

Anteunis, M., Tavernier, D. and Spiessens, L. Erythro-2,4-pentanedithiol: The Symmetry of its ^1H NMR Spectrum Versus the Symmetry of its Fischer Projection	1	Ernst, L. Determining the Relative Signs of Inter- benzylic J_{FF} by Changing the Solvent	32
Engle, J. Strike-Anywhere Matchbox.	3	Goldstein, J. H. and Babcock, E. E. R_{α} Structure and Orientation of Propargyl Chloride	34
Shindo, H. ^{31}P NMR of the A Form of DNA Fibers	5	Lippmaa, E., Puskar, J., Past, J. and Schraml, J. Inadequate Magic in ^{29}Si NMR.	35
Inubushi, T. and Becker, E. D. Super WEFT	8	Dybowski, C. R. Chemical-Shift Spectra of Oriented Poly(tetrafluoroethylene).	37
de Bruin, S. H., Haasnoot, C. A. G., Berendsen, R. G., van Boom, J. H. and Hilbers, C. W. Iminoprotons in Hairpin Loops	11	MacLean, C. and Ruessink, B. H. Evidence for Charge-Transfer Complexes by Electric Field NMR	39
Rinaldi, P. L. and Baldwin, N. J. Deuterium Decoupling on the Varian XL-200	13	Contreras, R. H. Transmission Mechanisms of Spin-Spin Coupling Constants	41
Khetrapal, C. L. The Influence of Bond-Polarisations on Molecular Conformation and Structure.	15	Erkelens, C., de Groot, J. A. and Lugtenburg, J. 4Z,9Z,15Z-2,3,17,18-Tetramethyl-1,19- [21H,24H]-bilindione	43
Rendall, K., Tiddy, G. J. T. and Trevethan, M. A. NMR of Soap Mesophases	17	Escanyé, J. M. and Canet, D. Frequency Dispersion of Water Proton T_1 in Tissues (in vitro)	45
Frye, J. S. Spinning Temperature Alteration for Preventing MAS Rotor Distortion	19	Bolton, P. H. Decoupling is Better than Refocusing in Proton-Carbon Two-Dimensional Correlation Spectroscopy	47
Huis, R., Alma-Zeestraten, N. C. M., Clague, A. D. H. and Hays, G. R. Vibration-Rotation Spectroscopy of the Magic Angle Spinning Assembly in High- Resolution Solid-State NMR	22	Emsley, J. W. 6th International NMR Meeting at Edinburgh, 10th - 15 July, 1983	49
Ray, G. J. An Unusual Phosphorus-Hydrogen Coupling Constant	25	Stilbs, P. JEOL Equipment Wanted	50
Lenkinski, R. E. ^{99}Ru NMR and WH-400 Probe Tuning Modification.	27	Shapiro, B. L. Subscription Renewals Due Now	51
Teklu, Y. and Storm, C. B. $^2\text{H}/^1\text{H}$ Isotope Effects on the ^{13}C NMR Spectrum of $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphin	29		

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All Newsletter Correspondence, Etc., Should be Addressed To:

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AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 287

Alma-Zeestraten, N.C.M.	22	Huis, R.	22
Anteunis, M.	1	Inubushi, T.	8
Babcock, E. E.	34	Khetrapal, C. L.	15
Baldwin, N. J.	13	Lenkinski, R. E.	27
Becker, E. D.	8	Lippmaa, E.	35
Berendsen, R. G.	11	Lugtenburg, J.	43
Bolton, P. H.	47	MacLean, C.	39
van Boom, J. H.	11	Past, J.	35
de Bruin, S. H.	11	Puskar, J.	35
Canet, D.	45	Ray, G. J.	25
Clague, A. D. H.	22	Rendall, K.	17
Contreras, R. H.	41	Rinaldi, P. L.	13
Dybowski, C. R.	37	Ruessink, B. H.	39
Emsley, J. W.	49	Schraml, J.	35
Engle, J.	3	Shapiro, B. L.	51
Erkelens, C.	43	Shindo, H.	5
Ernst, L.	32	Spiessens, L.	1
Escanyé, J. M.	45	Stillbs, P.	50
Frye, J. S.	19	Storm, C. B.	29
Goldstein, J. H.	34	Tavernier, D.	1
de Groot, J. A.	43	Teklu, Y.	29
Haasnoot, C. A. G.	11	Tiddy, G. J. T.	17
Hays, G. R.	22	Trevethan, M. A.	17
Hilbers, C. W.	11		

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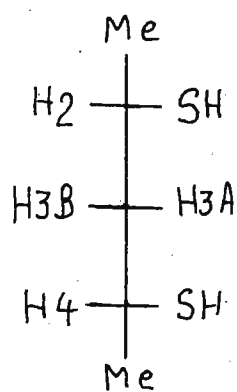
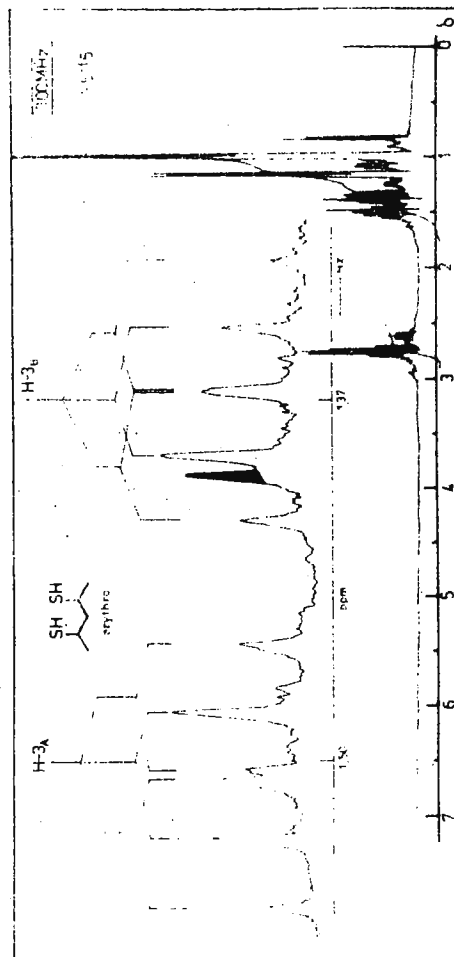
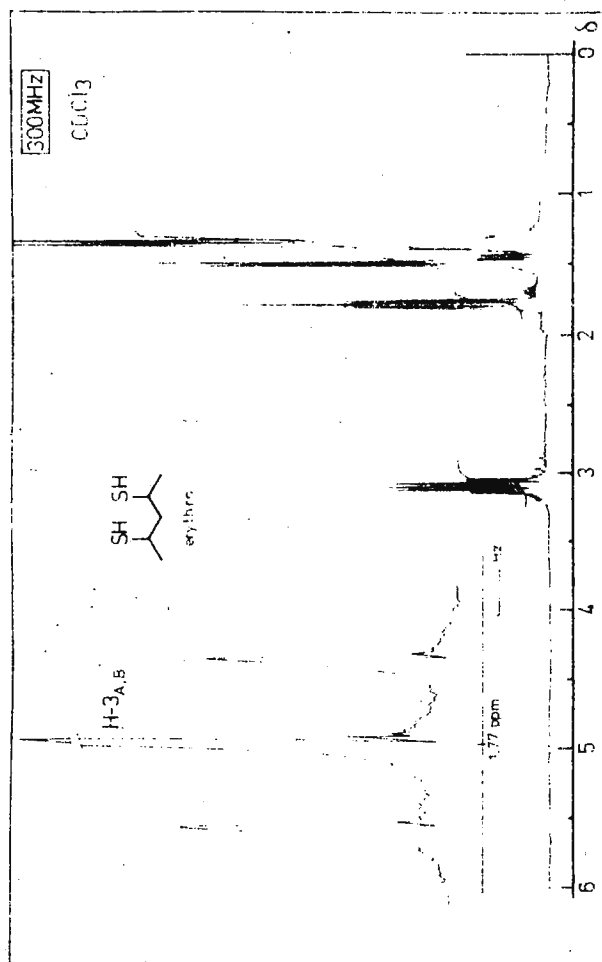
Prof. B.L. SHAPIRO
Texas A&M University
Dept. of Chemistry
College Station
TEXAS 77843 (U.S.A.)

Erythro-2,4-pentanedithiol : The symmetry of its ^1H NMR spectrum versus the symmetry of its Fischer projection.

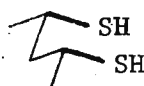
Dear Barry,

In Organic chemistry the Fischer projection serves to specify the configuration of a tetrahedral center of chirality. For compounds that have two identical chiral centers, e.g. the tartaric acids, the Fischer projection is also the traditional vehicle to explain the existence of an achiral "meso" (C_s symmetry) and a chiral "dl" (C_2 symmetry) form. The eclips (or "horse-shoe") conformation underlying this projection is actually of high energy but the same conclusion, the existence of a chiral and an achiral isomer, is obtained by considering the appropriate staggered conformations in rapid equilibrium. In NMR spectroscopy fast interconversion between conformations may lead to the effective equivalency of f.i. chemical shifts and coupling constants, and one is inclined to assume that these equivalences will be faithfully represented by the symmetry of the Fischer projection. But this is not necessarily so. Consider erythro-2,4-pentanedithiol. In the ^1H NMR spectrum, even at 300 MHz, the H3A, H3B and H2, H4 protons constitute an A_2X_2 system (shift equivalence + coupling equivalence). Yet in the Fischer projection H3A and H3B are diastereotopic, and one might have expected to find an ABX_2 system. The explanation is shown in the figure. There are seven plausible conformations of the erythro-dithiol: the achiral form, which has exactly the same symmetry properties as the Fischer projection, and three distinct pairs of enantiomers. The interconversion between two enantiomeric forms makes H3A and H3B shift and coupling equivalent. It is but the contribution of the aa form which makes, under rapid exchange, H3A different from H3B. If the aa conformer is not present, then the diastereotopicity of H3A and H3B, suggested by the Fischer projection, is fallacious. Under this condition it is NOT a good "mean" structure to represent the conformational averaging. Conversely the isochronism and the coupling equivalence of H3A, H3B is almost irrefutable evidence that the aa conformer is absent.

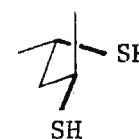
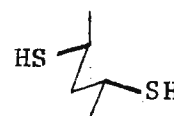
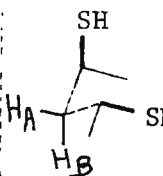
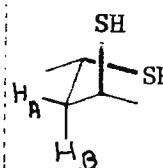
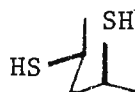
Two more points. $\text{SH}\cdots\text{SH}$ hydrogen bonding is known to be weak to non-existent, and the aa form is the only one allowing such bonding. The above discussed spectrum was taken in CDCl_3 , but in benzene solution an ABX_2 system is observed: H3A and H3B have different chemical shift and, important detail, the vicinal coupling constants of H3A and H3B are slightly different too. In benzene solution, there must be a small contribution from the aa form. It may be that in CDCl_3 , which is itself a donor in hydrogen bonding, the intramolecular $\text{SH}\cdots\text{SH}$ bonding is completely disrupted, but not in apolar benzene.



Fischer
projection



aa



M. Anteunis.

D. Tavernier.

L. Spiessens.

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

School of Medicine G4

DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

June 29, 1982

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

Strike-Anywhere Matchbox

Dear Barry,

We recently built this circuit for convenience in matching our probes to 50 ohms. A 50 ohm match is indicated by a minimum on the meter. The frequency range is from 15 to more than 400 MHz without adjustment. Any voltage of more than 3 Vpp will provide a useful indication. The voltage may be CW or pulsed, but I'd worry about diode D1 (Schottky) breakdown if the transmitter voltage were more than 200 Vpp or so. In theory the circuit may remain connected, although one might get some extra noise in the observe line. Unfortunately a lock transmitter will not deliver 3 Vpp, so a synthesizer of the right frequency must be used for the lock matching.

The first part of the circuit is an r.f. bridge which owes much to The Radio Amateur's Handbook. Opposite ends of the diode D1 are presented with voltages proportional to the load voltage and load current respectively. When the load is 50 ohms resistive (and the 34 pF has previously been adjusted at some convenient frequency for a null), then there is no r.f. difference voltage across the diode and no rectification takes place. Any deviation from 50 ohms will result in a detected D.C. and a deflection of the meter. The op amp feedback and meter circuit can be chosen to give a full scale reading with the op amp output beginning to saturate at the positive supply voltage and the input voltage to the op amp at about 50 mVdc.

I made a fairly dangerous transformerless power supply which I won't disclose here.

The r.f. wiring should be kept short. 50 ohm coax. should connect between the IN and OUT ports, with the toroid possibly surrounding the end of the center conductor (although I slipped it on in the middle). Of course the ground conductor must go outside of the toroid.

It's easiest to tell experimentally which is IN and which is OUT. The reverse sense will give you a measure of forward power (or its square root, rather).

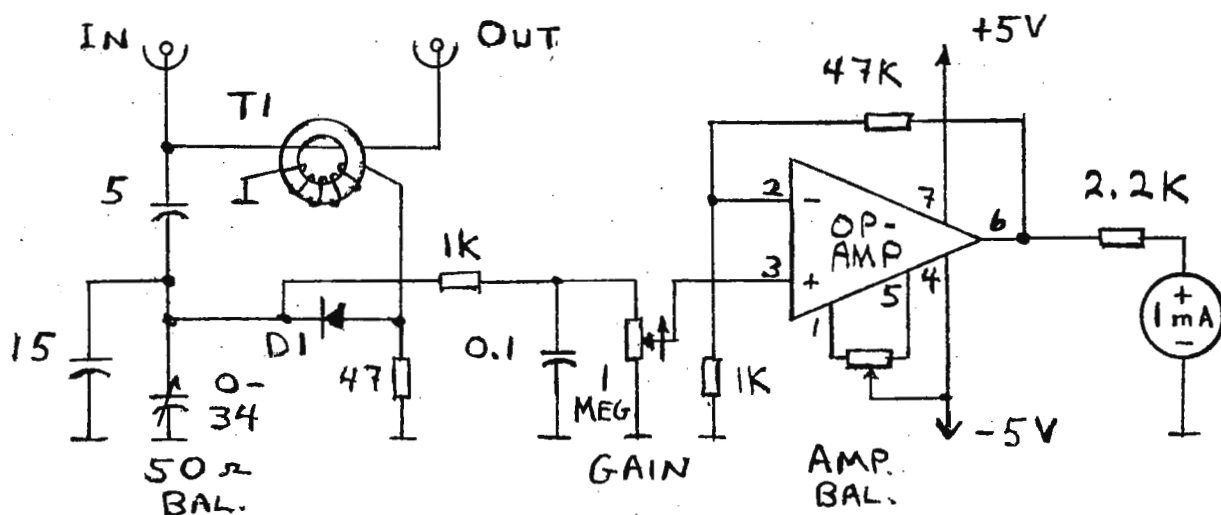
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Sincerely,

Jim

James Engle

P.S. The insertion loss is about 1 dB at 360 MHz; less at lower frequencies.



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TOKYO COLLEGE OF PHARMACY

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July 6, 1982

Professor B. L. Shapiro
 Department of Chemistry
 Texas A&M University
 College Station, Texas 77845

 ^{31}P NMR OF THE A FORM OF DNA FIBERS

Dear Barry:

We continue to work on DNA fibers to determine the orientation of the phosphodiester backbone of DNA. We had initially a difficulty in interpreting P- ^{31}P NMR spectra of the A form of natural DNA: the spectra were too broad and exhibited poorly defined patterns [1] (see the left spectra). We assigned such broadening of the lines to imperfect orientation of DNA within the fiber and to a little but observable reorientational motions. Later, we obtained somewhat better spectra from the A form of poly(dAdT) fibers [2]. B. T. Nall et al. [3] demonstrated that even natural DNA fibers show the highly resolved spectra at 97.2 MHz.

There are two major sources causing line broadening: one is a distribution of orientation of phosphodiester in DNA fiber and the other is dipole-dipole interactions (^{31}P - ^{31}P and ^{31}P - ^{23}Na). The former is associated with imperfect orientations of DNA molecules along the fiber axis. We recently measured at 40MHz spectra of the A form of salmon DNA (which was prepared in the same way as previously), which may be compared with the spectra obtained at 24.3 MHz. Apparent increase in resolution as increasing the field strength as shown below indicates that consideration of dipole-dipole interactions is important for interpreting the spectra patterns of solid DNA at least at low relative humidities, as suggested by Nall et al.

It seems to me that the statement that high field strength takes advantages over the low field strength may also be true for solid state NMR: we have to spend increasing cost to obtain better information !? It is unfortunate for sincere science, isn't it?

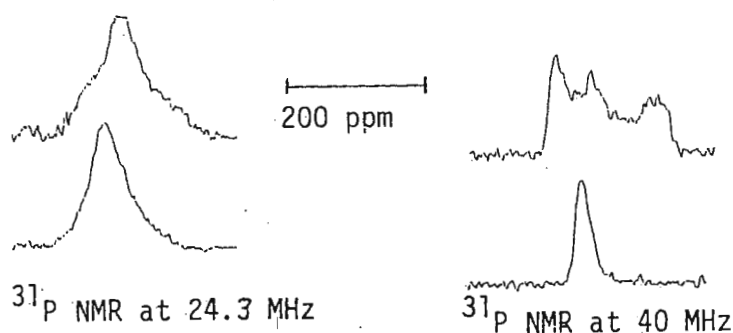


Fig. 1. The top spectrum: perpendicular and the bottom: parallel.

- [1] H. Shindo et al. Biochemistry, 19, 518(1980)
- [2] H. Shindo et al. Biochemistry, 20, 745(1981)
- [3] B.T.Nall et al. Biochemistry, 20, 1881(1981)

Sincerely Yours

H. Shindo
 H. Shindo

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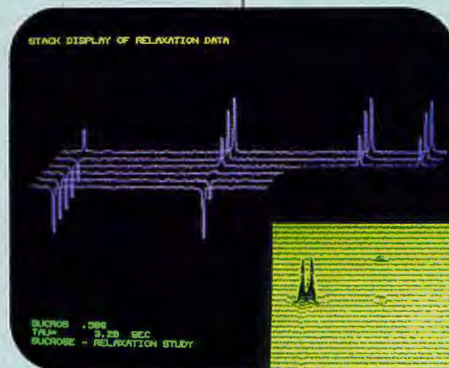
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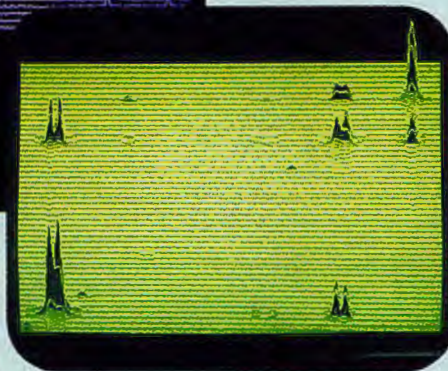
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JUN 30 1982

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Bethesda, Maryland 20205

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

Dear Barry:

Super WEFT

Of the many methods for minimizing interference from HDO or H₂O solvent lines, WEFT is one of the oldest and perhaps most commonly used. In applying this method to the study of contact-shifted proton resonances in several heme proteins, Toshiro Inubushi has developed a modification (dubbed "super WEFT") that offers considerable advantage. This modification, which is sketched in Figure 1, bears roughly the same relation to WEFT itself as the fast inversion-recovery method to the normal inversion-recovery method of measuring T₁. By limiting the repetition time of the pulse sequence -- 180°, t_A, 90°, t_B -- to much less than five times the T₁ of the solvent, many repetitions are possible within a given total experiment time. The period t_A is, of course, chosen to null the solvent signal for application of the 90° observation pulse. However, if t_B is rather short, the solvent signal is still quite small at the beginning of the next sequence, and at steady state t_A can be shortened also. The optimum ratio of t_A to t_B is given by the relation

$$e^{t_A/T_1} + e^{-t_B/T_1} = 2$$

where T₁ is the solvent (H₂O) relaxation time. Practical application of super WEFT is limited to cases in which the T₁'s of the lines to be observed are short. In fact, the minimum value of t_A should be greater than 5T₁(sample), so that the full sample magnetization is observed with the 90° pulse. Contact-shifted protons in heme proteins typically have T₁'s shorter than 50 ms, while T₁ for water in such protein solutions is about 1 s. While t_A is set to null only the water line, the rapid repetition of the sequence serves also to reduce substantially the intensity of the lines due to the diamagnetic parts of the protein (T₁ ≈ 0.3 - 0.5 s), which usually give considerable interference. Figures 2 and 3 give examples of the use of super WEFT in the study of two heme proteins. The advantage in signal/noise over published spectra is clear.

Best wishes for continued success of the Newsletter, which we all find extremely helpful.

Sincerely,

Toshiro Inubushi

Edwin D. Becker

Enclosures

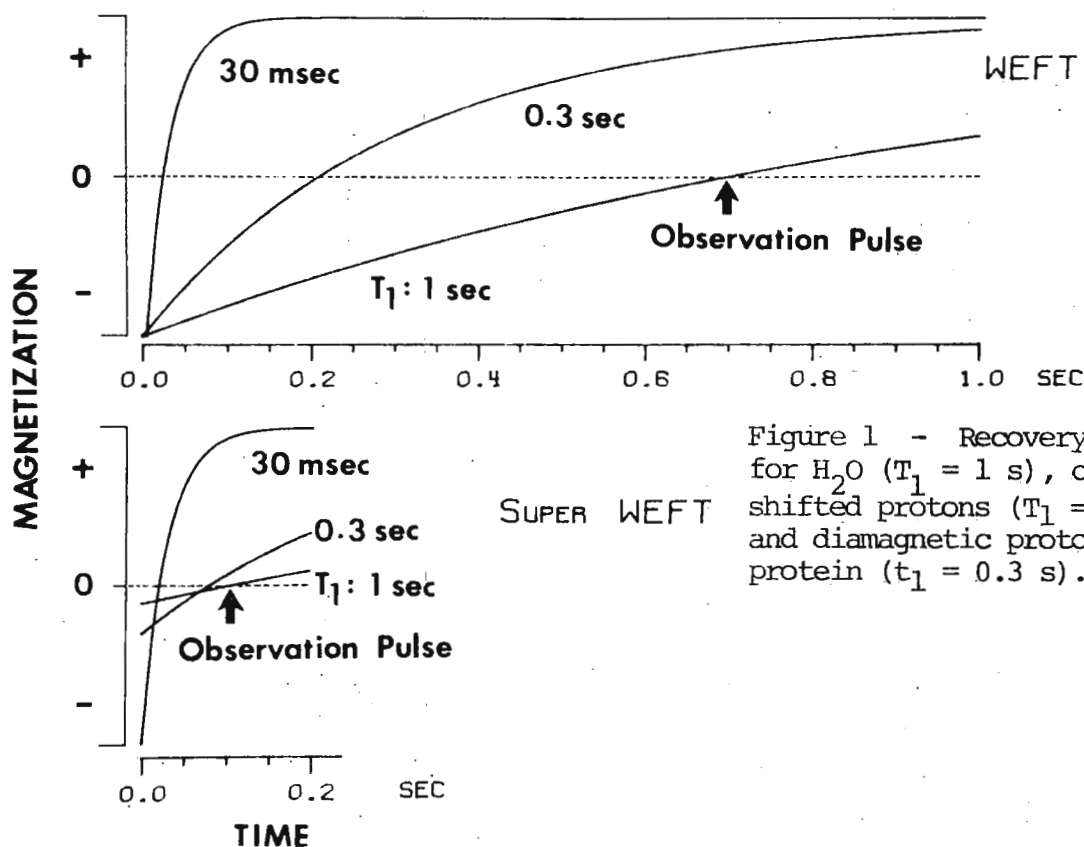


Figure 2

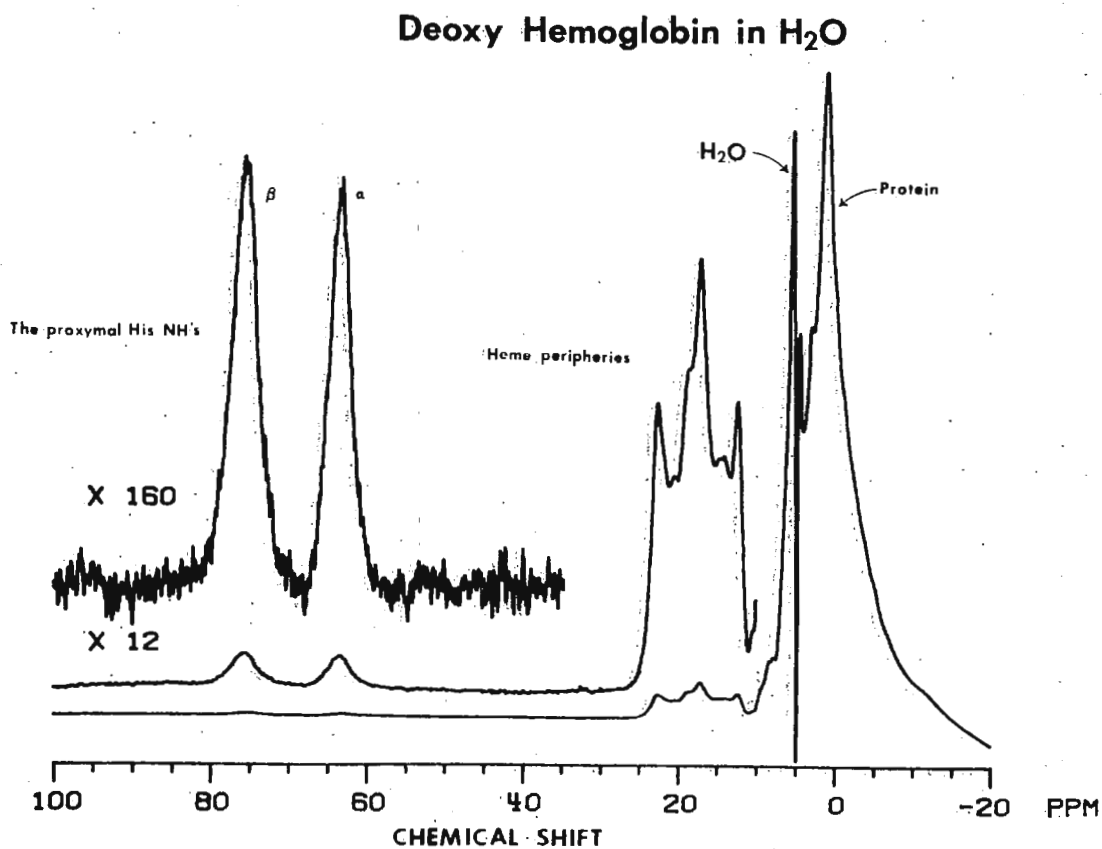


Figure 3

Ferric Cytochrome c**One-Pulse Sequence** $P2 = 9.5 \text{ us}$ $t_B = 233 \text{ ms}$

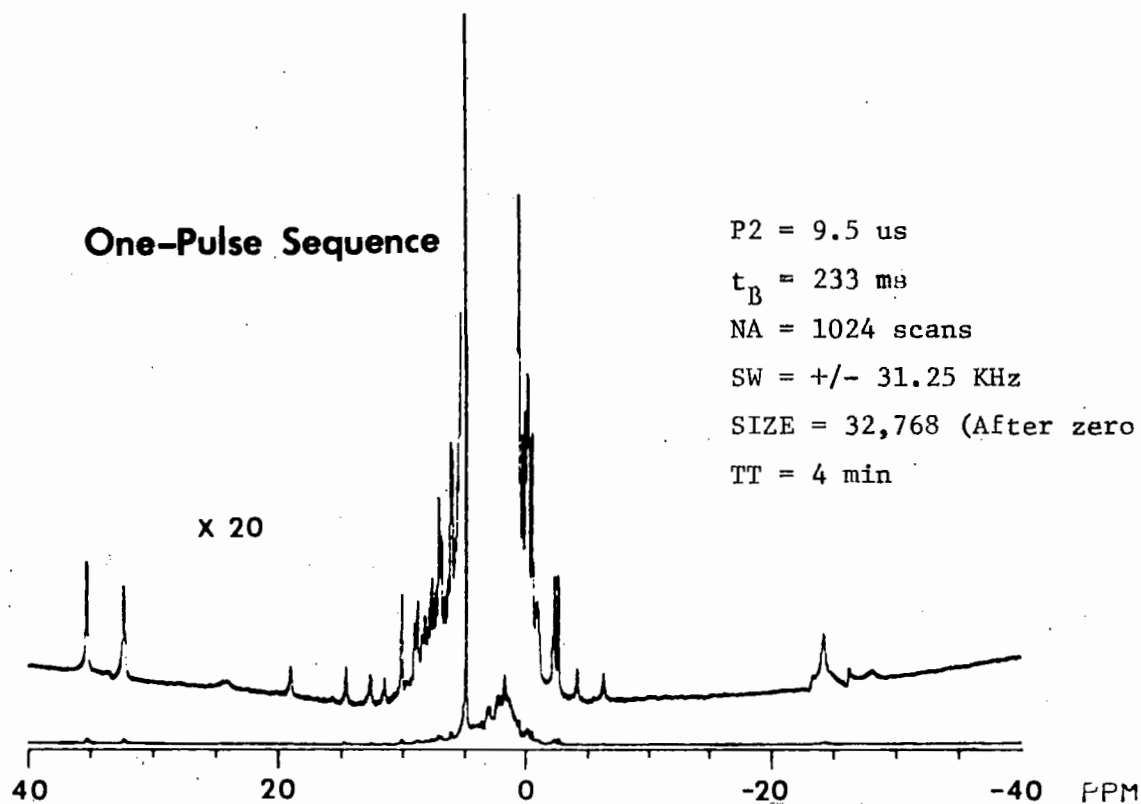
NA = 1024 scans

SW = $\pm 31.25 \text{ KHz}$

SIZE = 32,768 (After zero filling)

TT = 4 min

x 20

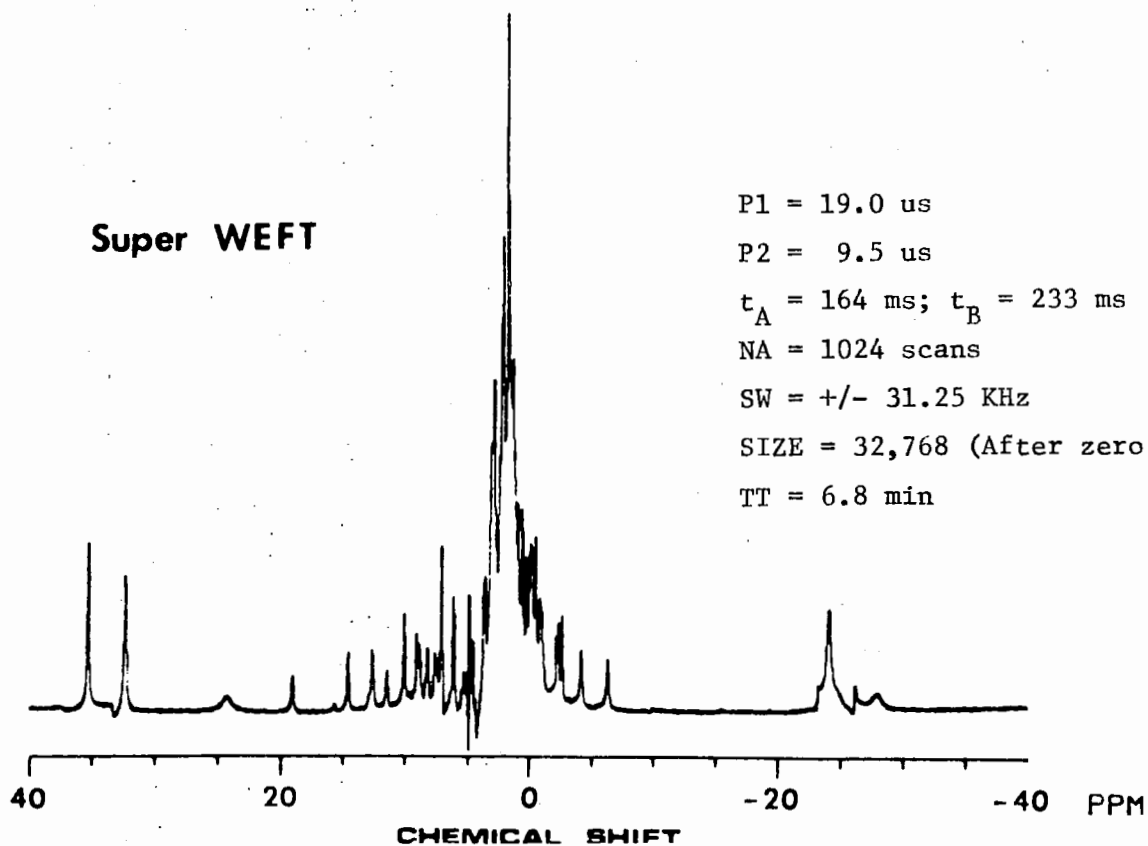
**Super WEFT** $P1 = 19.0 \text{ us}$ $P2 = 9.5 \text{ us}$ $t_A = 164 \text{ ms}; t_B = 233 \text{ ms}$

NA = 1024 scans

SW = $\pm 31.25 \text{ KHz}$

SIZE = 32,768 (After zero filling)

TT = 6.8 min





287-11

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

KATHOLIEKE UNIVERSITEIT
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Afdeling

Professor dr. Bernard L. Shapiro

Department of Chemistry

Texas A & M. University

College Station, TX 77843

U.S.A.

Uw kenmerk

Uw brief van

Ons kenmerk

82450/CWH/nk

Datum June 30, 1982

Onderwerp

Dear Professor Shapiro,

Hairpin loops are common features of the secondary structure of ribonucleic acids. In DNA the occurrence of loop structures seems less likely because of the complementary nature of the two strands. However, these structural features can be studied in synthetically prepared DNA fragments. Here we report on a DNA "hairpin" (see Fig. 1) formed by the synthetic oligonucleotide ATCCTATnTAGGAT.

The 500 MHz proton NMR spectrum of the iminoproton region (between 10 and 15 ppm downfield from the reference DSS) is shown in Fig. 2A. The numbering of the resonances below 12 ppm corresponds to the numbering of the basepairs in Fig. 1. The assignments of these resonances was accomplished by making use of Nuclear Overhauser Effects (NOE's) which are observed between the iminoprotons of adjacent basepairs.

A particularly interesting NOE is observable between an iminoproton from a thymine residue in the loop and the iminoproton signal arising from the A-T basepair 6. This result, in conjunction with the NOE's observed for other iminoprotons of the thymines in the loop, shows that these "loop"-iminoprotons are positioned within the interior of the loop at rather well defined distances. It also shows that the exchange rate of the "free"-iminoprotons in the loop is remarkably slow on the NMR time scale. This is a very interesting result as in thermodynamic considerations of hairpin formation it is tacitly assumed that bases in the loop remain freely accessible to water. The present experiments seem to invalidate this assumption.

Yours Sincerely,


S.H. de Bruin
C.A.G. HaasnootR.G. BerendsenJ.H. van Boom
C.W. Hilbers



KATHOLIEKE UNIVERSITEIT
NIJMEGEN

Geadresseerde Prof. Shapiro

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

Toernooiveld

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Telefoon (080) 55 88 33

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Ons kenmerk 82450/CWH/nk

Datum June 30, 1982

Blad No

FIGURE 1.

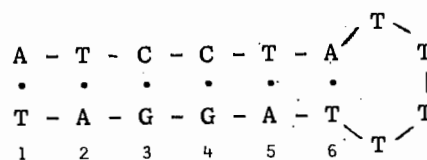
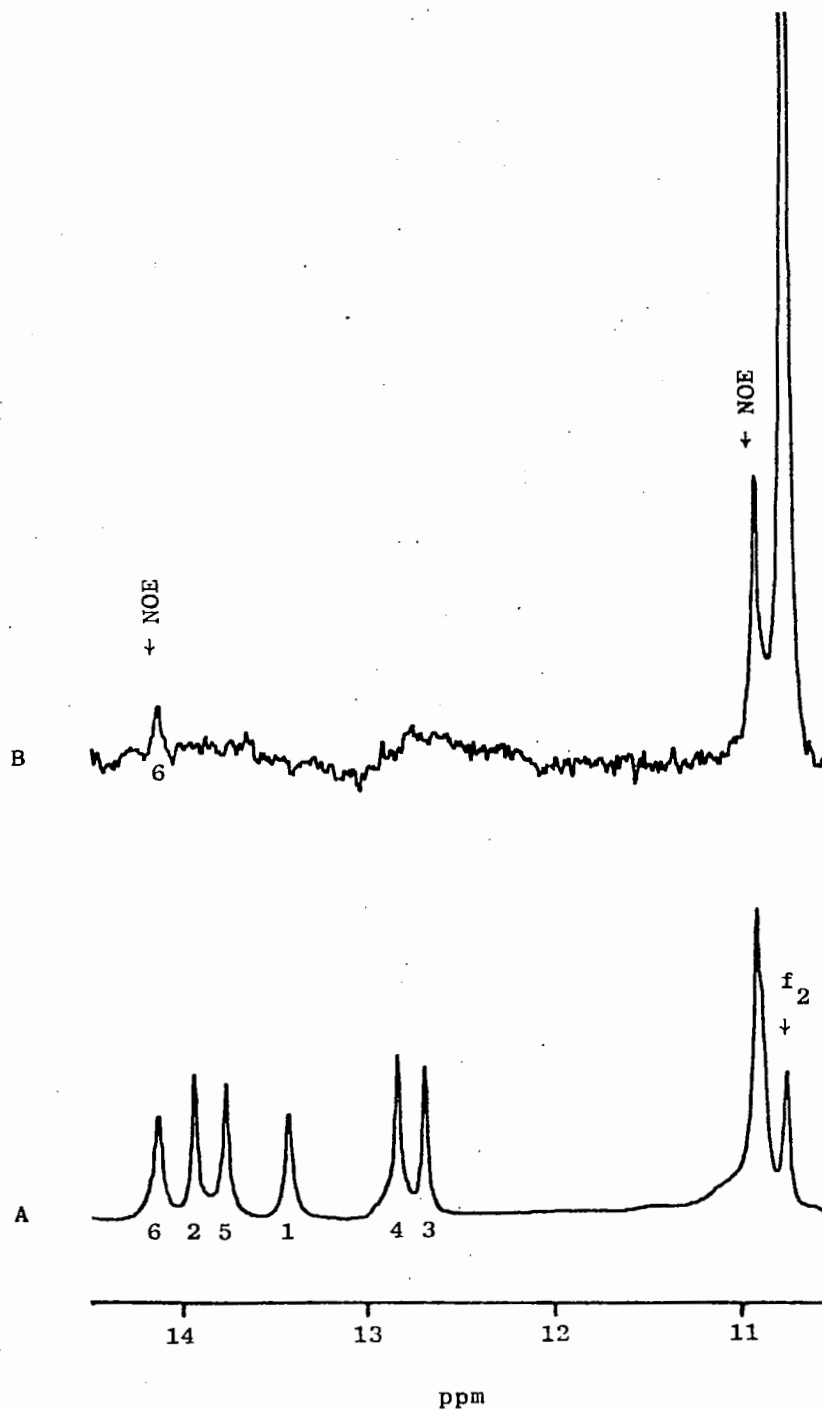
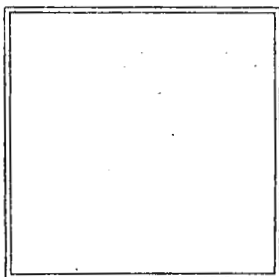


FIGURE 2.





July 6, 1982

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

Dear Professor Shapiro,

Associated with some of our work on labelled organic compounds, we have frequently found the need to obtain ^{13}C spectra with ^2H decoupling. This was easily implemented on our Varian XL-200 by switching the ^1H transmitter board with the ^2H transmitter board in the decouple and lock channels of the instrument. The decoupler is then attached to the lock channel of the standard Varian 10 mm broadband probe.

We found it necessary to filter the 30.7 MHz decoupler signal from the 50.3 MHz ^{13}C observe signal. This was accomplished by construction of the filters described in Schemes I - III. Initial values for the components in Schemes I and II were provided by Howard Hill of Varian. The 30.7 MHz band pass filter was placed at the input to the ^2H channel on the probe. The 30.7 MHz notch filter in Scheme II was found to be insufficient for our purposes, and so the two-stage filter shown in Scheme III was constructed for use in the observe channel. We emphasize that these components were most effective when used right at the bottom of the probe, so be careful that your components are non-magnetic.

With these filters in line we have obtained satisfactory ^{13}C $\{^2\text{H}\}$ spectra. Despite the fact that the ^2H channel of the probe is not optimized for high power decoupling, we obtain decoupling fields of ca. 1000 Hz, more than sufficient for use of broadband decoupling to collapse the 20-30 Hz one bond C-D couplings.

Please credit this contribution to the account of W. Ritchey.

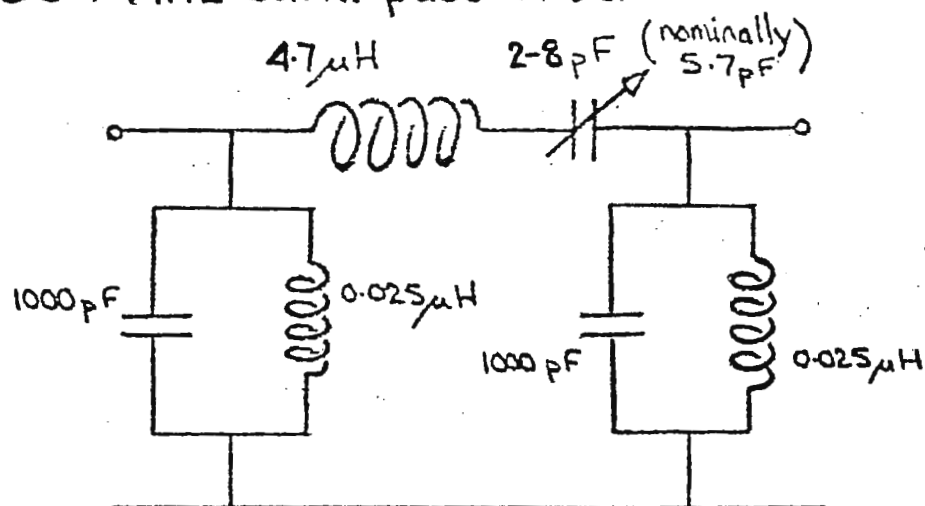
Yours sincerely,

Peter L. Rinaldi, Assistant Professor

Nicholas J. Baldwin, Research Assistant

arb

I) 30.7 MHz band pass filter

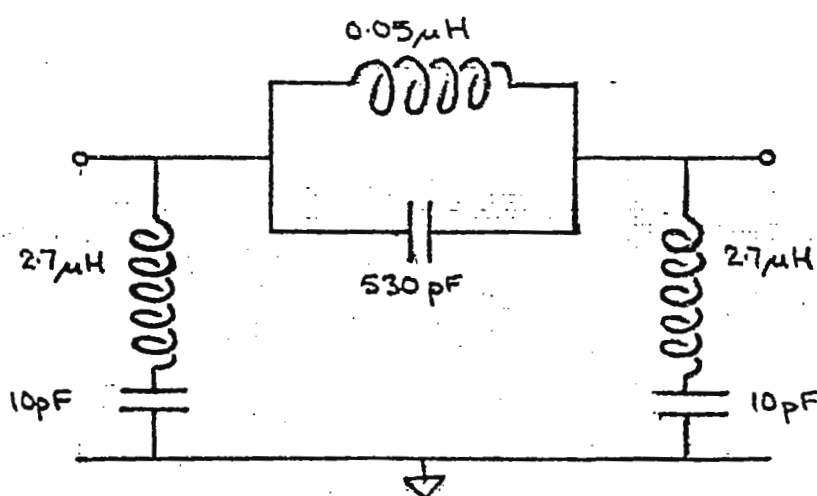


insertion loss

7 db at 30.7 MHz

22 db at 50.3 MHz

II) 30.7 MHz band reject filter

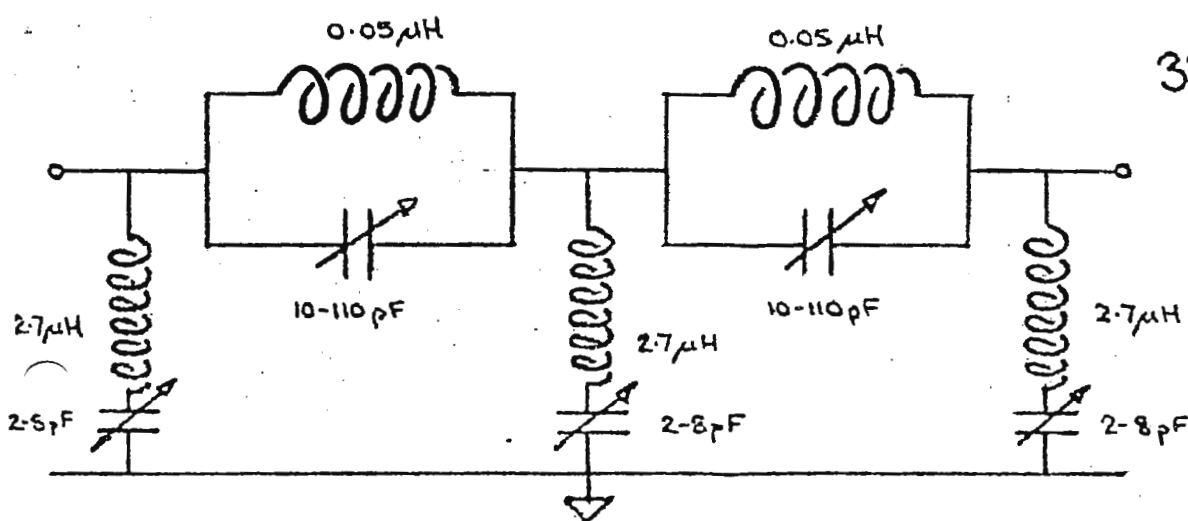


III) 30.7 MHz band reject filter (2 stages)

attenuation

32 db at 30.7 MHz

2 db at 50.3 MHz



RAMAN RESEARCH INSTITUTE

BANGALORE - 560 080. INDIA

Professor C.L.Khetrapal

July 6, 1982

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

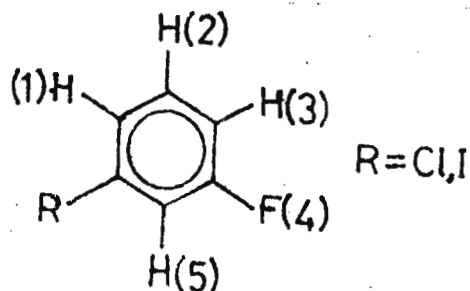
Title: The influence of bond-polarisations on molecular
conformation and structure

Dear Professor Shapiro,

Thank you very much for your green reminder of June 7, 1982. Before, it changes the colour, I submit the following contribution for the Newsletter.

Sometime back, we had studied the proton NMR spectrum of oriented phenylsilane¹ and interpreted the difference in the preferred conformations of phenylsilane and toluene in terms of opposite bond polarisations of the Si-H and the C-H bonds ($\text{Si}^{\delta+} \text{---} \text{H}^{\delta-}$ and $\text{C}^{\delta-} \text{---} \text{H}^{\delta+}$). The same hypothesis was later used to a number of systems (such as N:N-dimethyl uracil², 1-phenyl propyne³) containing one or more CH_3 groups, to predict their preferred conformations. The predictions based on the bond-polarisations are not only supported by the NMR results but theoretical minimum energy calculations are also in agreement.

In recent studies,⁴ we have applied these principles to m-halogen substituted fluorobenzenes and tried to interpret differences in relative internuclear distances, as a result of halogen substitution, in terms of simple electrostatic attractions. For example, in m-chlorofluorobenzene, r_{12}/r_{23}



is larger than in m-bromofluorobenzene. This is understood in terms of larger electrostatic pull of the $C^{\delta-} - H^{\delta+}$ bond by more electronegative chlorine than bromine. Other relative internuclear distances also behave as predicted by the bond-polarisation hypothesis.

The hypothesis seems to be fairly general in predicting the structure and preferred conformations of molecules.

1. C. L. Khetrapal and E.D.Becker, J.Mag.Res. 43, 8 (1981)
2. C. L. Khetrapal and A.C.Kunwar, J.Phys.Chem. (submitted)
3. C. L. Khetrapal and R.Highet, Org.Mag.Res. 16, 117 (1981)
4. N.Suryaprakash, A.C.Kunwar and C.L.Khetrapal, J.Mol.Struct. (submitted).

Yours sincerely,

C.L. Khetrapal

Table Values of T_{2eff} (CH_2 Groups), Δ (2H) and Δ ^{23}Na ($\pm 5\%$)
for various phases of sodium dodecanoate/water system at 82°C

<u>Phase</u>	<u>1H (μs)</u>	<u>Δ (2H) (Hz)</u>	<u>Δ Na (KHz)</u>
H _{1d}	180	840	3.8
Int(2)	300	560	7.5
La	120	1100	12.3

(T_{2eff} is time taken for 1H f.i.d. to decay to $1/e$ of original intensity.)



Unilever Research

Port Sunlight Laboratory
Quarry Road East
Bebington Wirral
Merseyside L63 3JW

Telephone 051-645 2000
Telex 627578



Prof B I Shapiro
Texas A & M University
Department of Chemistry
College Station
TEXAS 77843
USA

KR/GJTT/MAT/D

5 JUL 82

Dear Professor Shapiro,

NMR of Soap Mesophases

For a number of years we have been interested in using ^2H or ^{23}Na spectra of ionic surfactant mesophases to obtain information about micelle structure and water/counter-ion binding. The structures of the most important liquid crystals formed in these systems, the hexagonal (H_1) and lamellar (L_α) phases, are well known⁽¹⁾. Cubic phases also commonly occur with two major types being recognised, although the micelle architecture is not completely delineated^(2,3). In addition, numerous "intermediate" phases have been reported⁽⁴⁾ at compositions between hexagonal and lamellar phases. Their existence has yet to be fully established^(3,4).

In anisotropic media the spectra of quadrupolar nuclei ($I > \frac{1}{2}$) consist of $2I$ peaks with a separation Δ (the quadrupole splitting). Within a single phase, water ($^2\text{H}_2\text{O}$) and counter-ions exchange rapidly over all sites in the system, hence a single "average" spectrum is observed for these species. Where two (or more) phases are present then two (or more) spectra occur. This is of particular assistance when the separation of individual phases is difficult due to high viscosity. We have taken advantage of this property to study the "intermediate" phases of soap/water systems.

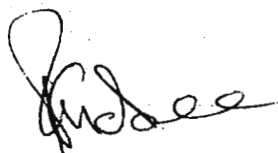
In a recent study of sodium dodecanoate (NaC_{12})/water by d.t.a., Madelmont and Perron⁽⁵⁾ have reported that two "intermediate" phases occur at compositions between the H_1 and L_α phases. The first (Int. 1) was reported to exist over the temperature range $60\text{--}150^\circ\text{C}$ at ca 56% NaC_{12} . The second (Int. 2) occurs at ca 60% NaC_{12} with the smaller temperature range of $64\text{--}90^\circ\text{C}$. We have made ^2H and ^{23}Na measurements on a range of $\text{NaC}_{12}/^2\text{H}_2\text{O}$ mixtures at 97°C and 82°C , where optical microscopy confirmed the existence of one or two "intermediate" phases.

At 97° we were unable to distinguish any two-phase spectra in the Int. 1 + H_1 compositions, while separate L_α and Int. 1 spectra were observed. The Δ values of ^{23}Na and ^2H in the Int. 1 compositions were continuous with those for the H_1 phase. Similarly, at 82°, no H_1 + Int. 1 two-phase region was observed while Δ values were similar to those at 97°C. Hence we conclude that the Int. 1 phase has a rod structure, which is the same as, or is closely related to, the normal H_1 phase.

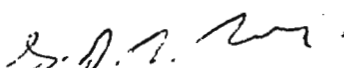
The second "intermediate" phase has first-order boundaries with both Int. 1 and the L_α phase since superimposed Int. 1 + Int. 2 or Int. 2 + L_α spectra are observed at appropriate compositions. This phase exists only over a narrow range of water compositions (ca 40-42% H_2O) where the Δ values are almost invariant with composition. The magnitudes of Δ for the Int. 2 and the adjacent Int. 1 or L_α phase are compared in the table. Also included are alkyl chain $T_{2\text{eff}}$ values which give a qualitative idea of alkyl chain alignment.

Any conclusions concerning the structure of the Int. 2 phase are obviously tentative in the absence of low angle X-ray diffraction data. Also, a detailed discussion of the factors that determine Δ (or $T_{2\text{eff}}$) is inappropriate here. We expect an increase in Δ by a factor of two at an H_1/L_α boundary provided that the structure of the head group/water region remains substantially unaltered. We suggest that the ^{23}Na values for the Int. 1/ Int. 2 transition indicate a rod/bilayer transition. The very low ^2H Δ values and large $T_{2\text{eff}}$ could arise from the existence of very thin bilayers, which attain their normal dimensions in the L_α phase. Clearly, further measurements are required to establish the structure of this new phase. It is also of interest to investigate the dependence of "intermediate" phase structure on the soap chain length and counter-ion.

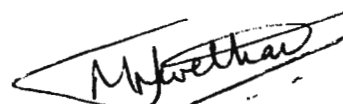
Yours sincerely



K RENDALL



G J T TIDDY



M A TREVETHAN

References

1. P A Winsor, Chem. Rev., 1968, 68, 1.
2. K Fontell, Mol Crystals Liquid Crystals,
3. G J T Tiddy, Physics Reports, 1980, 57, 1.
4. V Luzzati in "Biological Membranes", Ed. D Chapman, Academic Press 1968, Ch.3, p 71.
5. C Madelmont and R Perron, Bull. Soc. Chim. France, 1974, 430.

(See Table on page 287-16.)



Department of Chemistry

Colorado State University
Fort Collins, Colorado
80523

July 8, 1982

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

RE: Spinning Temperature Alteration for Preventing MAS Rotor Distortion.

Dear Barry:

Many labs doing C-13 magic angle spinning NMR use rotors machined from Kel-F. A disadvantage of this material is that it distorts, especially at and above room temperature. We have observed distortion resulting from excessive spin rate, heating due to high transmitter duty cycle, and stress from very high density samples. The current version of the bullet rotors¹ used in our lab, 3/8" O.D., 1/4" I.D., allows spinning rates around 3.8 kHz for ordinary samples and duty cycles. By passing the spinning air through a heat exchange coil in an ice bath we can lower the sample temperature about 10°C, which is sufficient to tolerate spinning speeds of 4.2 kHz or more extreme power and sample density with minimal rotor distortion. Our compressed air passes through a refrigerated drier at about 100 psig, so condensation in the heat exchange coil has not been a problem (calculated dew point -9°C).

The utility of this trick is offset by the inconvenience of replenishing the ice two or three times daily (4 L dewar). This can be alleviated by delivering a very slow trickle of liquid CO₂ from a siphon tank via a copper tube (warning: 1000 psi) through a needle valve immersed in the ice bath. A 50 lb (net) cylinder should last a couple of weeks of continuous duty if used to supplement a daily addition of ice. A common bath scale, chosen to provide a stable platform, will reveal the CO₂ level in the cylinder. This apparatus is much less expensive than a refrigerated bath and requires no power and very little space next to the magnet.

Please credit this contribution to Professor Maciel's subscription.

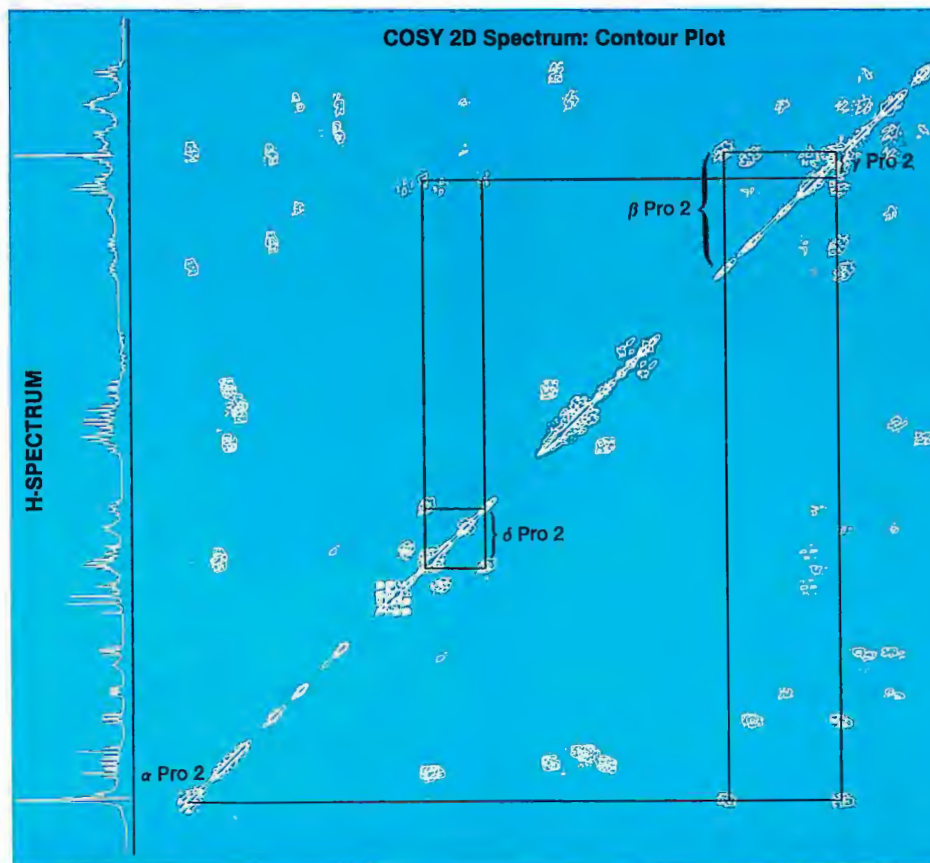
Sincerely yours,

James S. Frye
James S. Frye
CSU NMR Facility

¹V.J. Bartuska and G.E. Maciel, J. Magn. Res., 42, 312 (1981).

C₅₀H₇₃N₁₅O₁₁ by 2-D NMR

When complex molecules are submitted to analysis—e.g. the oligopeptide Bradykinin sample in this experiment—two-dimensional spectra such as proton correlated spectroscopy (COSY) can often produce dramatic simplification of seemingly intractable spectra, even at high magnetic field. Here is evidence:



Chemical Shift Assignments Using 2D Proton Correlated Spectroscopy (COSY).

The pulse sequence for COSY is given by:

$$90^\circ_x - t_1 - 90^\circ_{\pm x} - \text{Acq}(t_2) \quad (1)$$

The chemical shifts of mutually coupled protons can be extracted from over-lapping multiplets by means of a contour plot obtained from the COSY Experiment Data. The normal Proton Spectrum is represented along the diagonal axis, and the symmetrical off-diagonal cross peaks provide the clue to any coupled protons.

The COSY Contour Plot of Bradykinin triacetate (Arg-Pro*-Pro-Gly-Phe-Ser-Pro-Phe-Arg), illustrates the technique on the aliphatic moiety. With the known position of the H α -Pro 2 (*), the chemical shifts of all the six remaining protons (2 β ; 2 γ ; 2 δ) can easily be located as shown by the connecting lines.

(1) Ad Bax and Ray Freeman, JMR 44, p. 542-561 (1981)

Q.E.D. Both spectrum and contour plot of this COSY experiment were produced on a WM 400 at the Bruker Applications Laboratory. The WM Series of high-field NMR spectrometer systems comes with an extensive software system, including programs for 2-D processing display and plotting. A full-color graphic display processor further facilitates speed and clarity of stack and contour plots.

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In a short survey it is shown that for the last twenty years the instrumental development in the pulsed NMR field has been synonymous with the name of BRUKER and it is pointed out that the first commercially available Fourier Transformation (FT) spectrometers were developed by BRUKER in 1969. Since NMR tomography is based on both "pulsed" and "FT"-NMR, the unique experience of BRUKER in these fields represents the ideal basis for the recently developed imaging systems.

After a short introduction, the principles of NMR are described in the brochure followed by a short representation of the "Projection-Reconstruction-Technique". Due to the expected extraordinary importance of NMR tomography in the field of diagnostic medicine a comparison of the average X-ray tissue contrast with NMR data is given as well as some remarks about theoretically possible risks for patients. At the end of this brochure an "outlook" is given into new applications and of the expected development of NMR tomography.



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DEPT

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This method developed at the Griffith University by Drs. Bendall, Doddrell and Pegg can be performed on any BRUKER Spectrometer equipped with a CXP or high speed pulse programmer. Using this sequence the sensitivity in coupled spectra can be significantly increased or the multiplicity selection in ^{13}C spectra can be performed without the critical adjustments required for other polarization transfer pulse sequences.

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**Koninklijke/Shell-Laboratorium, Amsterdam****Shell Research B.V.**

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

Uw ref.:

Onze ref.:

AG

Amsterdam, 25th June, 1982
Badhuisweg 3
Tel. via telefoniste (020) 30 9111
Tel. rechtstreeks (020)
Hr/Mw

Dear Professor Shapiro,

VIBRATION-ROTATION SPECTROSCOPY OF THE MAGIC ANGLE SPINNING ASSEMBLY IN
HIGH-RESOLUTION SOLID-STATE NMR

Instability in the sample rotation of mushroom-shaped rotors can be a major problem in solid-state NMR, resulting on occasions in unnecessary (and unwanted) line broadening. Feeling for mechanical vibrations in the probe, listening for a 'clean' rotor sound and direct observation of the rotor are not ideal monitoring techniques when efficient and routine operation is required.

A very elegant method for measuring both the speed and the stability of spinning has been reported by Kendrick, Wind and Yannoni¹. Upon spinning the rotor becomes electrically charged due to frictional effects, before the air bearing is built up. These rotating charges will then induce an ac voltage in any non-grounded conductor in the vicinity of the rotor. Veeman² has successfully applied this technique, by monitoring the induced signal on the aluminium stator, which is of course isolated from earth by a foam-rubber cushion.

As an NMR spectrometer is basically a frequency analyser, we have applied its Fourier-transform capabilities to the problem, transforming the amplified signal into a Vibration-Rotation (VR) spectrum.

Figure 1 illustrates a very stable spinning system. The main peak occurs at the spinning frequency and higher harmonics (as well as low-frequency noise) are present. The two small peaks next to the main peak indicate minor instabilities (probably due to a slow nutation/precession).

Figure 2 shows the VR spectrum of a slightly unstable spinning system, where the intensity in the spinning frequency peak has become dissipated into the other two lines.

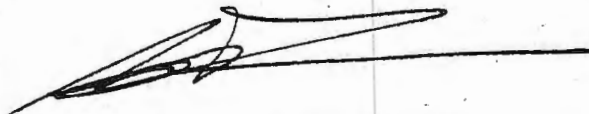
Although this is a diagnosis rather than a cure for spinning instability problems, it can serve as a warning before data acquisition is begun.

Yours sincerely,

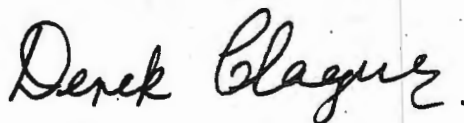
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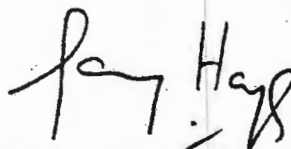
(R. Huis)



(N.C.M. Alma-Zeestraten)



(A.D.H. Clague)



(G.R. Hays)

P.S. Unfortunately, this will be Derek Clague's last contribution (at least for the foreseeable future) as he has forsaken NMR and Amsterdam for pastures new (Shell U.K. Thornton, Cheshire). The Newsletter subscription will be taken over by Gary Hays.

- 1) R.D. Kendrick, R.A. Wind and C.S. Yannoni, J. Magn. Reson. 40 585 (1980).
- 2) W.S. Veeman, University of Nijmegen, private communication.

Encl.: 2 Figures

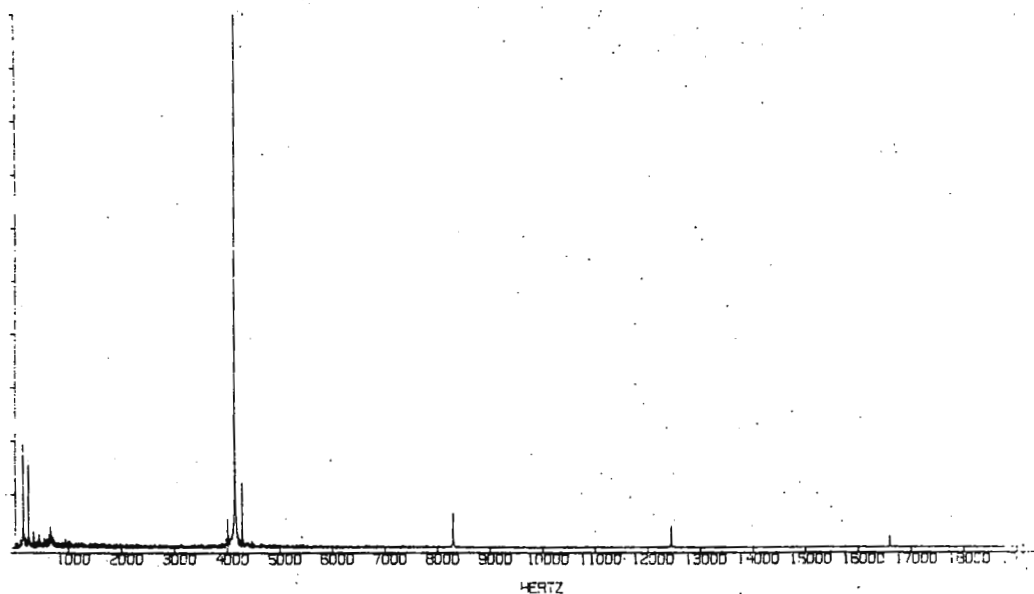


FIG. 1 VIBRATION-ROTATION SPECTRUM OF MAS ASSEMBLY
STABLE SPINNING AT 4.0 kHz

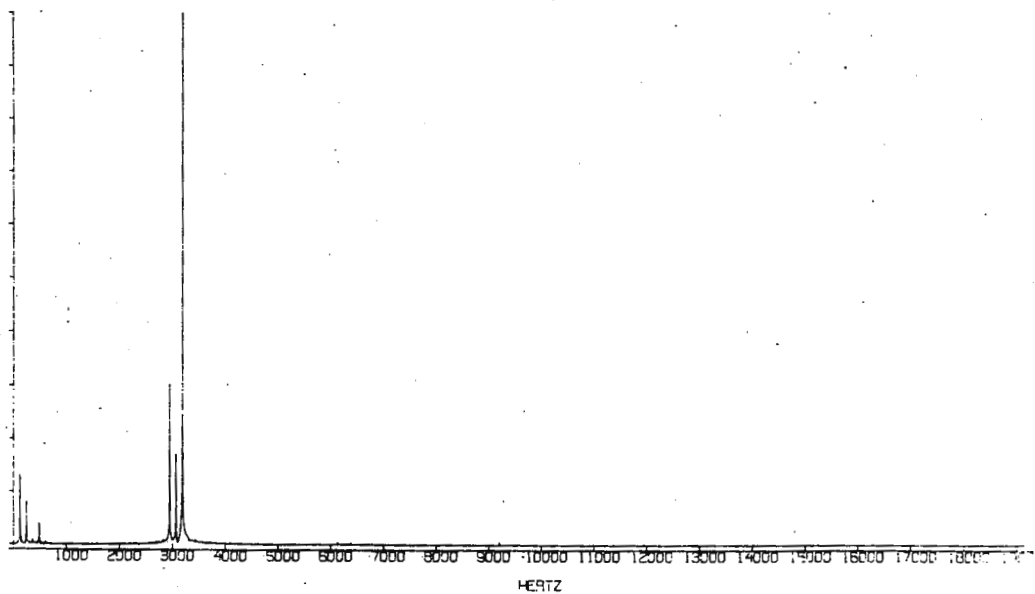


FIG. 2 VIBRATION-ROTATION SPECTRUM OF MAS ASSEMBLY
UNSTABLE SPINNING AT 3.1 kHz

Standard Oil Company (Indiana)

Amoco Research Center
Post Office Box 400
Naperville, Illinois 60566
312-420-5111

July 9, 1982

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

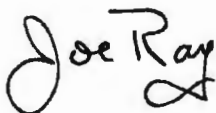
An Unusual Phosphorus-Hydrogen Coupling Constant

Dear Barry:

We recently encountered an unusual long-range coupling which appears to be rather general for secondary alcohol esters of dithiophosphoric acids. Figure 1 shows the ^{31}P spectra of bis(4-methyl-2-pentyl)dithiophosphoric acid, I. When broadband ^1H decoupling is used, two ^{31}P peaks are seen because I is a mixture of meso and racemic diastereoisomers which result from the chiral center at C-2 of the alkyl group. The coupled ^{31}P spectrum, surprisingly, consists of two triplets of triplets. A triplet from the coupling of H-2 in each of the two alkyl groups to phosphorus was expected. The additional triplet would, at first, appear to be the result of long-range, 5-bond coupling of phosphorus to H-4 in the two alkyl groups. However, we found that this is not the case but rather the coupling is due to one and only one of the methylene protons (H-3, H-3').

The ^1H spectrum of I is shown in Figure 2. The sample contains some unreacted alcohol as can be seen from the doublet at 1.2 ppm due to the C-1 methyl protons of the alcohol. Other alcohol resonances can be seen in the H-5 resonance. Assignments were made by noting the effect of homonuclear decoupling of H-5 and H-2. With single frequency decoupling at 4.6 ppm in the ^1H spectrum, the ^{31}P spectrum showed two triplets with a coupling of 3.0 Hz due to the four bond interaction of phosphorus with H-3'. Single frequency decoupling at 1.3 ppm gave two triplets ($J=12.3$ Hz) due to the expected three bond interaction of phosphorus with H-2. We do not understand why no coupling is observed between phosphorus and H-3 or H-1 and would welcome any comments readers may have on this matter. We have studied several other secondary alkyl esters of thiophosphoric acid as well as the 4-methyl-2-pentyl ester of phosphoric acid itself and in all cases this unusual four bond coupling was observed with values ranging from 1.5 to 3.0 Hz.

Sincerely,



G. J. Ray
Mail Station B-5

JH1:GJR/82082
attachment

Figure 1. ^{31}P NMR Spectra of $(\text{RO})_2\text{P}(\text{S})\text{SH}$,
 $\text{R} = 4\text{-methyl-2-pentyl}$

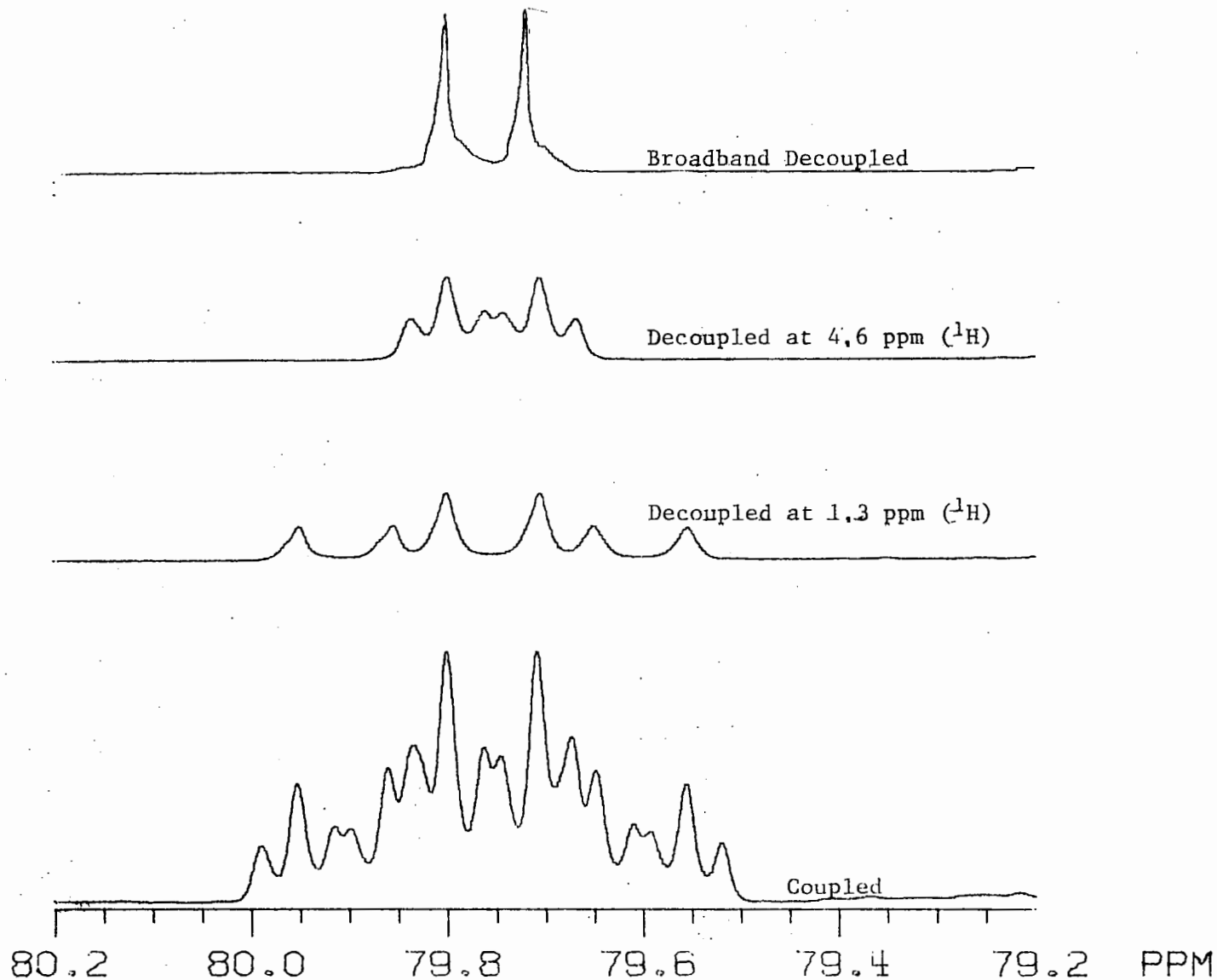
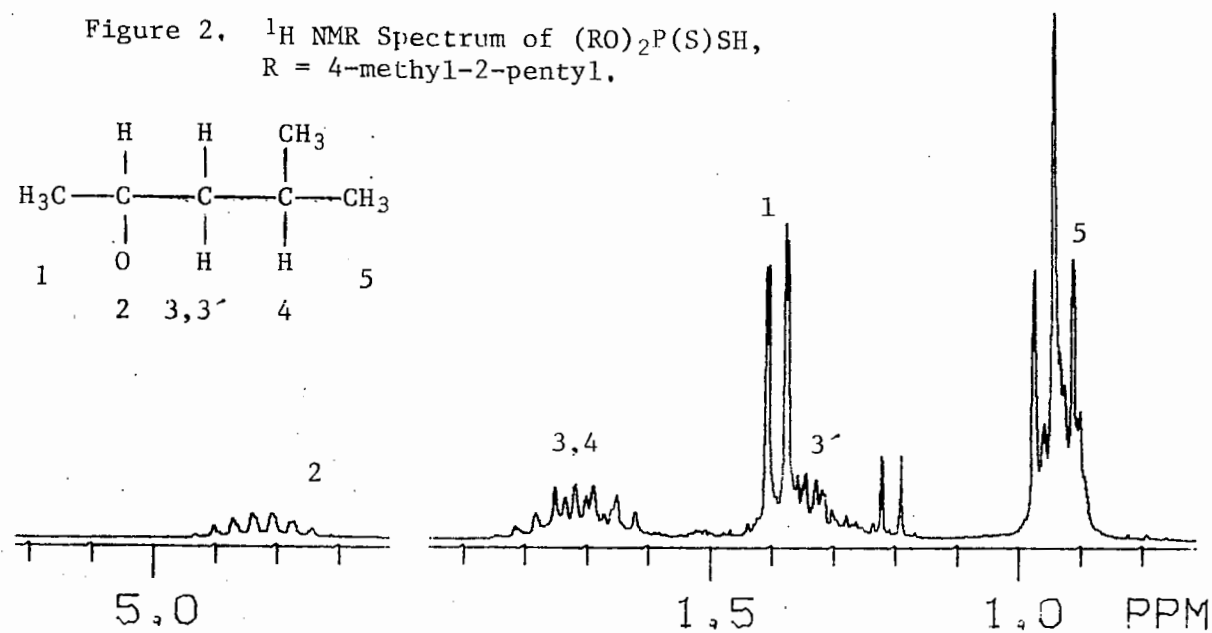
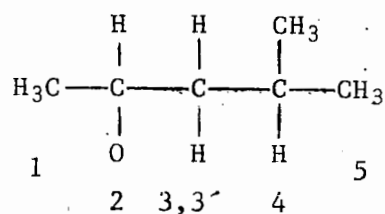


Figure 2. ^1H NMR Spectrum of $(\text{RO})_2\text{P}(\text{S})\text{SH}$,
 $\text{R} = 4\text{-methyl-2-pentyl}$.





The Guelph-Waterloo Centre for Graduate Work in Chemistry

Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1 519/824-4120

July 13, 1982

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

Title: ^{99}Ru NMR and WH-400 probe tuning modification

Dear Barry:

We have recently become interested in ^{99}Ru NMR. There have been several reports in the literature concerning the observation of this nucleus (1,2). From these reports it is clear that both the spin and frequency for ^{99}Ru listed in many NMR tables are incorrect. This can lead to frustrating experiences at the NMR console. For example, the "Bruker Almanac" lists the frequency of ^{99}Ru as 13.559 MHz at 9.359 T when in fact the correct frequency is 18.425 MHz. Once we discovered this error, finding ^{99}Ru resonances became easier.

We have adopted the same standard (RuCN_6^{4-}) that was suggested by Dykstra and Harrison(1). A typical ^{99}Ru spectrum run on our Bruker WH-400 is shown in Figure 1. We are currently exploring the feasibility of using ^{99}Ru NMR to characterize various Rh(0) compounds. We hope to be able to report on these results soon.

We have recently completed a modification to our WH-400 which may be of some interest to others. Since our frequency synthesizer (PTS-160) can only generate up to 159.99 MHz, we could not tune our high range 10 mm broadband probe to ^{31}P (162.00 MHz) directly. We found that, since the synthesizer frequency is multiplied by four in the console, we could tap this frequency directly. We used a coaxial BNC relay activated by a switch on the front panel in order to generate 4X the synthesizer frequency entered from the teletype. Since the signal generated in this way was 6 volts peak to peak, we attenuated it by 7db for tuning purposes. We can provide details of this modification to anyone who is interested.

Sincerely yours,

Bob Lenkinski

R. E. Lenkinski
Manager

REL/1a

1. R.W. Dykstra and A.M. Harrison, J. Mag. Res. **46**, 338 (1982).
2. C. Brevard and P. Granger, J. Chem. Phys. **75**, 4175 (1982).



99 Ru

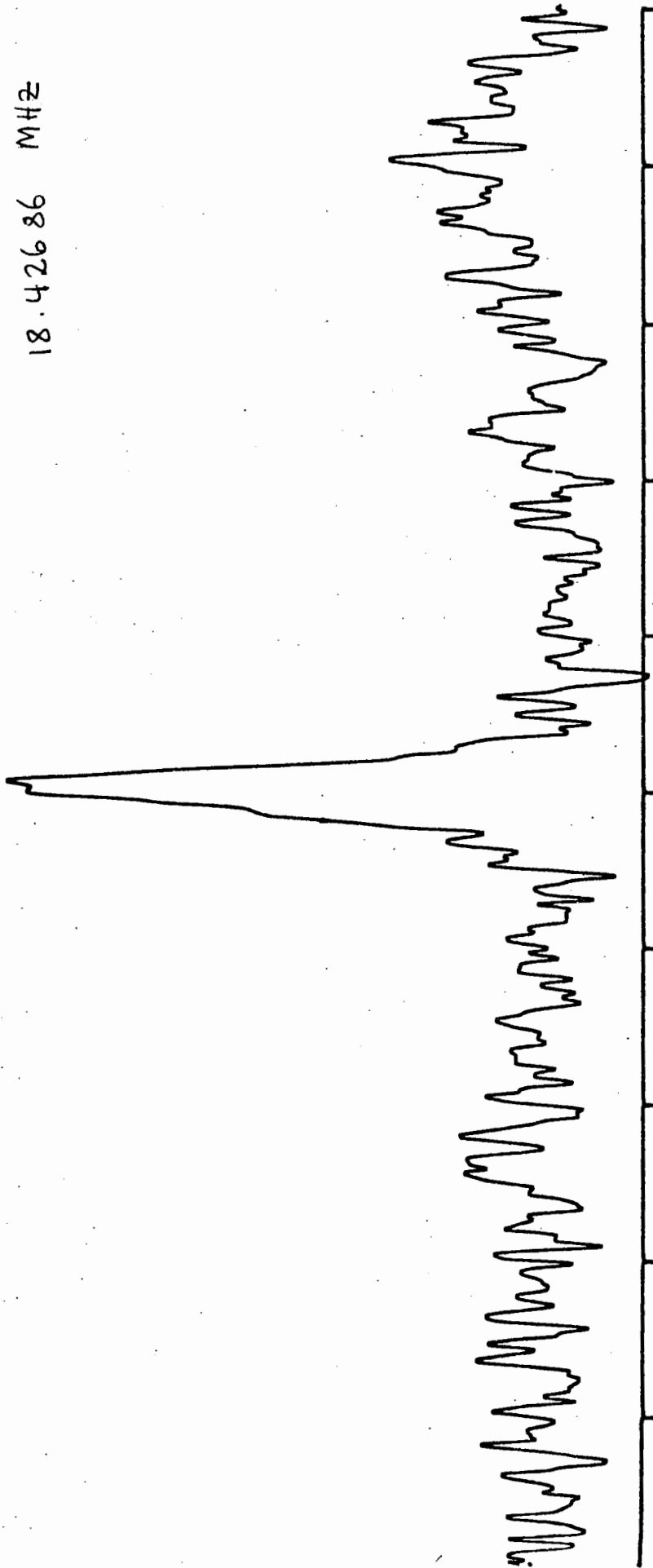
 $Ru(Bipy)_3^{2+}$

6024 SCANS

2K DATA POINTS

5000 Hz SWEEP

18.42686 MHz



500 Hz/div

200 Hz/cm

FIG. 1.

HOWARD UNIVERSITY

WASHINGTON, D. C. 20059

DEPARTMENT OF CHEMISTRY

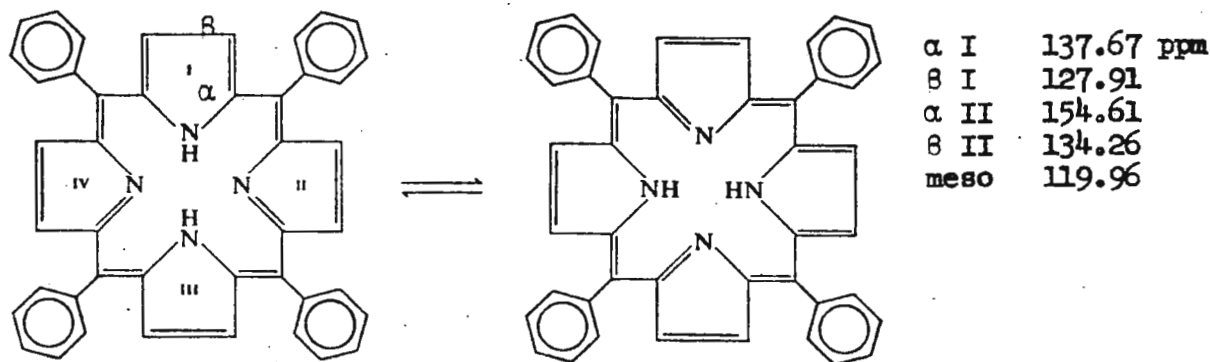
July 14, 1982

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

Dear Barry:

$^2\text{H}/^1\text{H}$ Isotope Effects on the ^{13}C NMR Spectrum of α , β , γ , δ -Tetraphenylporphyrin

The central protons in a porphyrin are strongly intramolecularly hydrogen bonded, as evidenced by the infrared stretching frequency at 3320 cm^{-1} and their slow rate of intermolecular exchange with water or alcohols. At room temperature the N-H tautomerism is rapid on the NMR time scale, at -60°C it is close to the slow exchange limit and the individual ^{13}C porphyrin resonances may be assigned (1).



When the central N-H's are exchanged for deuterium and the spectra at -60°C compared the ^{13}C resonances for the carbons in rings I and III are shifted to high field; α I, 0.2 ppm; β I, 0.05 ppm. The meso carbon resonance is only marginally effected. These shifts are normal for $^2\text{H}/^1\text{H}$ isotope effects on ^{13}C resonances. Evidently the strong intramolecular hydrogen bonding has no major influence on the magnitude of the isotope effect.

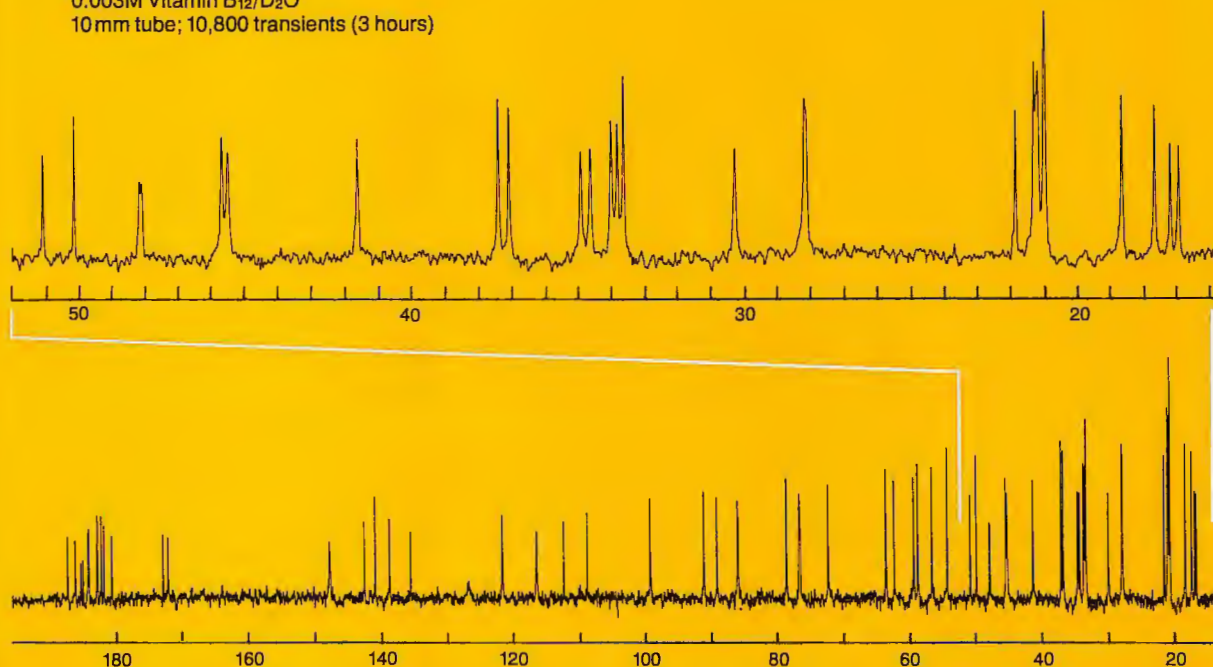
1. R. J. Abraham et al., J. C. S. Perkin II, 204 (1975).

Y. Teklu
 Y. Teklu

Sincerely yours,
C. B. Storm
 C. B. Storm

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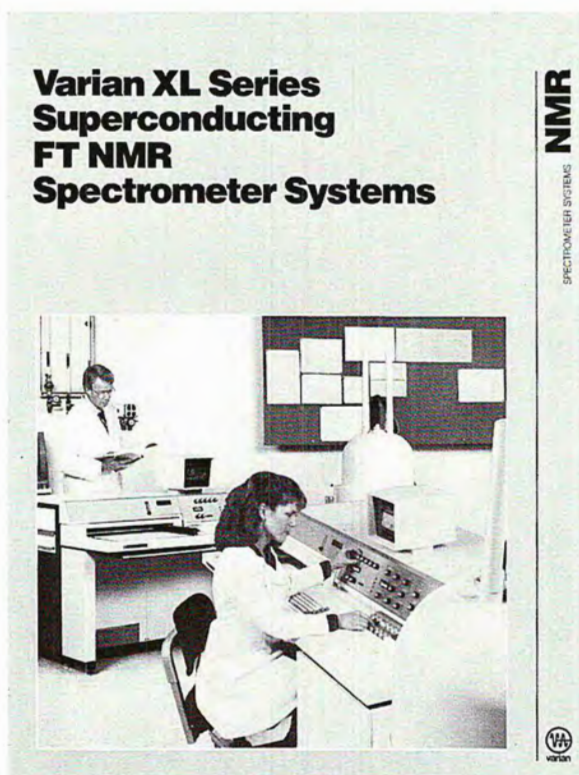
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Professor B.L. Shapiro
 Dept. of Chemistry
 Texas A + M University
 College Station, TX 77843
 USA

Gesellschaft für
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 Forschung mbH

Abteilung

Physikal.Meßtechnik

Ihre Nachricht vom
 July 6, 1982

Telefon 05 31/70 08-1

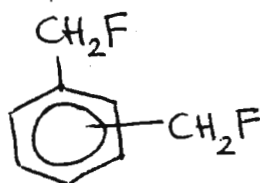
Telefondurchwahl
 05 31/70 08 306

Datum
 July 15, 1982

Determining the Relative Signs of Interbenzylic J_{FF} by Changing the Solvent

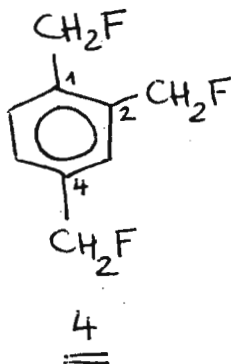
Dear Dr. Shapiro:

some time ago¹⁾, we found sizeable interbenzylic F,F-coupling constants in bis(fluoromethyl)benzenes 1 - 3 with ${}^6J_{FF}^{meta} \ll {}^5J_{FF}^{ortho}, {}^7J_{FF}^{para}$.



$$\left. \begin{array}{l} \underline{1} \text{ (ortho): } |{}^5J_{FF}| = 4.1 \text{ Hz} \\ \underline{2} \text{ (meta): } |{}^6J_{FF}| = 1.0 \text{ Hz} \\ \underline{3} \text{ (para): } |{}^7J_{FF}| = 4.8 \text{ Hz} \end{array} \right\} \begin{array}{l} \text{from } {}^{19}\text{F}\{^1\text{H}\} \\ \text{spectra in } \text{CDCl}_3 \end{array}$$

We were interested to see whether the relative signs of these couplings were the same as for the J_{PP} in the corresponding diphosphonates²⁾. However, spin tickling in the ${}^1\text{H}$ -coupled ${}^{19}\text{F}$ spectrum would have been very difficult. Therefore, we synthesized 4, expecting a tightly coupled ABC-type ${}^{19}\text{F}\{^1\text{H}\}$ spectrum which would give the relative signs from the spectral analysis.



We were displeased when we found that 4 in C_6D_6 (at 94 MHz) gave only an ABX spectrum: The shifts of F-1' and F-2' formed the AB part, so we obtained the relative signs of ${}^6J_{FF}^{meta}/{}^7J_{FF}^{para} < 0$. By experimenting with various solvents, we succeeded in producing a different ABX spectrum (in C_6D_{12}) in which F-1' and F-4' formed the AB part. This gave ${}^5J_{FF}^{ortho}/{}^6J_{FF}^{meta} < 0$. Thus,

Blatt

zum Schreiben vom 15.7.1982

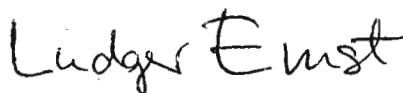
an Prof. B.L. Shapiro

GBF

${}^6J_{FF}^{\text{meta}}$ is of opposite sign to both ${}^5J_{FF}^{\text{ortho}}$ and ${}^7J_{FF}^{\text{para}}$, as is the case for the analogous J_{PP} coupling constants.

So changing the solvent saved us the otherwise required ${}^{19}\text{F}\{ {}^1\text{H}_{\text{BB}}, {}^{19}\text{F}_{\text{CW}} \}$ triple resonance experiment which we would not have been able to perform anyway because of lack of equipment.

Yours sincerely,



Ludger Ernst

- 1) L. Ernst and S. Pulmann, Org.Magn.Reson. 16, 63 (1981).
- 2) L. Ernst, TAMU-NMR-Newsletter 276, 27 (1981).

Structural and Orientational Results

 $\text{H}_1 - \text{C}_2 \equiv \text{C}_3 - \text{C}_4$

without vibrational corrections	27 °C	37 °C
r14/r12	3.404+0.002	3.401+0.001
r13/r12	2.088+0.001	2.087+0.001
Szz*	-0.171+0.001	-0.122+0.001
with vibrational corrections		
r14/r12	3.569+0.001	3.568+0.001
r13/r12	2.161+0.001	2.161+0.001
Szz*	-0.200+0.001	-0.146+0.001

* z-axis is coincident with the long axis of the molecule

References

1. S. Sykora, J. Vogt, H. Bosiger, and P. Diehl, J. Mag. Res. 36,53 (1979).
2. E. Haloui and D. Canet, Org. Mag. Res. 6, 537 (1974).
3. E. Haloui and D. Canet, Chem. Phys. Let. 26, 261 (1974).

EMORY UNIVERSITY

Department of Chemistry

1515 Pierce Drive
Atlanta, Georgia 30322
404/329-6585

July 14, 1982

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

Re: R_x Structure and Orientation of Propargyl Chloride


Dear Professor Shapiro:

As part of our continuing study of molecules oriented in liquid crystal solvents, we are currently investigating the structure of propargyl chloride (3-chloro-propyne). The proton spectrum of propargyl chloride oriented in ZLI 1167 was analyzed and the direct couplings obtained, including those of the natural abundance carbon-13 satellites. The structural analysis performed includes corrections to the direct couplings for the vibrational motion of the molecule. These corrections are generally understood to be of considerable importance for interactions involving directly bonded nuclei (1).

We have found a variation of as much as 5% between the vibrationally corrected and uncorrected distance ratios. Also, a brief temperature study was performed in which the distance ratios were found to be independent of the temperature. However, the order parameter defined as being coincident with the long axis of the molecule varied substantially with temperature. This dependency indicates a large orientation energy which is supported by the fact that the value of the orientation parameter is large. This order parameter also indicates that the long axis of propargyl chloride is oriented parallel to the optic axis of the liquid crystal, which is in agreement with the alignment observed for other acetylenic-type compounds (2,3). The structural and orientational results describing the linear portion of the molecule are provided in the table.

Sincerely,


J. H. Goldstein


E. E. Babcock



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AND BIOPHYSICS
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Lenini pstetsee 10, Tallinn 200001, USSR
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ИНСТИТУТ ХИМИЧЕСКОЙ И
БИОЛОГИЧЕСКОЙ ФИЗИКИ
АКАДЕМИЯ НАУК
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July 17, 1982 Ref.No. 33

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

Dear Professor Barry Shapiro,

"Inadequate magic in ^{29}Si NMR"

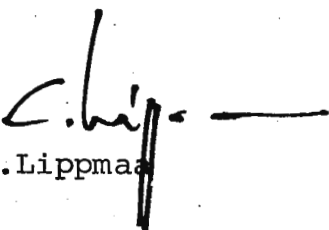
While developing the side-supported rotor probe for solid state high resolution NMR it was immediately clear that the double bullet design can be useful for both solids and liquids. The use for the study of suspensions is already mentioned in our U.S. Patent 4,254,373. We have recently used the same rotor for the study of nematic liquid crystals (OMR, in press) and solutions of proteins (Synergetics of enzyme action; to be written up). Since the whole liquid volume is located inside the rf coils and thus actively used, the sensitivity for the same amount of sample is about twice that of a conventional probe. Even if some precipitate is formed, it does not lead to any line broadenings.¹ The rf field homogeneity is excellent and since the whole sample is being measured, there are no convection and diffusion problems in relaxation studies. In order to try still other possibilities, we used this probe for the measurement of long range silicon-carbon spin-spin coupling constants using the INADEQUATE pulse sequence due to Ray Freeman.² The $90^\circ(x) - \tau - 180^\circ(y) - \tau - 90^\circ(x) - 90^\circ(x, \pm x)$ sequence worked well at the magic angle and showed that in neat triethylmethylsilane the couplings between central silicon and the ethyl carbons are 51.0 Hz and 2.2 Hz, respectively. It is very convenient that in the heteronuclear case we have to subtract two spectra that are excited by pulse sequences, identical for

the nucleus being measured with the only difference in the last 90° pulse which is applied to ^{29}Si along the x and -x axis, respectively. Thus any imperfections in the ^{13}C pulses cancel, leading to practically complete (300-fold) suppression of the central unwanted uncoupled ^{13}C lines. τ was 137 msec, which corresponds to $n = 0$ for the smaller and $n = 3$ for the larger heteronuclear coupling. The signal to noise ratio was 2.5×23 for the smaller "down-up" J doublet, registered with 2×20 4 sec scans.

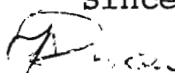
A CXP-200 NMR spectrometer was used with noise-modulated decoupling. The standard transmitter and receiver units were used for ^{13}C pulses. The ^{29}Si pulses were synthesized from the phase-shifted pulses available at 60 MHz in the HP decoupler and amplified using an Amplifier Research 200 L broadband amplifier.

With best regards,

Sincerely yours,



E. Lippmaa



J. Puskar

J. Past*

J. Schraml**

* Presently at Bruker, Karlsruhe, BRD.

** Institute of Chemical Processes Fundamentals, Prague, Czechoslovakia.

¹ M. Alla

² Ad Bax, R. Freeman and S. P. Kempell, J. Am. Chem. Soc. 102, 4849 (1980).

UNIVERSITY OF DELAWARE
NEWARK, DELAWARE
19711

DEPARTMENT OF CHEMISTRY

July 19, 1982

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

Chemical-Shift Spectra of Oriented Poly(tetrafluoroethylene)

Dear Professor Shapiro:

It appears to be my turn to report for the Blue Hen NMR Complex. As you know, many spectroscopists spin solid samples at the magic angle to make their spectra look like those of a liquid. While this produces a lovely spectrum, it discards some very useful solid-state information, namely the chemical-shift dispersion. Slow-spinning sideband analysis can give information back on the dispersion in random polymers.

The chemical shift dispersion can, like many other anisotropic interactions, be put to good use in analyzing the effects of partial alignment, in a manner analogous to studies of deuterium spectra by Spiess, Samulski and others. We have looked at the ^{19}F multipulse spectra of PTFE, as are shown in the left side of the figure as a function of the angle, β , between H_0 and the direction of uniaxial stress. The right side shows the calculated spectra for the same angles for an appropriate probability distribution of crystallite axes. The calculated central region deviates from the experimental central region only by virtue of the presence of the resonance of the nuclei in the regions of the amorphous sections of the sample. Otherwise, the fit is quite good. In principle, one should be able, by selection, to obtain spectra of both the amorphous and crystalline regions. Thus, one could study orientation in both regions in a manner similar to deuterium studies.

The study of chemical shift dispersions may be useful for characterizing orientations in various polymer blends, as well as in studying processes such as shrinkage and curing. The main requirement is the ability to observe a single resonance, either by virtue of simplicity of the polymer or enrichment. Of course, one must not spin the sample.

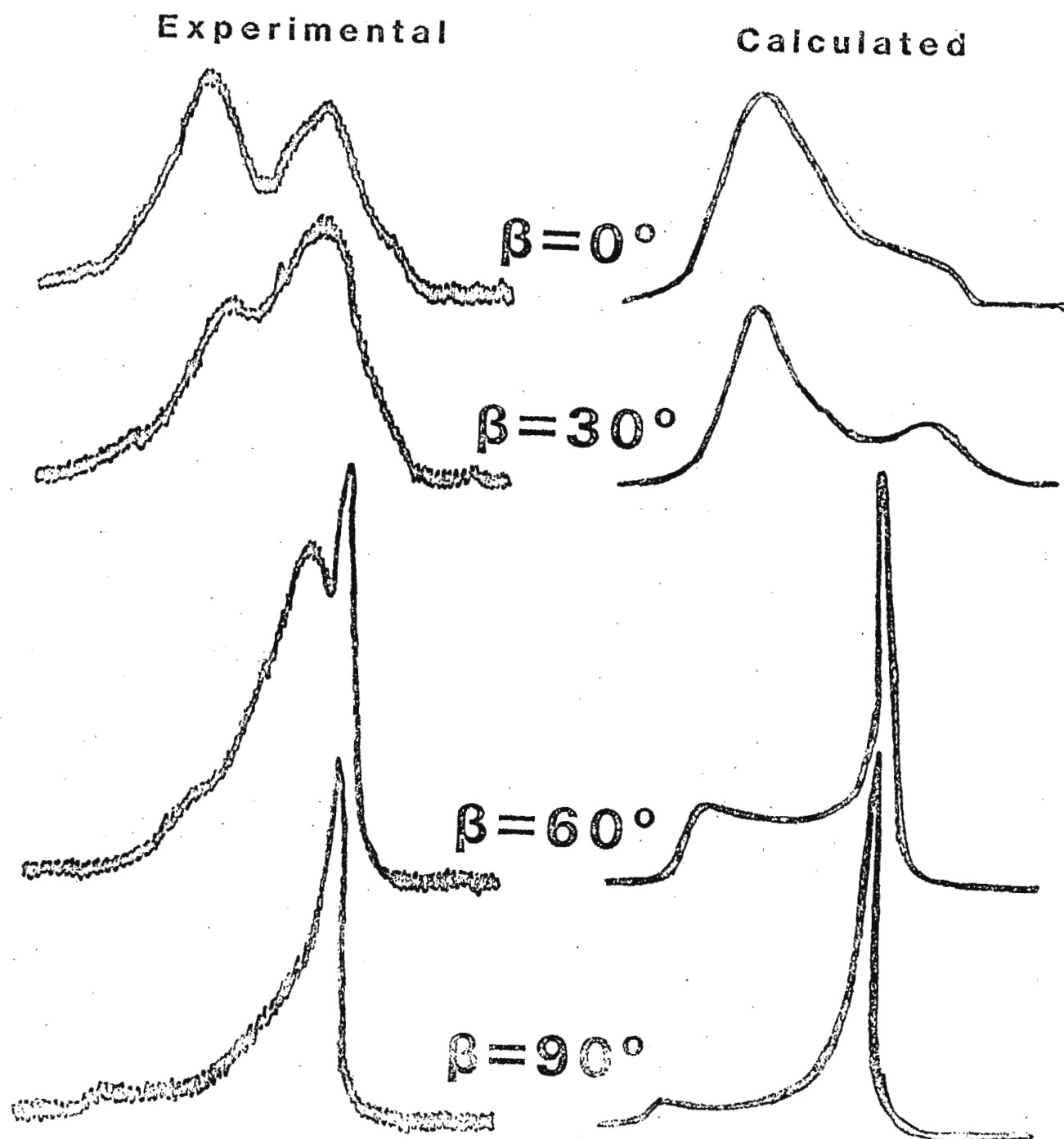
Yours truly,

Cecil Dybowski

Cecil R. Dybowski
Associate Professor of Chemistry

sr

Computer Simulation of Spectra





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Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
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Texas 77843
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uw kenmerk

uw brief van

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datum

July 19, 1982

bijlage(n)

onderwerp

Dear Professor Shapiro,

Evidence for charge-transfer complexes by Electric Field NMR

Polar molecules in a liquid are aligned by a strong electric field. In a molecule like nitrobenzene- d_5 (fig. (1)) this alignment becomes visible by the quadrupolar line-splittings in the 2H NMR spectra. For neat nitrobenzene- d_5 the ratio r of the para-deuterium splitting and the ortho (or meta) deuterium splitting is close to eight. Assuming the same q.c.c. for the different 2H nuclei and a zero asymmetry parameter of the electric field gradient tensor, this ratio can very well be understood in terms of the angles γ between the C-D bonds and the direction of the dipole moment (namely in the aromatic plane, parallel to the symmetry-axis).

Deviations from the value $r = 8$ in a number of binary mixtures with nitrobenzene have previously been interpreted in terms of small changes in geometry and changes in the asymmetry parameter η ¹⁾. The orientation of the dipole moment in the molecular frame was assumed to be the same as described for neat nitrobenzene.

Recently we studied binary mixtures of nitrobenzene- d_5 and mesitylene (fig. (2)). The value of r was as high as about 20 for a mixture with 24 mole% nitrobenzene and about 40 for a mixture with 54 mole% nitrobenzene. Changes in the molecular geometry and of η have to be improbable in order to account for the high r values: $\gamma_m \approx 53^\circ$, $\eta_{o,m} \approx -0,46$ (24 mole % mixture). When, however, we allow the dipole moment to turn away from the direction assumed

1) T.M. Plantenga, P.C.M. van Zijl, C. MacLean, Chem. Phys., 66, 1, 1982

in pure nitrobenzene and calculate the ratio r as function of the angles α (relative to aromatic plane) and β (relative to symmetry axis), values higher than 8 are indeed possible. (fig. (3)). The reason for this change in direction of the dipole moment is no doubt molecular association between mesitylene and nitrobenzene. The origin of this association is charge-transfer interaction, mesitylene being the electron donor and nitrobenzene the acceptor.

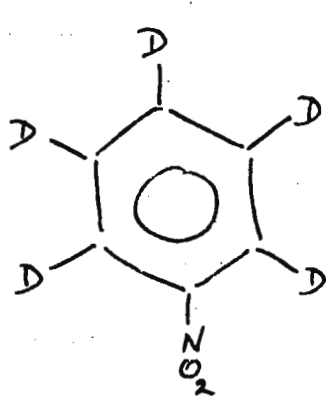
So, the species we are aligning in the electric field is in fact the charge-transfer complex between mesitylene and nitrobenzene, having an effective dipole moment that has turned away from its pure nitrobenzene direction.

We are now investigating ^{14}N NMR spectra of the same mixture. The nonzero asymmetry parameter for the nitrogen field gradient tensor offers in principle extra information concerning α and β . Our final goal is to solve for α and β and then we have an NMR tool to determine the direction of dipole moments in molecular associates.

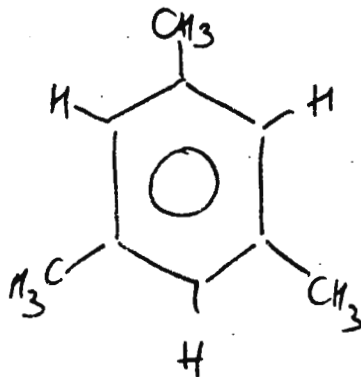
Sincerely yours,

C. MacLean

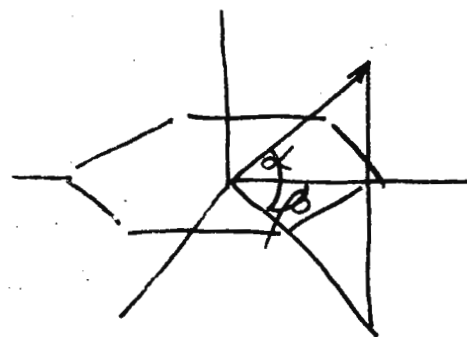
B.H. Ruessink



①



②



③



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Departamento de Física

Ciudad Universitaria, P. 1

1428 Buenos Aires, Argentina

Buenos Aires, July 20, 1982

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

Dear Prof. Shapiro:

"Transmission Mechanisms of spin-spin coupling constants"

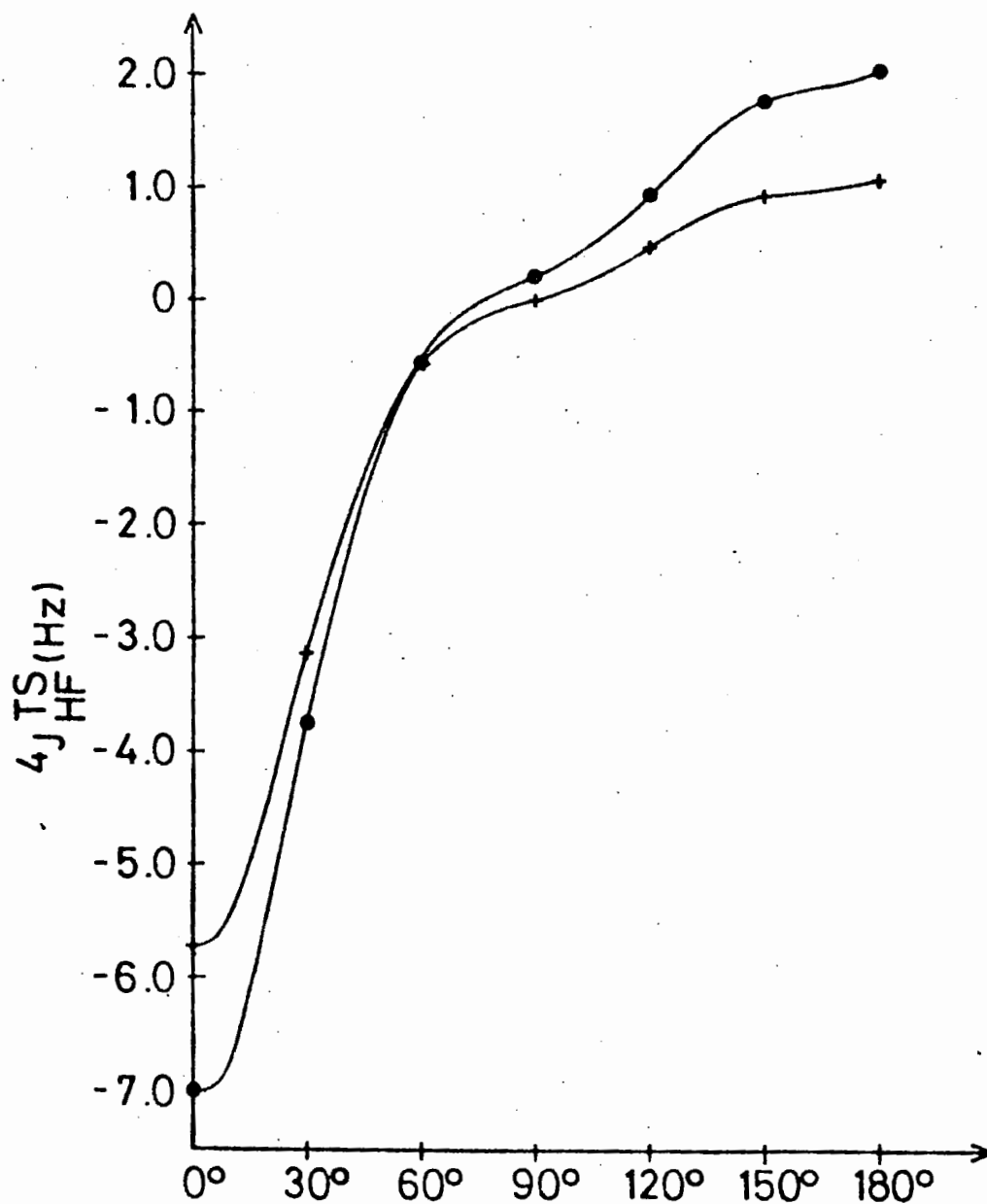
In our Laboratory we were, during the last few years, devoting much work to study transmission mechanisms of spin-spin coupling constants. In this way, we introduced the ideas of performing partially restricted molecular orbital calculations (PRMO). At the INDO and MNDO levels of approximation, we have already reported a series of results (1). At present, we have reasons to believe that π -transmitted components calculated at the INDO level of approximation are, in many instances, reliable in an almost quantitative sense. When the PRMO ideas were applied to study through-space transmitted coupling constants, very promising results were also found (2) at the same level of approximation. However, from the very beginning we were quite aware of two shortcomings underlying this method. They are, respectively, a lack of a sound theoretical base, and that no possibilities are envisioned to extend this method to more accurate calculation schemes. Very recently, a breakthrough to these problems was achieved by one of our collaborators, Lic. A. R. Engelmann, at present working in the Quantum Chemistry Group at the University of Uppsala. The novel approach is to use inner projections of the polarization propagator. For the time being it was formulated within the Coupled Hartree-Fock approximation (CHF). The first reported results were obtained using the INDO method (3). As an example of this approach, results for through-space components of F-H couplings are shown in the figure, where they are compared for cis-fluoropropene and ortho-fluorotoluene. The peculiar behaviour of this component in both compounds indicates that several through-space mechanisms are operating, all of them increasing in magnitude when shortening the C-C bond distance when going from the aromatic to the vinylic compound. This behaviour strongly supports the physical meaning of the through-space interaction calculated with this method.

Please, credit this contribution to the subscription of Prof. V. J. Kowalewski.

- 1) A. R. Engelmann, R. H. Contreras and J. C. Facelli, Theoret. Chim. Acta, 59, 17 (1981); A. R. Engelmann and R. H. Contreras, QCPE Bull. 2, 14 (1982); J. C. Facelli, C. G. Giribet and R. H. Contreras, Org. Magn. Reson., in press; G. E. Scuseria, A. R. Engelmann and R. H. Contreras, Theoret. Chim. Acta, 61, 49 (1982); A. R. Engelmann, G. E. Scuseria and R. H. Contreras, J. Magn. Reson. In press.
- 2) D. G. de Kowalewski, R. H. Contreras, A. R. Engelmann, J. C. Facelli and J. C. Durán, Org. Magn. Reson., 17, 199 (1981).
- 3) A. R. Engelmann and R. H. Contreras, 4th International Congress of Quantum Chemistry, Uppsala, June 14-19 (1982).

Sincerely yours,


 R. H. Contreras



The through-space components of the corresponding four-bond F-H coupling constants in cis-fluoro-propene and ortho-fluoro-toluene are compared for different values of the dihedral angle θ . ● : cis-fluoro-propene; + : ortho-fluorotoluene.

STATE UNIVERSITY LEIDEN - THE NETHERLANDS
GORLAEUS LABORATORIES - DEPARTMENT OF CHEMISTRY

P.O. Box 9502, 2300 RA Leiden

Phone: 71-148333, extension: 3921

Your letter:

Your ref.:

Our reference: Dr. J. Lugtenburg

Subject:

LEIDEN, July 22, 1982.

Prof. Bernard L. SHAPIRO

Department of Chemistry
Texas A & M University

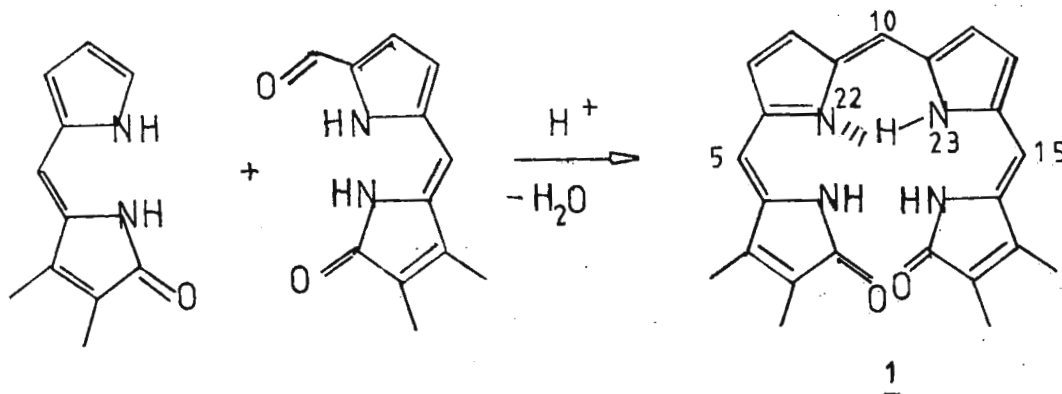
College Station
TX 77843

U.S.A.

Dear Professor Shapiro,

4Z,9Z,15Z-2,3,17,18-Tetramethyl-1,19-[21H,24H]-bilindione

For our studies in the bile pigment field we needed a model for biliverdin. This model 2,3,17,18-tetramethyl-1,19-[21H,24H]-bilindione (1) could be obtained according to the reaction scheme.



1 Is obtained as a blue crystalline material (λ_{max} (MeOH): 359 nm, 601 nm) with a molecular ion of m/z : 386.1743 (calculated 386.1743). The 300 MHz 1H NMR spectrum in $CDCl_3$ shows a symmetrical structure due to a N_{22} to N_{23} hydrogen shift, that is rapid on the NMR time scale.

¹H NMR data of 1 (CDCl₃; δ rel. to TMS)

δ	multiplicity	number of H's	assignment
1.91	s	6	2 + 18 CH ₃
2.12	s	6	3 + 17 CH ₃
6.03	s	2	5 + 15 H
6.55	AB	2	8 + 12 H
6.79	s JAB=4.2 Hz	1	10 H
6.95	AB	2	7 + 13 H
8.5	bs	3	21 + 22 + 24 H

The system can occur in two symmetrical isomeric forms. That it occurs in the 4Z,15Z form could be established by the NOE between 3 + 17 CH₃ and the 5 and 15 H. The central bond is also in the Z configuration because otherwise the NMR spectrum could not have been so symmetrical and all known pyrromethenes, the central part of the molecule, occur in the Z form; 1 has the 4Z,9Z,15Z form. This agrees well with the crystal structure of biliverdin itself which has the 4Z,9Z,15Z configuration (see W.S. Sheldrick, J.C.S. Perkin II, 1457, (1976)).

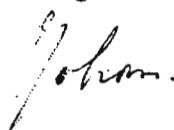
Sincerely,

C. Erkelens

J.A. de Groot

J. Lugtenburg





D. CANET
Professeur

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

Frequency dispersion of water proton T_1 in tissues (in vitro)

July 23, 1982

Dear Professor Shapiro

Thank you for your numerous remainders. During the last few months, we have performed, among other things, a series of water proton T_1 measurements in different mice tissues as a function of the Larmor frequency. This has been made possible by our old HX-90 magnet and we could easily investigate the 6-90 MHz range. It turns out that the data (at ambient temperature) pertaining to a given tissue can be rationalized by :

$$A/T_1 = A/\sqrt{\nu} + B$$

Within a two state model, A is related to "bound" water whereas B leads to the value of "free" water relaxation time as determined by progressive deshydration of a muscle tissue (B.M. FUNG Biochim. Biophys. Acta 497, 317 (1977)).

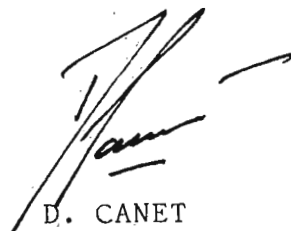
This is exemplified in the joined figure which shows relaxation data of one of the groups studied (tumor bearing C3 H male mouse).

We are currently investigating the behavior of non-freezable water (around -8°C) in order to have a better insight in the meaning of the A and B parameters.

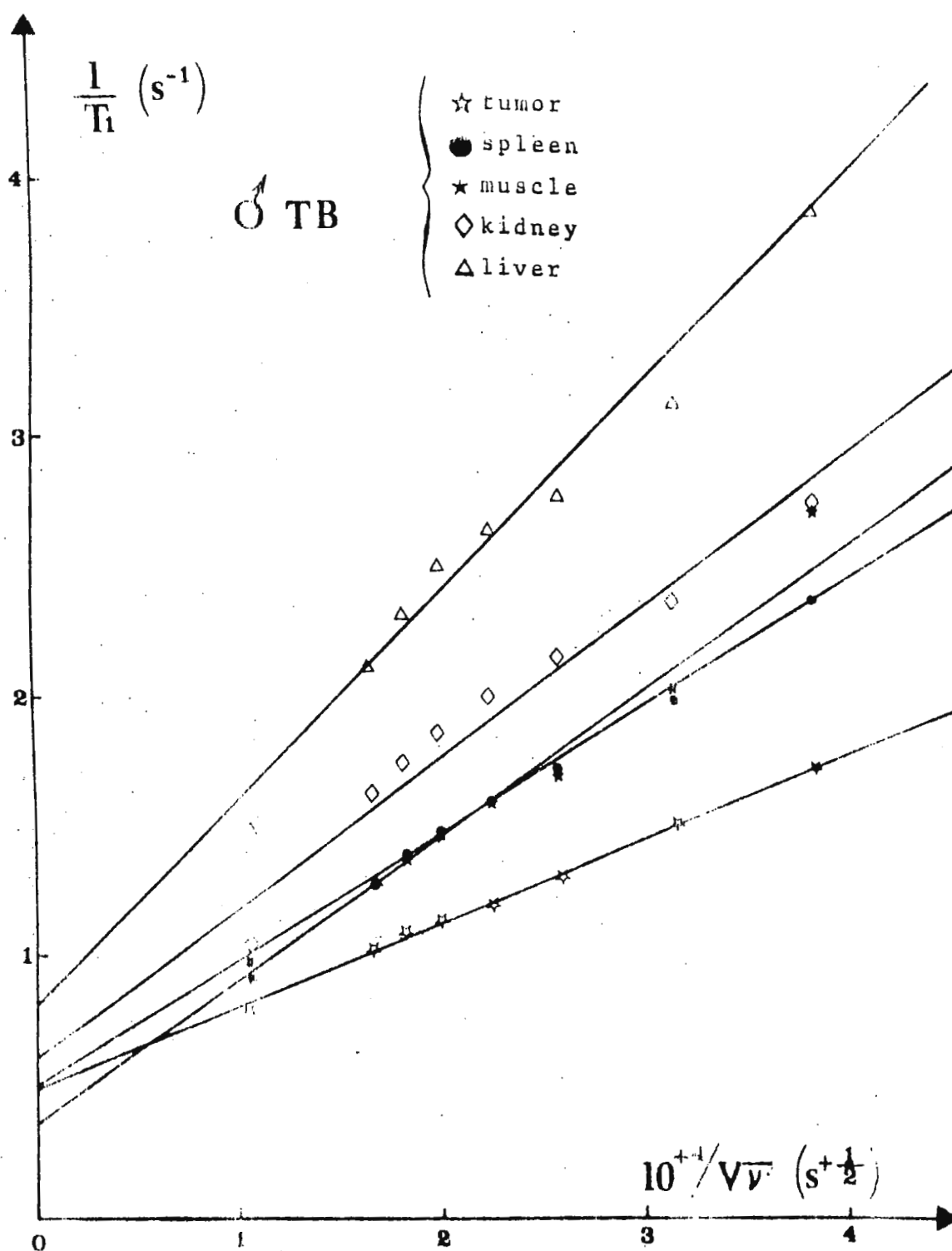
Yours sincerely,



J.M. ESCANYE



D. CANET





HALL-ATWATER LABORATORIES

MIDDLETOWN, CONNECTICUT 06457

TEL.: (203) 347-9411

DEPARTMENT OF CHEMISTRY

July 24, 1982

"Decoupling is Better than Refocusing in Proton-Carbon
Two-Dimensional Correlation Spectroscopy"

Dear Barry:

Many dim years ago the gyromagnetic ratio of carbon-13 in solution was determined by observing the collapse of the proton multiplet of enriched methyl iodide when an rf field was applied near the resonant frequency of the carbon-13. This pioneering experiment of Royden's, *Phys. Rev.* 96, 543 (1954), is an NMR classic and her experiment has now been superseded by heteronuclear two-dimensional NMR. When correlating the chemical shifts of carbon-13 and protons it is common to decouple the carbon-13 from protons and to refocus the carbon-13 coupling of the protons as shown in pulse sequence A. This method can lead to unwanted signals in the data.

Some spectra obtained with refocusing of the heteronuclear coupling are shown in the figure. It is seen that there are anomalous peaks at the chemical shifts of nearby protons. The anomalous peaks can have intensity of 1/3 or more of the proper signals. These blights in the data arise from strong coupling of in the carbon-13 satellite subspectra. That is, the high field subspectrum of H_2 is strongly coupled to H_3 and the high field subspectrum of H_3 is strongly coupled to H_4 and so on. Refocusing does not remove the strong coupling effects since it does not affect precessional frequencies.

The spectra can be cleaned up by the substitution of carbon-13 decoupling for carbon-13 refocusing using pulse sequence B. The resulting data shows the superiority of decoupling. A MLEV-4 sequence was used for carbon-13 decoupling. A more thorough presentation has been submitted to *J. Magn. Reson.*

Sincerely,

Philip H. Bolton

Figure notes: Bottom shows the timing for pulse sequences A and B. The delay times are the usual ones. The phase sensitive data is for 1-pentanol in $CDCl_3$ and contrasts the signals obtained using refocusing with those using decoupling. A XL-200 was used for the experiments.

REFOCUSED

DECOUPLED

287-48

C_5

1H_5

C_4

1H_4

C_3

1H_3

C_2

1H_2

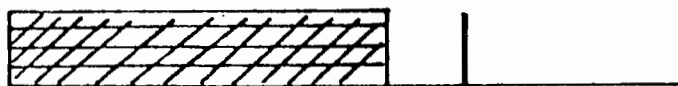
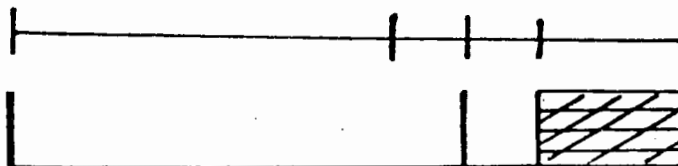
t_1

$\Delta_H \Delta_C$

AT



A



B

Chairman: J. Emsley, Dept. of Chemistry, University of Southampton, Southampton.
Telephone (0703) 559122

Secretaries: I.R. Jones, Bruker Spectrospin, 209 Torrington Avenue,
Coventry CV4 8HN. Telephone (0203) 463770
D. Shaw, Oxford Research Systems Ltd., Osney Mead,
Oxford OX2 0DX. Telephone (0865) 724240

Treasurer: P. Beynon, Kodak Ltd., Research Division, Harrow,
Middx HA1 4TY. Telephone 01-427-4380.

NMR DISCUSSION GROUP



JWE/HN

20th July, 1982.

Professor B.L. Shapiro,
Department of Chemistry,
TEXAS A and M UNIVERSITY,
College Station,
Texas - 77843,
UNITED STATES OF AMERICA.

Dear Barry,

6th International N.M.R. Meeting at Edinburgh
10th - 15 July, 1983

The meeting will comprise eight symposia with the following Chairmen and Invited Speakers.

Symposium	Chairman	Invited Speakers	
1. Applications in Biology	J. Feeney	I. Campbell	K. Wuthrich
2. Applications in Organic Chemistry	J. Saunders	I Staunton A.I. Scott	D.H. Williams
3. N.M.R. Imaging	D. Shaw	W. Moore	G. Radda
4. N.M.R. Methods	G. Morris	R. Freeman	R. Kaptein
5. New Developments	N. Boden	R.R. Ernst	A. Pines
6. High Resolution in Solids	R.K. Harris	C.A. Fyffe	D.M. Grant
7. Applications in Inorganic Chemistry	G.E. Hawkes	P.D. Ellis	P. Sadler
8. Relaxation Studies	K.J. Packer	M. Bloom	V. McBrierty

... continued ...

From Dr. J.W. Emsley,
Southampton University.

To Professor B.L. Shapiro,
Texas A and M University.

Oral presentations will be confined to the above topics and anyone wishing to have a talk considered for inclusion in the program should send an abstract to the appropriate chairman, or to me. There will be a Poster Session which will be open to any topic in N.M.R. and intending contributors should send abstracts to me.

The first circular for the meeting will be available soon and will be sent to the attendees at the York and Exeter meetings. Anyone else wishing to receive the circular should write to Dr. John F. Gibson, The Royal Society of Chemistry, Burlington House, Piccadilly, London, W1V 0BN.

Best wishes,

Jim

J. W. EMSLEY.



UPPSALA UNIVERSITET
FYSIKALISK-KEMISKA INSTITUTIONEN
UPPSALA

Uppsala 20/7 1982

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

JEOL equipment wanted

Dear Professor Shapiro,

I would be interested in hearing from anyone who would like to sell a used JEOL FX-100, in whole or in parts.

Sincerely,

Peter Stilbs

/Peter Stilbs/

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Thunbergsvägen 5

Telefon
018-13 94 60

TEXAS A&M UNIVERSITY

DEPARTMENT OF CHEMISTRY

COLLEGE STATION, TEXAS 77843

2 August 1982

Have you initiated payment (and/or informed us) for
the October 1982 - September 1983 subscription year?
If not, please do so now! Thanks.

B. L. Shapiro



Apples-to-apples comparison of NMR sensitivity

To make a long story short, Nicolet's 300 MHz spectrometer offers the industry's highest ^{13}C sensitivity by a significant margin.

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This is an apples-to-apples comparison, since both of the S/N specifications above are based on ASTM samples; and as you can see, the Nicolet 300WB delivers 67% more sensitivity. How do we *know* our 500:1 S/N is for real? We do it by computer determination. Computer calculated values are inherently more precise, because RMS noise is calculated directly from the digitized data. In fact, Nicolet's computerized S/N ratio calculation is the accepted industry standard. With the Nicolet 300WB you can reduce run time, and you'll still be able to identify smaller peaks.

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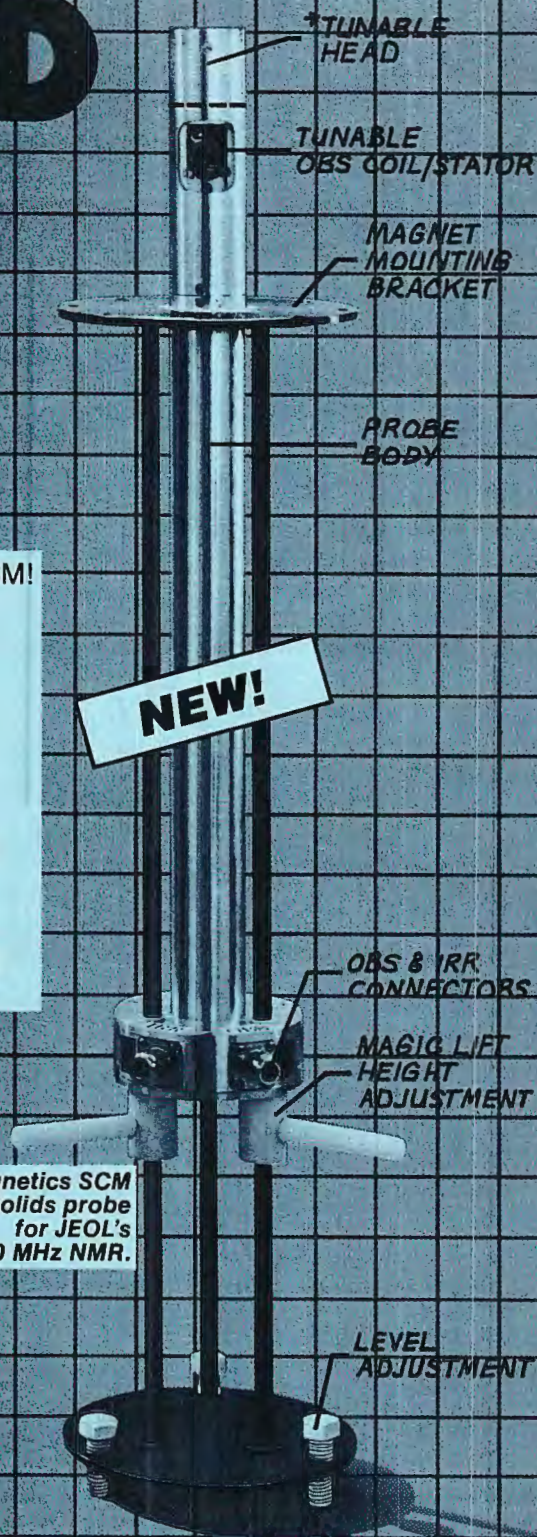
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