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Newsletter

CT
No. 240

September, 1978

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DEADLINE DATES: No. 241: 2 October 1978
 No. 242: 6 November 1978

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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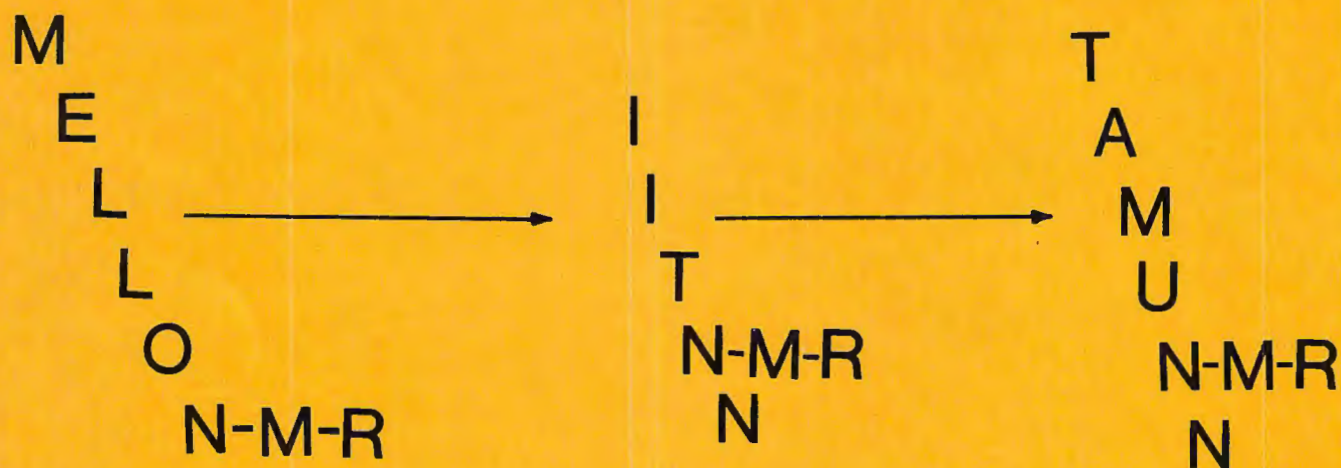
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No. 240, THE 20TH BIRTHDAY ISSUE

SEPTEMBER 1978

SEE PP. 46 - 59

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

August 7, 1978

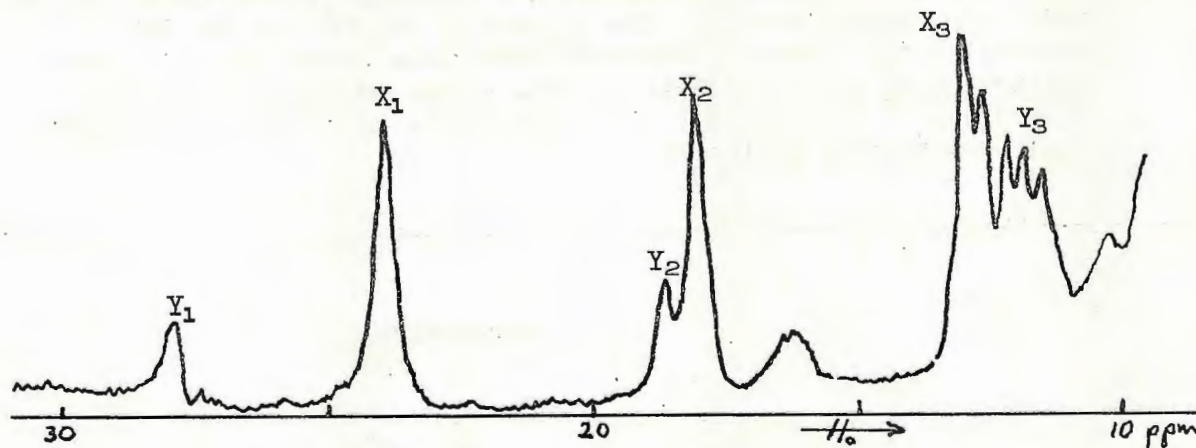
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Molecular Heterogeneity in Hemoproteins/Postdoctor position available

Dear Barry,

The general belief is that hemoproteins reconstituted with chemically modified porphyrins retain a unique solution structure, as found for the native proteins. Current studies in our laboratory, however, are indicating that this is generally not the case.

Sperm whale myoglobin reconstituted with deuteroporphyrin IX, deut-Mb, yields a proton nmr spectrum in both the deoxy ($S = 2$) and met-cyano ($S = 1/2$) forms which is consistent only with two species. The downfield portion of the trace for deut-metMbCN, where the porphyrin methyls resonate, is illustrated below. Specific



deuterium labeling (in collaboration with K. M. Smith of our Department) reveals that X_1 , X_2 , X_3 are methyls for the major isomer, while Y_1 , Y_2 , Y_3 are methyls for the minor isomer. Since the set of X and Y peaks interconvert readily, the two forms represent different versions of the same protein. The nature of the deuterium labeling pattern indicates that the two forms differ by having their porphyrin oriented differently by 180° .

Our current efforts are directed toward characterizing the thermodynamics and kinetics of the interconversion between the two forms and the consequence of this molecular heterogeneity for oxygen binding.

Postdoctoral Position Available

Two positions to start between October 1, 1978 and March 1, 1979, are open in my research group. Our present work focuses on the characterization of the molecular/electronic structure of hemoproteins using a variety of ^2H and ^{13}C labeled porphyrins, and the use of extrinsic metal ion probes to assign specific resonances in proteins.

We have available excellent nmr equipment with the recent acquisition of a narrow-bore Nicolet 360 MHz and wide-bore Nicolet 200 MHz spectrometers, as well as our "old" Jeol PFT-100. Probes include ^1H (100, 200, 360 MHz), ^2H (55 MHz), ^{13}C (25, 50 MHz) ^{31}P (40.5, 81 MHz) and ^{19}F (188 MHz).

The candidates should have a strong interest in biophysical chemistry. Some experience in nmr spectroscopy and/or protein handling is highly desirable but not absolutely necessary. The appointments are for one year and are renewable for a second year by mutual agreement. The stipend is \$9,500-\$10,500 depending on experience. Potential candidates should send me their curriculum vitae and arrange to have forwarded three letters of reference. The University of California is an Affirmative Action/Equal Opportunity Employer.

Sincerely,



Gerd N. La Mar
Professor of Chemistry
Co-director, UCD Biological
Magnetic Resonance Facility

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DEPARTMENT OF CHEMISTRY

DAVIS, CALIFORNIA 95616

August 7, 1978

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

NMR Staff Research Associate Position Available

Dear Barry,

Our new Biological Magnetic Resonance Facility (Nicolet narrow-bore NT-360 and wide-bore NT-200) is seeking a candidate for the NMR Staff Research Associate position described below. The position is to back up our Operation Manager who is in charge of the Facility.

STAFF RESEARCH ASSOCIATE to operate NMR instruments in Biological Magnetic Resonance Facility consisting of superconducting 200 and 360 MHz Spectrometers. Duties involve consultation with potential users, sample preparation, running spectra, and interpretation of spectra; collaborative research is encouraged. Also included are routine maintenance, and training and scheduling users under supervision of faculty. Candidate must have at least B.S. degree in a physical science and four years experience in spectroscopy, at least two in FTNMR and preferably in superconducting systems, and a working knowledge of FTNMR principles; some experience in rf electronics and/or computer programming is desirable. Starting salary will be \$16,032-17,568 dependent upon qualifications and experience. Send resume and three letters of reference to Prof. G. N. La Mar, Department of Chemistry, University of California, Davis, CA 95616. The final filing date of application will be October 1, 1978. The University of California is an Affirmative Action/Equal Opportunity Employer.

Sincerely,

Gerd N. La Mar
Professor of Chemistry
Co-director, UCD Biological
Magnetic Resonance Facility

GNL:jkg

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312-420-5111

August 10, 1978

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

Dear Barry:

1,4-cyclohexadienes and the Dihomoallylic Coupling Constant

In the past few years, the relationship between the conformation of 1,4-cyclohexadienes and the dihomallylic coupling constant has been a topic of considerable interest.¹ We have been studying two closely related systems; 1,4-dihydrophthalic acid (I) and 2,5-dihydrotrimellitic acid (II). Compound I gives a spectrum similar to those reported in the literature¹ in that H_4 and H_4' have identical chemical shifts and most of the coupling constants were too small to be resolved. Spins 1, 3, 4 and 4' combine to give an AM_2X spectrum with the coupling constants $J_{1,4} = J_{1,4'} = 6.8$ and $J_{3,4} = J_{3,4'} = 3.8$. All other couplings were too small to be resolved. The fact that $J_{3,4} = J_{3,4'}$ indicates that the $H_4-C_4-H_4'$ bond angle is bisected by the C_3-H_3 bond and this implies a planar ring structure. The ratio of the dihomallylic coupling constants, $J_{1,4}/J_{1,4'}$, is unity which does not agree with the value 1.29 determined experimentally¹ and by INDO calculations^{2,3} for a planar system. However, H_1 , H_4 , and H_4' probably form a deceptively simple ABX pattern where $J_{14} \neq J_{14'}$, a problem common to these systems.⁴

Compound II, in stark contrast to compound I, gave a well resolved spectrum in which all couplings could readily be obtained. Only the value of $J_{2,6}$ was not directly observable. This value was obtained by varying $J_{2,6}$ until the calculated lineshape (Nicolet NMRCL program) for the H_2 resonance agreed with the experimental lineshape. The signs of the coupling constants were determined by INDOR and $J_{5,5'}$ was assumed to be negative. To our knowledge, this is the first determination of the sign of the dihomallylic coupling. The value of $J_{2,5}/J_{2,5'}$ is consistent with a highly puckered boat conformation¹ for II with the CO_2H group at C_2 in a quasiequatorial position. This assignment is supported by the relative magnitudes of the vicinal couplings. A surprising and unexplained result was the size of $J_{3,6}$.

Compound II was reacted with trifluoroacetic anhydride to give III. It is interesting to note that $J_{2,5}$ and $J_{2,5'}$ both increase in magnitude but the ratio $J_{2,5}/J_{2,5'}$ reduces to 1.9 from 4.1 in II. Also $J_{2,3}$ and $J_{2,6}$ both increase in size. This is probably due to a distortion of the boat format due to formation of the anhydride

Professor Bernard L. Shapiro
August 10, 1978

between the carboxyl groups at C₁ and C₂.

We are attempting to make the anhydride of I since that should convert the planar ring to a boat conformation and give further data on the dihomoaallylic coupling.

Sincerely,

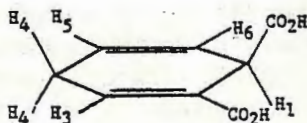
Joe Ray

G. J. Ray
Mail Station F-9

Bill Dunlap

R. W. Dunlap
Mail Station F-9

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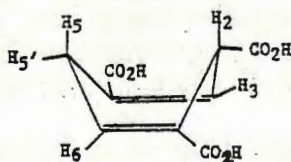


$\delta_1 = 4.06$
 $\delta_3 = 7.15$
 $\delta_4 = 2.95$
 $\delta_4' = 2.95$
 $\delta_5 = 5.90$
 $\delta_6 = 5.90$

$J_{1,3} \sim 0$
 $J_{1,4} = -6.8$
 $J_{1,4'} = 6.8$
 $J_{1,5} = 0$
 $J_{1,6} = 0$

$J_{3,4} = 3.8$
 $J_{3,4'} = 3.8$
 $J_{3,5} = 0$
 $J_{3,6} = 0$

$J_{4,4'} = 0$
 $J_{4,5} = 0$
 $J_{4,6} = 0$
 $J_{5,6} = 0$

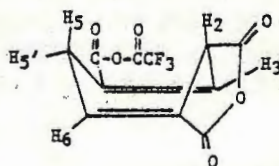


$\delta_2 = 3.72$
 $\delta_3 = 7.56$
 $\delta_5 = 2.77$
 $\delta_5' = 3.13$
 $\delta_6 = 7.23$

$J_{2,3} = -0.6$
 $J_{2,5} = 10.5$
 $J_{2,5'} = 2.9$
 $J_{2,6} = 0.2$

$J_{3,5} = 0.7$
 $J_{3,5'} = 0.0$
 $J_{3,6} = 1.3$

$J_{5,5'} = -19.6$
 $J_{5,6} = 3.1$
 $J_{5',6} = 6.1$



$\delta_2 = 4.03$
 $\delta_3 = 7.54$
 $\delta_5 = 2.84$
 $\delta_5' = 3.33$
 $\delta_6 = 7.73$

$J_{2,3} = 3.3$
 $J_{2,5} = 18.2$
 $J_{2,5'} = 9.6$
 $J_{2,6} = 1.0$

$J_{3,5} = 1.1$
 $J_{3,5'} = 0$
 $J_{3,6} = 1.0$

$J_{5,5'} = -19.6$
 $J_{5,6} = 2.7$
 $J_{5',6} = 6.4$

- (1) P. W. Rabideau, *Accts. of Chem. Res.* 11, 141(1978).
- (2) P. W. Rabideau, *et al.*, *J. Chem. Soc., Perkin Trans. 2*, 842(1977).
- (3) J. L. Marshall, *et al.*, *J. Am. Chem. Soc.*, 99, 321(1977).
- (4) J. L. Marshall, *J. Org. Chem.*, 35, 2038(1970).



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מחלקת איזוטופים

August 8, 1978

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

Title: Assignment of Secondary Carbons

Dear Prof. Shapiro:

Recently, Dr. K. Roth (1) has presented, yet another method, whereby identification of secondary carbons is made possible, using $^{13}\text{C}\{\text{H}\}$ Noise Off-Resonance Decoupling (NORD). It is based on the fact (2) that at low decoupler power the triplet component of an A_2X spin system is smeared out, while the singlet component is not being affected. Thus, sharp signals for secondary carbons can be observed. The reduction of the effective decoupler power is obtained by placing the decoupling band at an off-resonance position.

We have been using this technique for sometime now in our lab, but with a minor difference. Instead of obtaining a reduction in the effective decoupler power by way of choosing an appropriate decoupler position, we employ on-resonance conditions and in fact reduce the decoupler output power.

Using on-resonance conditions with reduced decoupler power has a number of advantages: a) Uniformity of the effective decoupler power over all the spectrum, enabling better distinction between secondary carbons bearing equivalent protons and those bearing non equivalent protons. b) It is possible to establish an optimum decoupler power for a given family of compounds. c) Methyl and methine carbons are smeared out simultaneously (see spectrum). d) The On-Resonance Partial Decoupling (ORPD) method is easy to perform, and it is adaptable to all FTNMR instruments including "antiques", where the decoupler position is not being controlled by software gear.

Finally the use of this technique provides an additional method for carbon peak assignment which is sometimes superior to the usual Single Frequency Off-Resonance Decoupling (SFORD) method. In particular, for those

cases where the assignment is hempered by severe overlap of multiplets (e.g. steriods).

Please credit this modest contribution to the account of Dr.
R. Poupko.

Sincerely yours,

Elisha Berman

Elisha Berman

(1) K. Roth, Org. Mag. Resonance, 10, 56 (1977).

(2) R.R. Ernst, J. Chem. Phys., 45, 3846 (1966).

90% Ethyl Benzene

1 pulse (90°)

Decoupler Band ~ 1500 Hz

Decoupler Power:

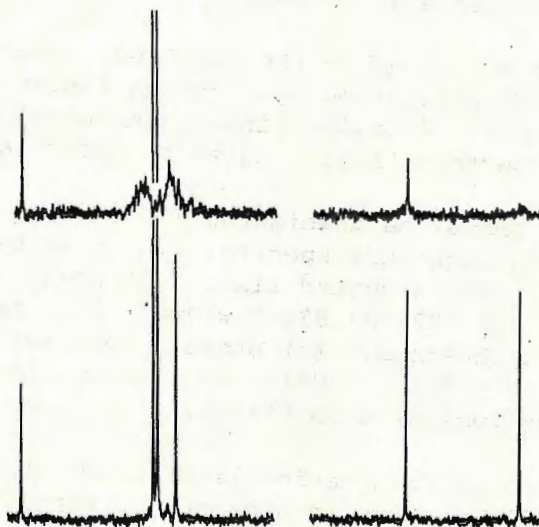
Upper = 0.1 V

Bottom = 5.0 V

S/N Reuction:

Experimental = 4.5

Theoretical = 4.0



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BMNC/78/31

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

Dear Professor Shapiro

An order of magnitude better, or who needs phase angles?

The letter from the Stanford Magnetic Resonance Laboratory (232-15) has prompted us to try resolution enhancing magnitude spectra using a Gaussian deconvolution process (J. Mag. Res. in the press). This procedure, in absorption mode, converts Lorentzian lines into Gaussians and also allows a reduction in the line-width.

As an example we chose a sample of mixed deuterated n.m.r. solvents and observed the proton signals from residual acetone- d_5 and acetonitrile- d_2 . Some $Eu(fod-d_9)_3$ was added to broaden the acetone signal and to provide a suitable chemical shift difference at 90 MHz.

In order to remove the wings of the magnitude spectrum and to retain the same line-width as in the unfiltered spectrum an insignificant trade-off in signal-to-noise was observed. Allowing line width reductions, quite dramatic enhancements are possible but the sensitivity begins to suffer a little.

The top trace (a) shows the unweighted FID and, in the frequency domain, the absorption mode and magnitude spectra. The true baseline in the magnitude spectrum is marked with a dotted line. (b) shows the result of multiplying the same FID with $\exp(32t - 37.82t^2)$ where t runs from zero to one. Here the same line-width is obtained. (c) shows a more extreme example with a weighting function $\exp(15t - 9.94t^2)$. Here the line-widths have been reduced by ~30% with a significant loss of sensitivity.

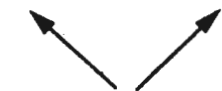
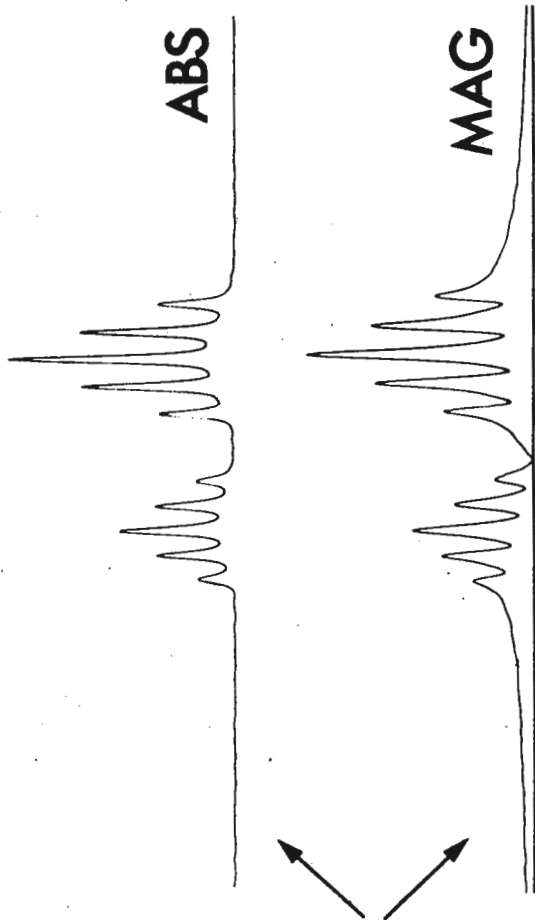
A clear application of this method lies in two dimensional FT n.m.r. where spectra are normally plotted in a magnitude representation.

Yours sincerely

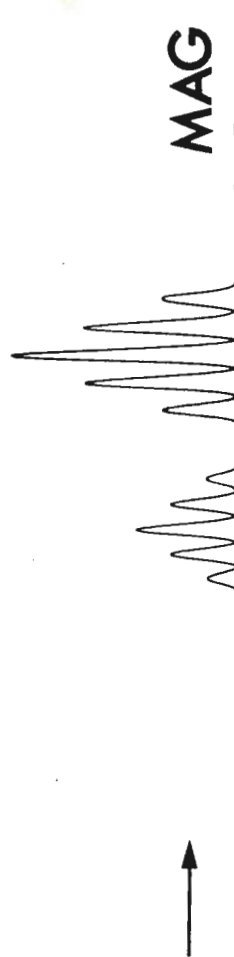
J. C. Lindon

A. G. Ferrige

DEPARTMENT OF PHYSICAL CHEMISTRY



a



b



c



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Asilomar, California, February 19-23, 1979

20th EXPERIMENTAL NMR CONFERENCE

The 20th ENC will be held at Asilomar, California February 19-23, 1979. Everyone who attended any one of the meetings in 1975, 1976, 1977, or 1978 is on the mailing list and will receive registration information and a copy of the preliminary program which will be mailed about December 10. If you are not on the mailing list or fail to receive meeting information by the first week of January contact Aksel Bothner-By, Secretary.

POSTER SESSIONS

If you would like to talk about your work, taking advantage of the selectivity and intimacy which a poster presentation offers, you are invited to contact the Poster Session Chairman, Dr. Michael J. Albright, JEOL, 235 Birchwood Avenue, Cranford, New Jersey 07016 for further information.

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Department of Chemistry
telephone: (516) 246-5050 / 5051

August 17, 1978

Dear Barry:

Postdoctoral Position

I would like to announce the availability of a postdoctoral position in my laboratory starting around the first of next year. The work involves NMR studies of model biological membranes particularly focusing on mediated ion transport facilitated by either small molecules or membrane proteins. Some of this work is described in the abstract of the talk I presented at the 19th ENC at Blacksburg in April. I would be happy to discuss details with those interested. I can be reached at 516-246-5057 (or 516-246-5050 (leave message)). The State University of New York is an equal opportunity affirmative action employer.

Sincerely,

Charlie Springer

Charles S. Springer, Jr.
Associate Professor of Chemistry

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August 23, 1978

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

Computer Program DNMR5

Dear Barry:

We have recently completed the documentation for our iterative NMR bandshape program DNMR5 and submitted it to QCPE; a summary is reproduced below. The program will probably be announced by QCPE in their November 1978 Newsletter. The people at Atlas Computer Laboratory at East Anglia also have plans to include it in their library. A paper describing the theoretical background of the algorithm is tentatively scheduled to appear in *JMR* in October 1978. A companion paper, to be published in the same issue, will present experimental examples.

ABSTRACT

DNMR5 is the iterative version of DNMR3 (QCPE No. 165). It uses an improved and simplified DNMR3 as a subroutine. Up to 16 parameters (chemical shifts, coupling constants, populations, effective transverse relaxation times, exchange rate constants, 2 baseline parameters and the spectral origin) may simultaneously be optimized by the least-squares fitting of a theoretical bandshape to experimental digitized CW NMR signal intensities. The optimization is constrained by the total experimental bandshape integral corrected for baseline increment and baseline tilt. The iterative minimization algorithm is based on a judicious interpolation between the gradient and Gauss-Newton parameter correction vectors with respect to direction as well as length. In standard operation the experimental spectrum is to be supplied as 10200 16-bit integer data words on a 9-track magnetic tape prepared by a modern NMR spectrometer system. For users lacking the capability to prepare such a tape, two alternative optional input routines are provided. The raw bandshape data are smoothed and truncated prior to the iterative calculation. The program outputs information about the progress of the iteration, an error analysis of the final parameters and an agreement factor based on a calculated RMS noise figure, and optionally produces plots of the original spectrum, of the smoothed and truncated spectrum and of the computed spectrum, either on separate sheets or as superimposed traces.

The most complicated case we have tackled so far is that of 1,4-dinitrosopiperazine. There are 2 isomers, 4 nuclear configurations and 8 spins, falling into 2 groups of 4 each, whose weak mutual interaction can be accounted for by choosing appropriate effective transverse

A

1,4-DINITROSOPIPERAZINE 130C

COMPUTED ON SMOOTHED

B

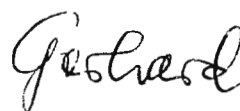
1,4-DINITROSOPIPERAZINE 130C

relaxation times. Part A of the figure shows the experimental 100 MHz spectrum at 130°C recorded with a density of 40 points/Hz. The iteration proceeds from the smoothed spectrum truncated to 999 points. The 4 shifts, the population ratio, 2 of the independent rate constants, the baseline increment and the baseline tilt were treated as free parameters in the iteration. Total CPU time was 2.5 minutes on a CDC CYBER 175. The superposed plots (part B of the figure) show the degree of agreement between theory and experiment that can be achieved with this approach.

Sincerely yours,



David S. Stephenson



Gerhard Binsch

UNIVERSITY OF CALIFORNIA, SAN DIEGO

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SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY, M-001
LA JOLLA, CALIFORNIA 92093

August 21, 1978

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

$^{31}\text{P}\{^1\text{H}\}$ NOE OF PHOSPHOLIPIDS IN MIXED MICELLES AS MODEL MEMBRANES

Dear Professor Shapiro:

In response to the pink sheet, we wish to inform you that we have been continuing our NMR studies on the conformational details of phospholipids in mixed micelles as model membranes (1,2). Because of the phenomenon of "specificity reversal" (3), whereby phospholipase A_2 hydrolyzes phosphatidyl-ethanolamine (PE) significantly only in the presence of phosphatidylcholine (PC), we wished to know if the two phospholipids specifically interacted in mixed micelles. Recently, Yeagle et al. (4) used $^{31}\text{P}\{^1\text{H}\}$ NOE's to explore the interactions of the polar portion of phospholipids in mixed phospholipid bilayers. They found that the major contribution to the NOE of the PC phosphorus (and of the PE phosphorus in mixtures with PC) is from the choline methyl protons. This was explained by intermolecular interactions between the positively charged N-methyl moiety of one molecule of PC and the negatively charged phosphate on a neighboring molecule of either PC or PE.

We have now examined the proton frequency dependence of the $^{31}\text{P}\{^1\text{H}\}$ NOE for PC, PE, and a binary mixture of the two phospholipids in mixed micelles with Triton X-100. As shown in the Figure, the NOE maximum occurs at the ^1H -irradiation frequency corresponding to the methylene protons adjacent to the phosphorus for both PC and PE in the binary mixture. Thus, in contrast to the case with phospholipid bilayers (4), there is no evidence in the mixed micelles for an intermolecular interaction between PC and PE.

Sincerely yours,

Mary F. Roberts

Edward A. Dennis

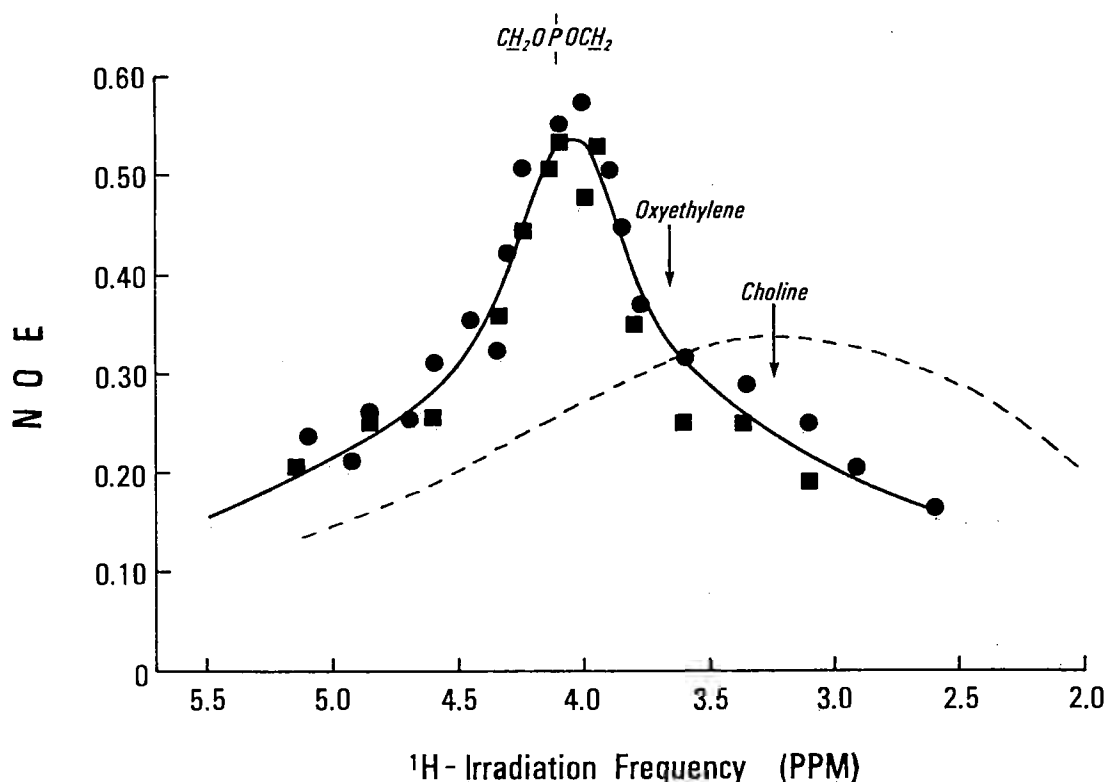


FIGURE: Frequency dependence of $^{31}\text{P} \{^1\text{H}\}$ NOE of egg phosphatidylcholine (●) and egg phosphatidylethanolamine (■) in mixed micelles with Triton X-100 plotted as a function of the CW proton decoupler frequency. The NOE data was obtained on a JEOL PFT-100/Nicolet 1085 system using weak continuous wave broad band decoupling. The chemical shifts for choline methyl groups and methylene groups adjacent to the phosphate of the phospholipid and Triton oxyethylene groups are indicated in ppm from tetramethylsilane. The dashed line superimposed on the data is taken from the results of Yeagle *et al.* (4) for phospholipid vesicles.

1. M.F. Roberts and E.A. Dennis, *J. Am. Chem. Soc.*, **99**, 6142-6143 (1977).
2. M.F. Roberts, A.A. Bothner-By, and E.A. Dennis, *Biochemistry*, **17**, 935-942 (1978).
3. M. Adamich and E.A. Dennis, *Biochem. Biophys. Res. Comm.*, **80**, 424-428 (1978).
4. P.L. Yeagle, W.C. Hutton, C-H. Huang, and R.B. Martin, *Biochemistry*, **16**, 4344-4349 (1977).

THE UNIVERSITY OF BRITISH COLUMBIA
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DEPARTMENT OF CHEMISTRY

17 August, 1978

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

DISPERSION VERSUS ABSORPTION:(DISPA):
A New Method for Distinguishing a
Distribution in Chemical Shift from
a Distribution in Line Width.

Dear Barry,

We have recently pointed out¹⁻⁵ that a plot of dispersion versus absorption in NMR provides a simple graphical means for identifying and quantifying several different line-broadening mechanisms, using the data from a single accumulated F.I.D.

In this note, I wish to report that I have now been able to prove that essentially any distribution in chemical shift will lead to displacement of an experimental DISPA curve above its reference semicircle, while any distribution in line width will lead to displacement of the experimental DISPA curve below its reference semicircle. This provides a near-trivial means for distinguishing between these two most general types of line-broadening in NMR. The proof will appear shortly in J. Phys. Chem. While there are certainly other means for distinguishing between these two types of line-broadening (e.g., spin-echo or other multiple-pulse methods), none is as simple or rapid (in data acquisition) as the DISPA analysis.

Our own experimental interests are in biological applications. Fig. 1 shows a DISPA plot constructed from the broad ³¹P FT-NMR signal from ribosomes (raw data courtesy of Prof. Ian M. Armitage at Yale University). The data points are clearly displaced below the reference semicircle (diameter = absorption-mode maximum peak height), showing that this sample exhibits appreciable heterogeneity in line width of its individual components, probably due to variation in flexibility of the phosphodiester linkages in the various RNA components.

Although it is a bit early to make general conclusions, our preliminary ¹H DISPA plots suggest that the broad signals from polymers themselves (e.g., polymethyl-methacrylate) seem to be dominated by distribution in line width of the component peaks, while the broad signals from small adsorbed molecules (e.g., H₂O in gels or in biological cells; benzene on silica gel) seem to be due to distribution in chemical shifts. We are pursuing further applications for broad-line ¹H systems, and would welcome suggested problems from other workers.

Sincerely,

Alan G. Marshall D. Christopher Roe

Alan G. Marshall*, D. Christopher Roe, and R. LeBlanc

References:

1. A. G. Marshall and D. C. Roe, Anal. Chem. 50, 756 (1978).
2. D. C. Roe, A. G. Marshall, and S. H. Smallcombe, Anal. Chem. 50, 764 (1978).
3. A. G. Marshall and D. C. Roe, TAMU 231, 9 (1977).
4. A. G. Marshall, J. Phys. Chem., in press.
5. A. G. Marshall and D. C. Roe, J. Magn. Res., in press.

* Please credit to account of A. G. Marshall.

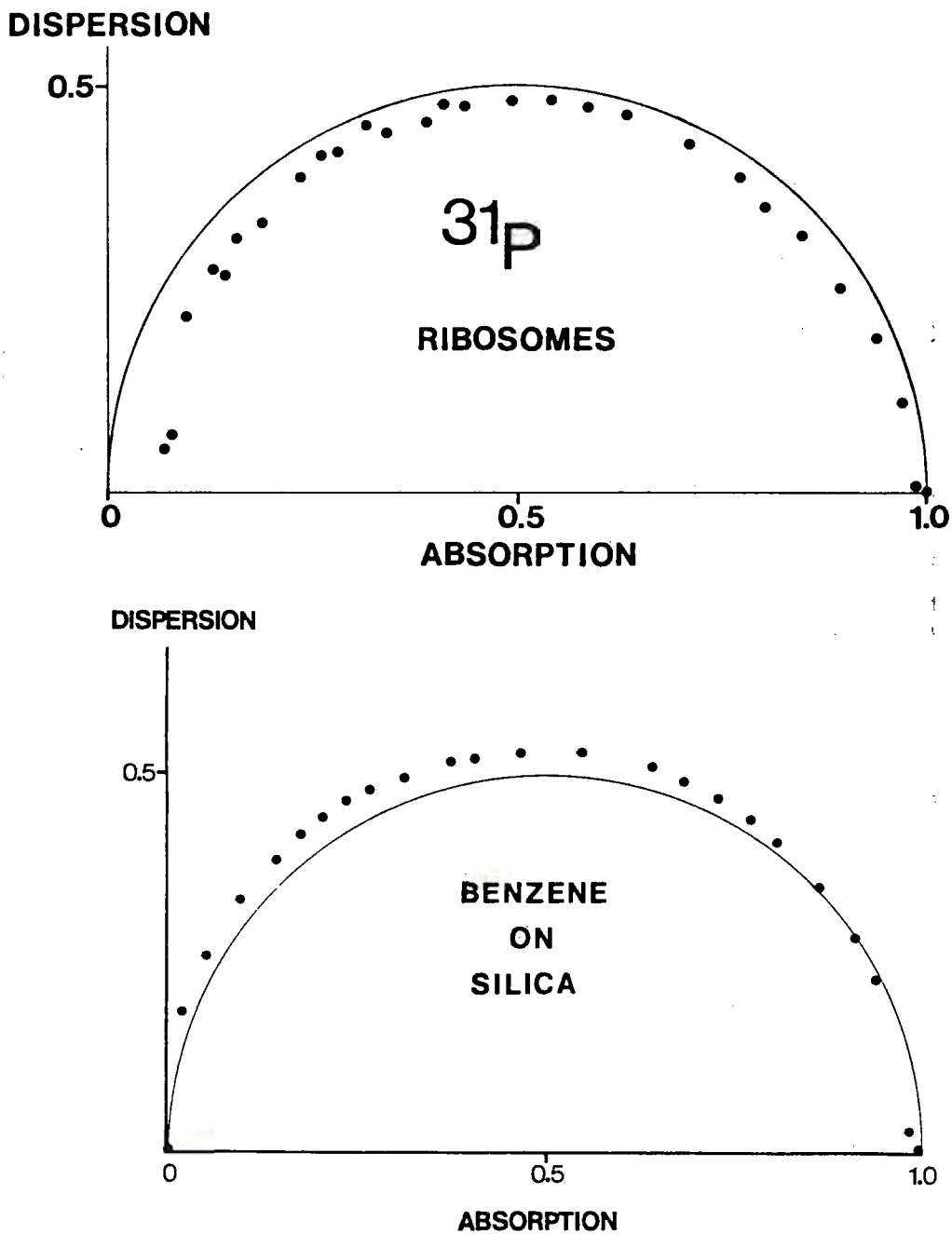


Figure 1. Plots of NMR Dispersion versus Absorption (DISPA). Solid line represents a reference semicircle whose diameter is set equal to the experimental absorption-mode peak height (see References).
 Top: ^{31}P data from *E. coli* ribosomes. The DISPA plot indicates a distribution in T_2 for the component phosphate resonances.
 Bottom: ^1H data for benzene adsorbed onto silica gel. The DISPA plot indicates a distribution in chemical shift for the adsorbed benzene molecules.

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19104

School of Medicine G3

DEPARTMENT OF
BIOCHEMISTRY AND BIOPHYSICS

August 17, 1978

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

Dear Barry:

We have reported an ^{18}O isotopic shift on ^{31}P of inorganic phosphate(1) and have applied to the study of the mechanisms of several enzymatic reactions(1,2). The ^{18}O shift on ^{31}P was independently reported by Lutz et al.(3). Recently we have synthesized a number of ^{18}O labeled species of adenosine triphosphate and have found that the magnitude of the isotopic shift depends on which phosphorus is observed and whether the ^{18}O is in the bridge or non-bridge position as illustrated for two species of ATP in Fig. 1. The results of all measurements made thus far are summarized in Table I.

Table I

P of ATP	Oxygen Position	Shift in ppm per ^{18}O atom
α	α - β bridge	0.017
β	α - β bridge	0.017
	non-bridge	0.028
	β - γ bridge	0.016
γ	β - γ bridge	0.016
	non-bridge	0.023

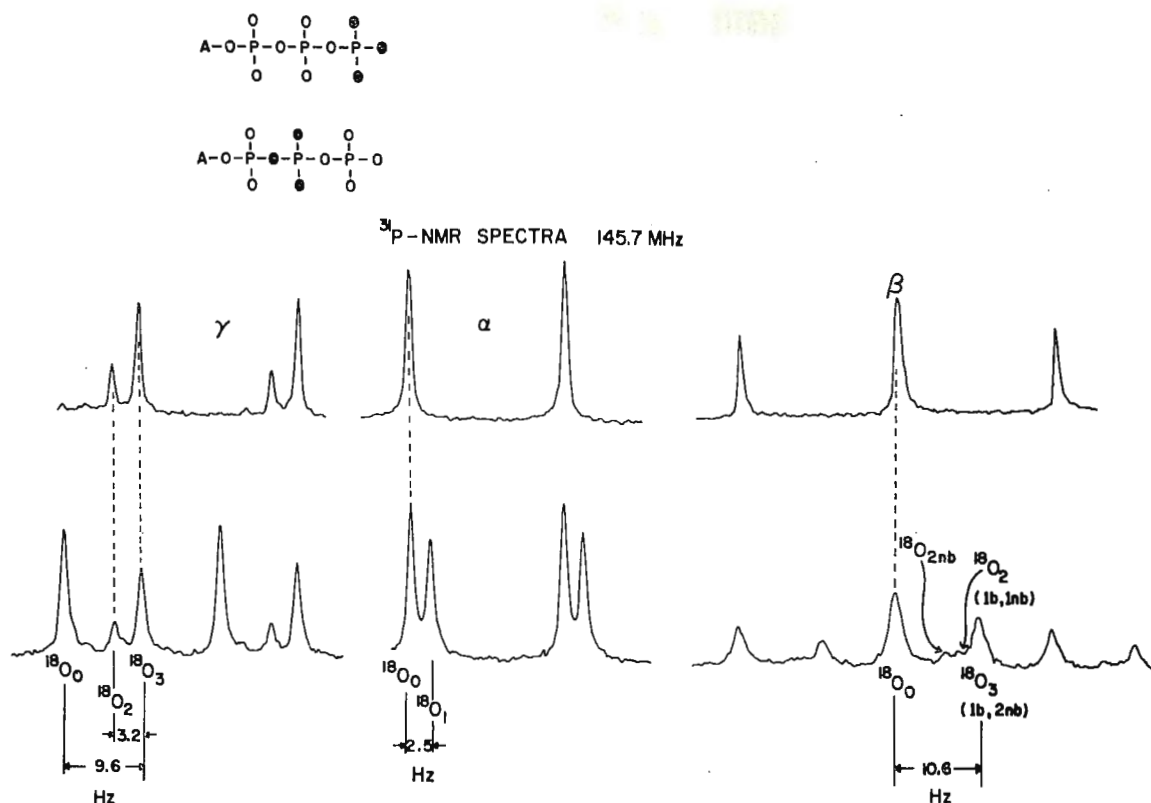


Fig. 1

The filled symbols in the formulae indicate the positions of ^{18}O .

Upper spectrum - ATP, 89% ^{18}O in 3 non-bridge positions of γ -P.

Lower spectrum - Mixture of ATP(^{16}O), ATP(γ $^{18}\text{O}_3$), ATP(β $^{18}\text{O}_3$) and small amounts of ATP(γ $^{18}\text{O}_2$) and ATP(β $^{18}\text{O}_2$). There are two peaks for the last species (β $^{18}\text{O}_2$) corresponding as indicated to 2 non-bridge oxygens (2 nb) and to 1 non-bridge and 1 bridge oxygen (1 b, 1 nb) respectively. The $^{18}\text{O}_2$ species arise from the binomial distribution since the compounds were synthesized from inorganic phosphate, 89% ^{18}O .

Sincerely yours,

Mildred
Mildred Cohn

References

- 1) Cohn, M. and Hu, A. (1978) Proc. Nat. Acad. Sci. U.S.A. 75, 200-203
- 2) Bock, J.L. and Cohn, M. (1978) J. Biol. Chem. 253, 4082-4085
- 3) Lutz, O., Nolle, A. and Stachewski, D. (1978) Z. Naturforsch. 33a, 380-382



Instruments, Inc.

MANNING PARK
BILLERICA, MASSACHUSETTS 01821
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25 August 1978

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

Dear Dr. Shapiro:

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Phone (416) 625-2374

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

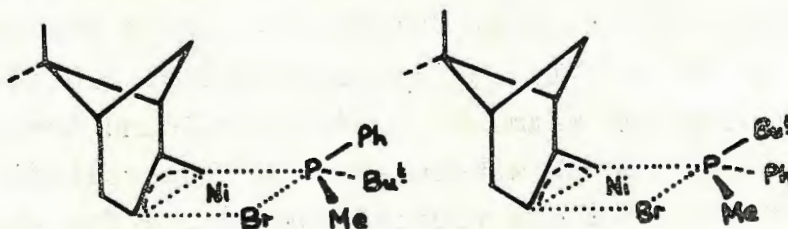
Dear Professor Shapiro,

A Simple Spectroscopic Method to Determine the Optical Purity
of Horner Phosphines

In earlier work in this Institute, Behrens and Wilke¹ described the method to resolve Horner phosphine enantiomers (PRR"R") by complexation with $(\eta^3-(+)-(1R,5R)\text{-pinenyl})\text{nickel bromide}$. They obtained 1:1 complexes in which the methyl groups of the pinenyl residue are directed away from nickel and phosphorus is trans to C_3 (see Figures 1 and 2).

We were interested to find out by how much the carbon-13 spectra of such diastereomeric complexes differ from each other and therefore measured the spectra of methyl-t-butyl-phenyl phosphine (Table 1) and its corresponding complexes.

Figure 1.

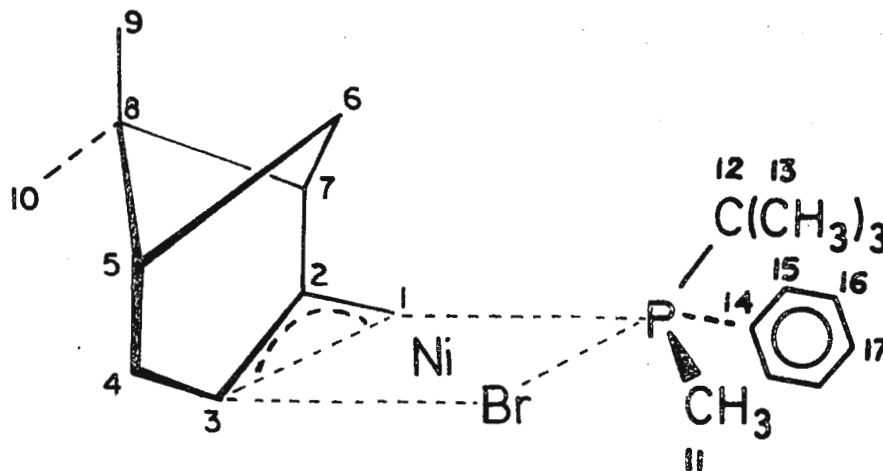


The first sample of complex to be examined contained one component enriched to 87%. This was the same diastereomer as that for which an X-ray determination of the absolute configuration has been carried out.² Seventeen signals are to be expected in the carbon-13 spectrum and all were found. Multiplicities and $^1J_{CH}$ were obtained from a gated decoupled spectrum; the quaternary carbons C_8 and C_{12} were confirmed by recording a low-power broad-band decoupled spectrum. All signals could be assigned unambiguously (Table 1). C_6 (in the cyclobutane ring) and C_4 have practically the same chemical shift (29.6 and 29.3 ppm) but could be assigned using the proton-carbon coupling constants ($^1J_{CH} = 138$ and 129 Hz, respectively). $|^2J_{PC_3}|$ (trans) is 20.7 Hz, $|^2J_{PC_1}|$ (cis) is 4.8 Hz.

A second sample, containing both diastereomers in approximately equal amounts, was measured to obtain the diastereomeric splittings. All the signals give a resolvable splitting! (See Table 2.) The largest is for C_{11} (1.16 ppm) and the smallest for C_9 , C_{10} , C_{16} and C_{17} (0.07 to 0.04 ppm). The respective phosphorus-carbon coupling constants are generally the same in both diastereomers within experimental error.

Figure 2.

Labelling of
the carbon atoms



The relative concentrations of the diastereomers in a given sample gives the optical purity of the Horner phosphine. Thus a phosphine whose optical purity is to be determined can be reacted with a small excess of $(\eta)^3$ -(+)-(1R,5R)-pinenyl)nickel bromide and its carbon-13 nmr spectrum measured.³ We have found that carbon-13 has the advantage over phosphorus-31 that the splittings are usually better resolved and moreover are found for several centres in a given complex. In the first of the samples discussed here, the enantiomeric excess of the phosphine was found to be 75%; the error was estimated to be $\pm 3\%$. A parallel determination by optical rotation gave 74%. Normally such a determination requires considerably more work than the method described here.

Please credit this contribution to the account of Professor Hoffmann.

Yours sincerely,

Richard Mynott

Table 1.

Complex ^a				Free Phosphine ^b		
Carbon	δ , ppm	Mult.	J_{PC} , Hz	δ , ppm	J_{PC} , Hz	, Hz
1	49.44	t	4.8			
2	128.63	s	-			
3	81.12	d	20.7			
4	29.31	t	2.6			
5	39.99	d	-			
6	29.62	t	-			
7	46.39	d	-			
8	39.15	s	-			
9	26.03	q	-			
10	21.32	q	-			
11	7.82	q	23.8	5.01	19.4	
12	31.10	s	19.7	28.20	13.1	
13	26.73	q	4.7	26.92	14.2	
14	134.37	s	33.3	137.43	20.2	
15	132.89	d	10.8	133.42	19.5	
16	128.06	d	8.7	127.75	6.8	
17	129.82	d	1.9	128.55	-	

a. 30% solution in C_6D_6 (major component), 30°, rel. int. TMS

b. 50% solution in C_6D_6 .

Spectrometer: Varian XL-100-15A, ^{13}C frequency 25.2 MHz.

Table 2. Diastereomeric Splittings

Carbon	ppm	Carbon	ppm	Carbon	ppm
1	0.26	6	0.13	11	1.16
2	0.12	7	0.20	12	0.16
3	0.34	8	0.18	13	0.30
4	0.09	9	0.07	14	0.84
5	0.07	10	0.06	15	0.35
				16	0.07
				17	0.04

References:

- (a) O. Behrens, Dissertation, Ruhr-Universität Bochum, 1973.
(b) B. Henc, H. Pauling, and G. Wilke, Justus Liebigs Ann. Chem., 1820 (1974).
- C. Krüger, Chem. Ber., 109, 3574 (1976).
- R. Mynott, J. Richter, and G. Wilke, manuscript in preparation.

240-27

Université de Nancy I

NANCY, le August 10, 1978

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~~XXXXXXXXXXXXXXXXXXXX~~

Tel. (28) 28.93.93 poste 20.18

Dr. D. CANET

Professor B.L. SHAPIRO
Texas A&M University
Department of Chemistry
College of Science

COLLEGE STATION, Texas 77843

U.S.A.

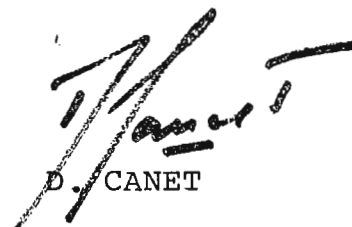
Title : *Unexpected effects due to selective pulses.*

Dear Professor Shapiro

In looking to possible applications of selective pulses in FT-NMR, we met with a rather amazing phenomenon. As shown in the enclosed figure, the inversion of a methyl triplet may result in the disappearance of one peak belonging to the methylene quartet. Repeating this type of experiment on other systems, we found that this effect was systematic : intensity alterations are observed as long as there exists a J-coupling with the nucleus (or the nuclei) corresponding to the inverted multiplet. This is essentially due to the r.f. amplitude that we used for the selective pulses and which is, in our experiments, of the same order of magnitude as the J-coupling.

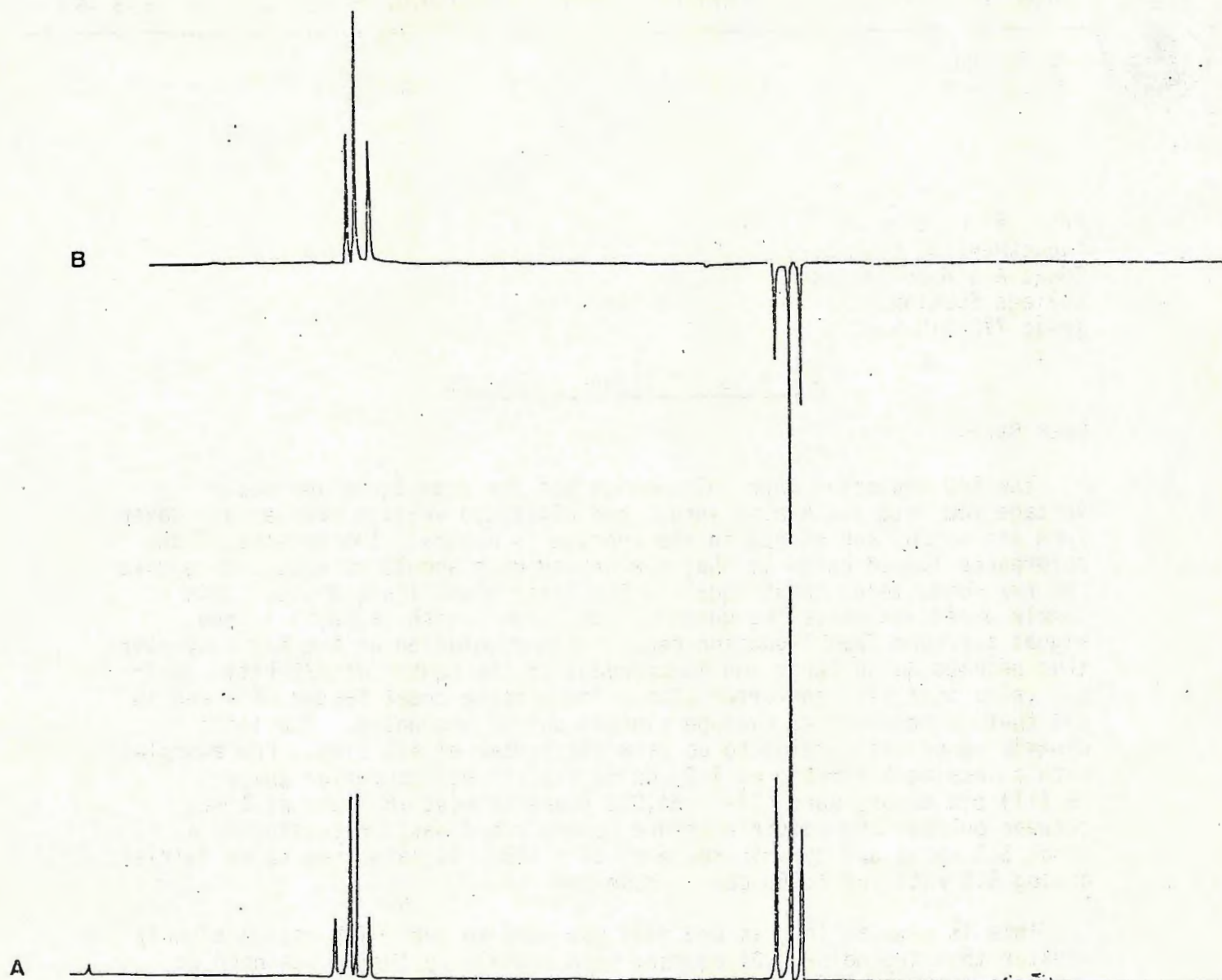
The whole story will appear in the Journal of Magnetic Resonance.

Yours sincerely



D. CANET

Encl. 1



A. Normal spectrum

B. Spectrum obtained after the selective inversion of the triplet



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NEW BRUNSWICK

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Physics Department
(506) 453-4723

August 10, 1978.

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

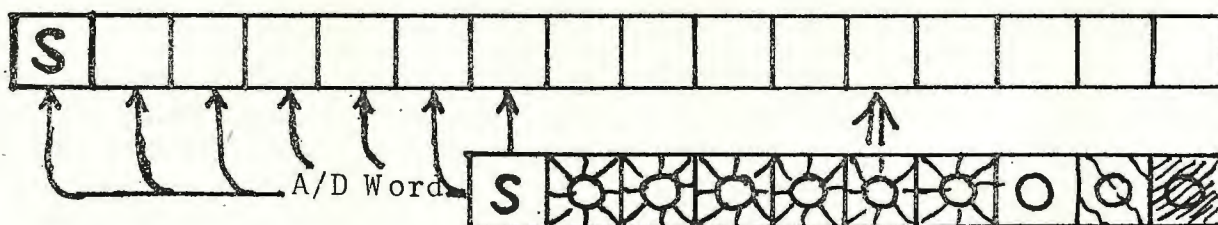
A/D BITS AND SIGNAL AVERAGING

Dear Barry:

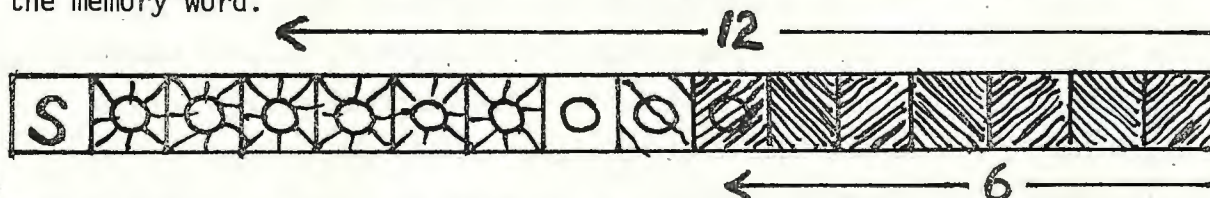
The A/D converter under discussion has the free induction decay voltage fed into its analog input, and digitized voltage samples are taken from its output and stored in the averager's memory. The message of the references listed below is that the analog gain should be adjusted to make the rms noise level about equal to the least significant digit. This simple expedient makes the quantization noise vanish (almost) in the signal averaged free induction decay. The resolution of the A/D converter thus becomes quite large and independent of the number of A/D bits. A 3-bit (plus sign bit) converter allows for a noise crest factor of 4 and is all that is required to average signals out of the noise. The final dynamic range has nothing to do with the number of A/D bits. For example, with an analog S:N ratio of 1:2, using a 3(+1) bit converter and a 15(+1) bit memory word, $2^{16} \approx 64,000$ scans (almost 18 hours at 1 sec between pulses) are possible before memory overflows, resulting in a final S:N ratio and dynamic range of $2^7 = 128$. Signals down to an initial analog S:N ratio of 1:256 can be observed.

This is fine as long as one does not need to deal with analog signals greater than the noise. Of course, such signals by themselves need no averaging. The real problem arises when one has both large and small signal components carrying information, or simply when one wants to acquire a strong spectrum in a single scan. In these cases, the converter needs $\log_2(S/N)$ bits so that it can handle the sum of all signal component amplitudes when the analog level is adjusted as before to make the noise fill the least significant bit.

Still, there is no need to signal - average the strong components, and the easiest way to separate them from the weak ones is to ignore them in the averaging process. The memory word will overflow and spill most of the strong signal information, but that information can be recovered in a single extra scan. The procedure is illustrated below for the case of an initial S:N ratio of 512:1 for which a 9(+1) bit A/D converter is required. Initially, the situation with a 16 bit memory and two's complement arithmetic is this:

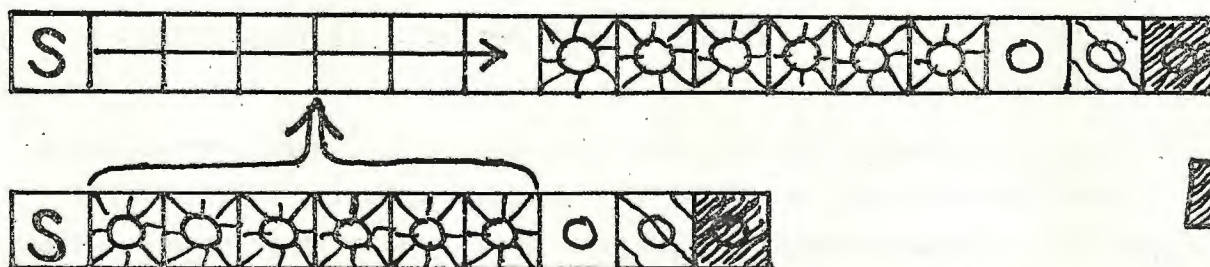
Memory
Word

The arrows indicate algebraic addition of the A/D word to the memory word existing at each scan. It is possible in this example to accumulate a maximum of $2^{12} = 4096$ scans. After this, the signal has been shifted left by 12 bits so that 6 bits have been spilled out of the high end of the memory word.



The noise level has been shifted left 6 bits, and $12 - 6 = 6$ bits of signal have been recovered out of the noise.

To restore the information lost in the overflow, a 6 bit right shift is first performed, followed by one extra scan. In the right shift, only noise is lost but a 6 bit space is created on the left into which the previously lost information can be moved from the A/D word in the extra scan.



The result is then a final S:N ratio and dynamic range of 2^{15} that fully utilizes the 16 bit memory word, and detection of signals down to an initial analog S:N ratio of 1:64.

Other cases are not quite so favourable but the foregoing example illustrates the principle. We have played with this scheme on a mini-computer, there is some hassle in taking care of the 'carry' when joining the extra scan into the memory, but the 3 guard bits between signal and noise appear to be adequate.

Sincerely,

R. Kaiser.

Ref: G.J. Diebold, Rev. Sci. Instr. 48, 1689 (1977)
R.R. Ernst, J. Mag. Resonance 4, 293 (1971)

UNIVERSITY OF DURHAM

DEPARTMENT OF CHEMISTRY

Science Laboratories,
South Road,
Durham. DH1 3LE

28th July, 1978.

Dear Professor Shapiro,

^{13}C , ^{19}F and electron density foray

As part of a ^{13}C study of some aromatic hydrocarbons, we have recently measured the ^{19}F and ^{13}C chemical shifts of twelve chlorofluoropyridine of the type $\text{C}_5\text{Cl}_n\text{F}_{5-n}\text{N}$, in the hope that we might clarify the origin of large low field shifts for fluorines adjacent to nitrogen in aromatic heterocycles such as pentafluoropyridine. On plotting the ^{19}F shift versus the ^{13}C shifts we obtained two parallel lines (top figure) and to be brief, our plot for C3,4,5 sites followed a set of more general correlations in substituted pentafluorobenzenes (Briggs and Randall, J.C.S. Perkin Trans. II, 1789, 1973) and as such it is not new. But the data for the C2,6 sites indicates that the ring nitrogen is causing a constant shift deviation of the adjacent C2 and/or F2 shifts.

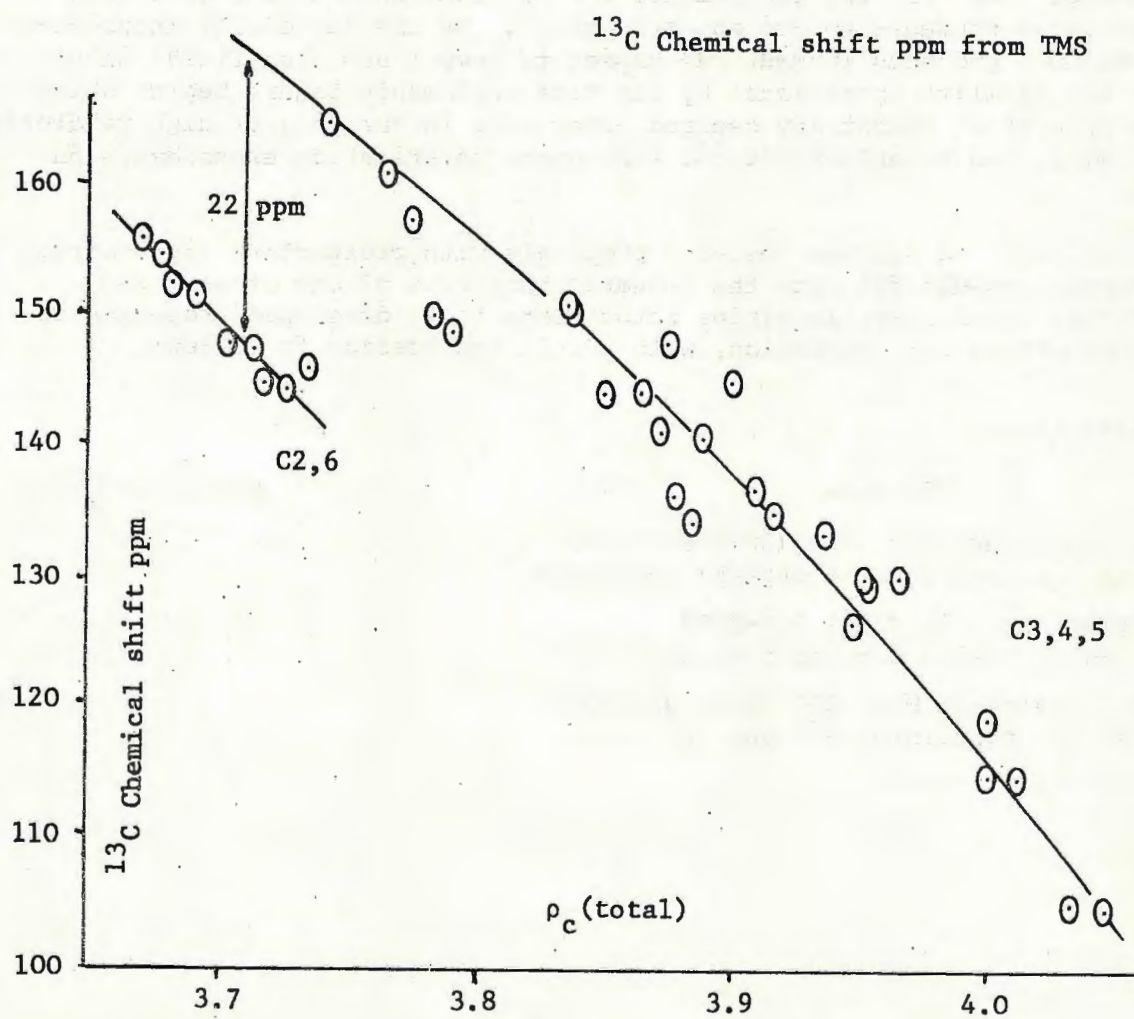
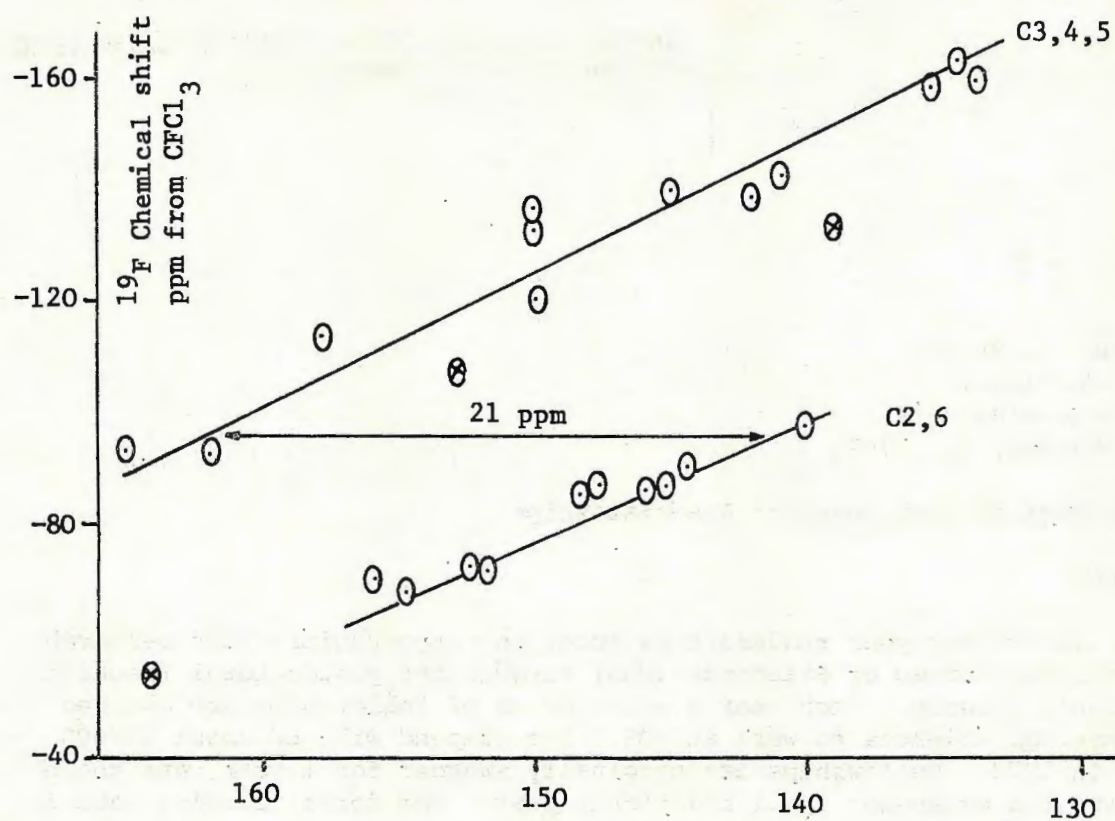
In order to ascertain the origin of the deviation we made further plots of ^{13}C shifts with electron densities (ρ_c) calculated by the CNDO/2 method and found that $\rho_c(\text{total})$ served our purposes best. Again there were two lines (bottom figure), one for the C2,6 data and one for the C3,4,5 data where the former was 22 ppm upfield of the latter. This value is fortuitously close to the original difference of 21 ppm and implies that the shifts of C2 and C6 suffer a constant local effect, the origin of which is uncertain.

In conclusion it seems reasonable to expect that the low-field ^{19}F shifts are dominated by the local changes in electron density and that the ^{19}F shifts are proportional to electron densities in this case. A reasonable correlation of ^{19}F shift versus $\rho_c(\text{total})$ supported this argument. The crossed points represent the comparable shifts in 2-, 3- and 4-fluoropyridines* indicating the argument may be more general.

* (Lichter and Wasylishen, J.A.C.S. 97, 1808, 1975; Thomas and Griffin, Org. Magn. Resn., 2, 503, 1970; Desai, J.C.S. Perkin Trans. 1, 1865, 1973).

Yours sincerely,

Ray. S. Matthew *Raydon*





UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

August 29, 1978

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

NBS - NRC Postdoctoral Research Associateships

Dear Barry:

We would like to let your readers know about the opportunities for research at the National Bureau of Standards (NBS) through the postdoctoral research associateship program. Each year a score or so of fellowships are awarded in the physical sciences to work at NBS. The stipend will be about \$19000 per year in 1979. Fellowships are originally awarded for 1 year, and there is a chance for extension for 1 additional year. The formal closing date is approximately Jan. 15, but the competition is keen, and it is a good idea for interested students to get an early start. We are especially interested in the various projects in NMR. We expect to have a new high field, multi-nuclear NMR facility operational by the time fellowship tenure begins which will be able to do almost any desired experiment in the area of high resolution NMR; it will also be able to do ^{13}C {'H} cross polarization experiments on solids.

We will be happy to discuss research proposals with prospective applicants. The proposals should fit into the research interests of one of us. We suggest that preliminary inquiries rather than fully developed proposals be sent to one of us for discussion, with a full application to follow.

Yours very truly,

Rolf

Bruce

David

Rolf B. Johannesen Div. 561 (301) 921-2040
NMR of inorganic & metal - organic compounds

Bruce Coxon Div. 552 (301) 921-2867
NMR of carbohydrates & other organics

David L. VanderHart Div. 563 (301) 921-3344
NMR of solids containing ^{13}C and 'H

A hot performer at a cool 4.2°K



Varian introduces: The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

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The XL-200's data management system tops all conventional concepts of versatility and convenience. There are two processing units working in tandem—one 32 bits wide and very fast for data acquisition, the other programmed in a high-level language and extremely flexible for data manipulation. Both operate continuously and, together with the XL-200's full complement of built-in I/O devices, offer you unique multi-tasking capability and high sample throughput.

And that's only the beginning of a long list of features which could read like your own NMR wishlist:

- 47-kG Nb-Ti superconducting magnet with 50-mm bore
- 25 liters liquid He dewar capacity; 3-month refill interval
- 35 liters liquid N_2 dewar capacity; 14-day refill

interval (45 days with optional refrigerator)

- 5- and 10-mm samples standard; other sample sizes optional
- Broadband probes covering 20-80 MHz and 188-212 MHz ranges
- Flexible mix/match RF system with fixed-frequency sources such as ^1H , ^{13}C , ^{19}F , and ^{31}P
- Compatible with RF synthesizer for broadband multi-nuclear operation
- 50-kHz spectral widths with quadrature phase detection
- Automatic ^2H internal field/frequency stabilization with exclusive AutoLock™ circuit
- ^1H homo/heteronuclear decoupler for a wide variety of gated modes
- Programmable 32K CPU for data processing and multi-tasking
- Independent 32-bit parallel processor with dedicated random-access memory for spectrometer control and data acquisition
- Built-in I/O devices include solid-state keyboard; 5M-word moving-head disk with dual platter (one removable); high resolution raster scan storage/display oscilloscope; 32-column line printer; 500 x 240 mm X-Y recorder.



If you would like the balance of the features to compare with your wishlist, write Varian Associates, Inc., Box D-070, 611 Hansen Way, Palo Alto, CA 94303.

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THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

August 21, 1978

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

Suggested Title: Postdoctoral Position

Dear Barry,

I anticipate a postdoctoral opening in my research group beginning early in 1979. The position can involve any of several projects in the general area of magnetic resonance and optical studies of membranes and liquid crystals. Specific areas include proton NMR of diffusion in model membranes (including drug effects), cross polarization ^{13}C NMR in membranes, deuterium NMR in phospholipid multilayers, NMR relaxation in liquid crystals, fluorescence of chemical carcinogens in model membranes and in cells, and time resolved (nanosecond and picosecond) optical studies of molecules in membranes.

The NMR work will involve two spectrometers in my laboratory plus a wide bore multinuclear superconducting magnet spectrometer the Department is presently purchasing. Much of the optical work will be done at the Center for Fast Kinetics Research, an NIH Biotechnology Center on our campus.

The position requires a person capable of independent progress, but previous experience with NMR or with optical techniques is not necessary. The salary will be in the range \$10,000-12,000 depending on qualifications. Renewal of the position past the first year is possible with mutual agreement. The University of Texas is an equal opportunity employer.

Candidates should arrange to have sent to me three letters of reference plus their resume.

Please distribute this to anyone you think might be interested.

Yours truly,

Chuck, RK

Chas. G. Wade
Associate Professor of Chemistry

DEPARTMENT OF PHYSICS
INSTITUTE OF CYBERNETICS ACADEMY
OF SCIENCES OF THE ESTONIAN SSR

Lenini puistee 10, Tallinn 200 001, USSR
Tel. 440 640, 605 729, 605 745, 605 759

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№ 21

27 July 8 197

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

Dear Professor Shapiro,

High Resolution in One Dimension

Thank you once again for your multicolored letters. During the past months we have been observing high resolution ^{13}C spectra of liquid crystals and solids with one-dimensional conductivity. The latter present an interesting case where dipolar interactions cannot be completely suppressed by decoupling and sample spinning, and lead to some interesting line splittings in the ^{13}C spectrum of the TTF-TCNQ complex, enriched to 31% ^{13}C in the cyano groups. The Knight-shifted 2:1 doublet of lines at -253 and -402 ppm (at 300K in a 9.4 kG field) corresponds to the TCNQ^- cyano groups, and a weaker line at 159 ppm, to the non-complexed TCNQ^0 . The non-complexed line persists through recrystallizations, and indicates a slight inherent non-stoichiometry. The unsymmetric 1.50 kHz wide TCNQ^- doublet is actually a 1:1:1 triplet, caused by dipolar splitting of the ^{13}C resonance by ^{14}N . Quadrupole interaction with electric field gradients in the TCNQ^- ion radical tends to fix the ^{14}N spin moment in some definite orientation in the principal axis system of the molecule, and mechanical rotation of the sample tends to drag along the spin moments of quadrupole nuclei. The extent of this rotation-synchronization, and of the ensuing dipolar splitting, depends upon the ratio of the ^{14}N Zeeman and quadrupole interaction energies. The splitting is temperature-independent between 163 and 396K, but field-dependent, and the low-field value (1.50 kHz) is very close to the value (1.56 kHz), calculated by taking $r = 1.151 \text{ \AA}$ for the mean $-\text{C}\equiv\text{N}$ distance in the complex and using 3.395 MHz in the closely similar TCNQ^-K^+ salt for the quadrupole interaction. The ^{14}N T_1 value in the TTF-TCNQ complex appears to be much longer than in most diamagnetic or paramagnetic nitrogen compounds.

Yours sincerely

E. Lippmaa

E. Lippmaa

M. Allas

E. Kundla

E. Kundla

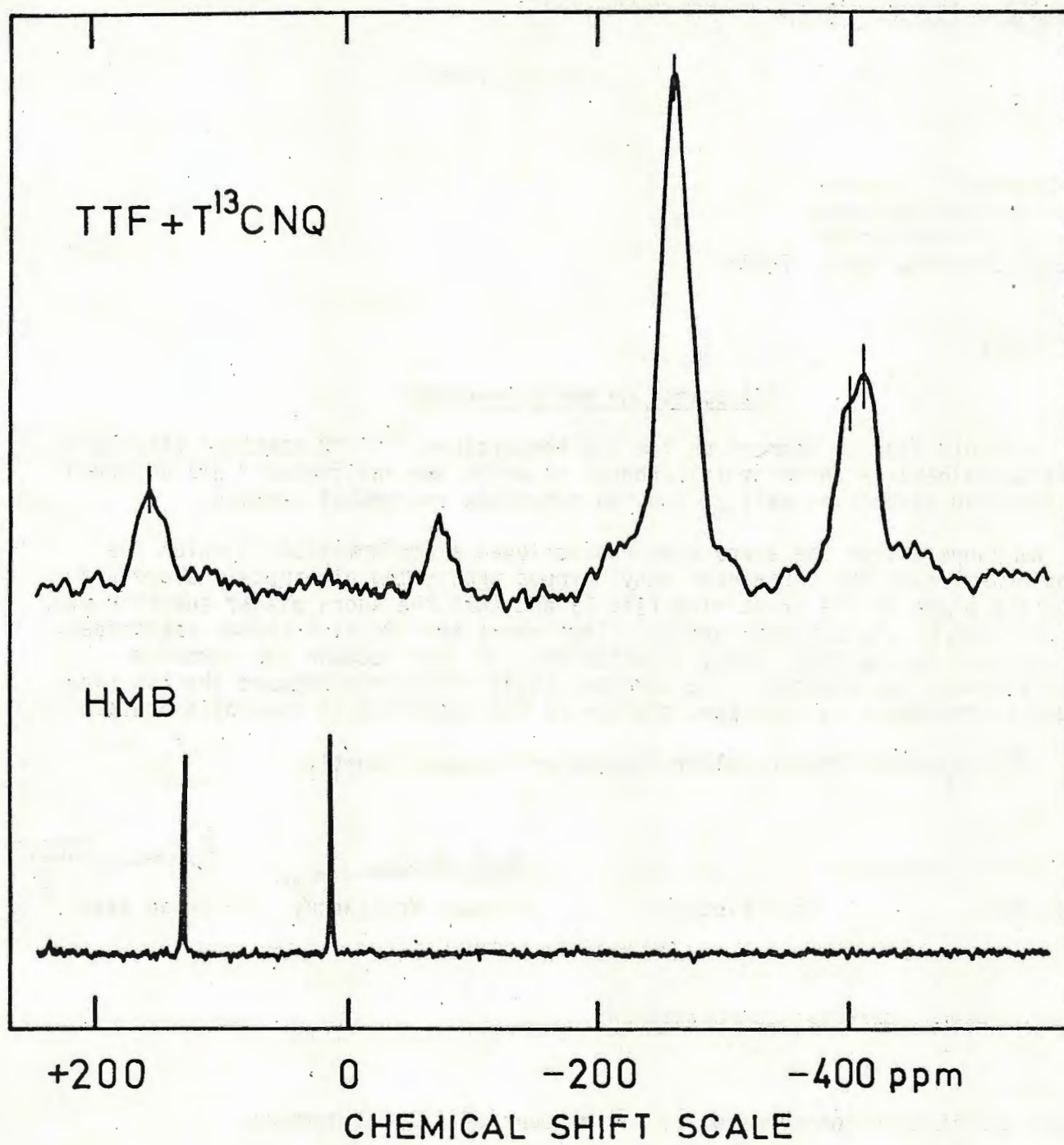
R. Teeäär

R. Teeäär

I. Heinmaa

I. Heinmaa

*presently Dept. of Chemistry, University of California, Berkeley





McMASTER UNIVERSITY

Department of Chemistry

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

Telephone: 525-9140

July 18, 1978

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

Dear Barry:

Stopping the Merry-Go-Round

We would like to comment on the low temperature ^{13}C NMR spectrum (fig 1) of hexaethylbenzene chromium tricarbonyl in which two environments are observed for the ring carbons as well as for the methylene and methyl carbons.

We suggest that the arene ring has achieved a conformation in which the hexapodous ligand has tentacular ethyl groups projecting alternately above and below the plane of the arene ring (fig 2) and that the supra planar substituents are eclipsed by the carbonyl groups. Thus there are two ring carbon resonances, not only due to the ethyl group orientation, but also because the chromium-arene rotation has stopped. The chemical shift difference between the two ring carbon environments is ca 8 ppm, similar to that obtained in the solid state.¹

It is expected that a fuller account will appear shortly.

Alex Bain

John Fletcher

Michael McGlinchey

Brian Sayer

1. J.S. Waugh, personal communication

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

/rg

FIG. 1.

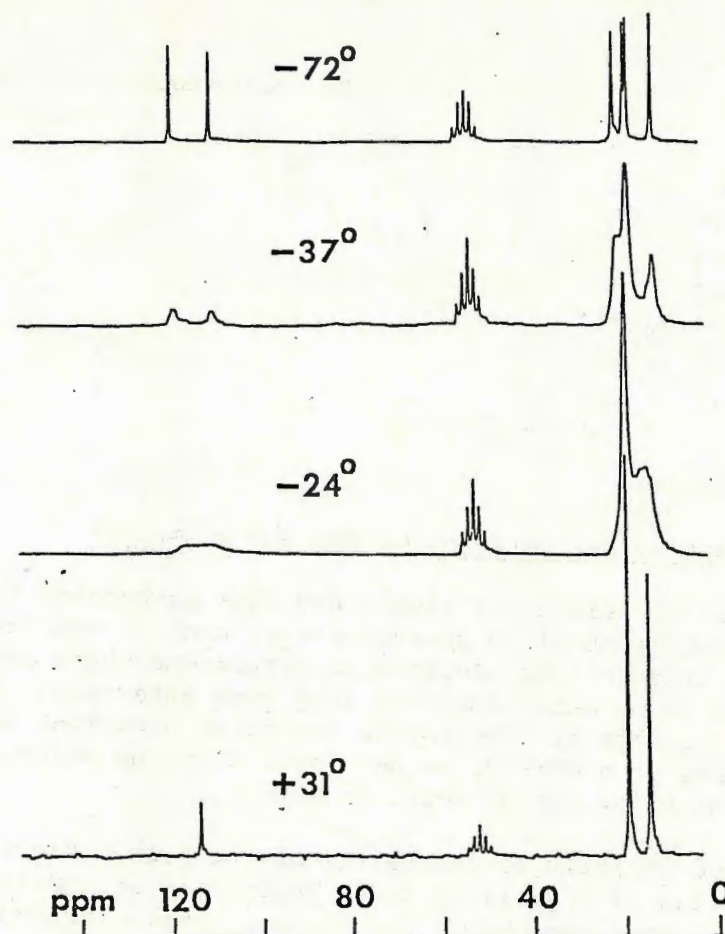
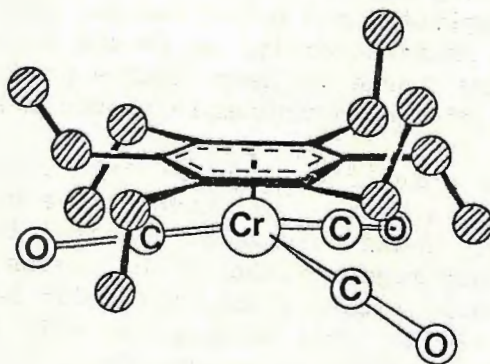


FIG. 2.





University of Canterbury Christchurch 1 New Zealand
Department of Chemistry

18 August 1978

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

Dear Professor Shapiro

Long-term Low Temperature Operation of NMR Spectrometers

Those who have had experience of liquid air heat exchanging units for variable temperature control in spectrometers, such as the Varian range, will know of the frustrations involved in situations where below-ambient temperatures need to be maintained for long time intervals. Faced with the prospect of a number of experiments requiring overnight accumulations at low temperatures on a CFT-20, we developed a system which permits unattended operation for twelve hours or more.

Cold air is passed directly to the bottom of the probe, via insulated tubing, from the top of a 25 litre dewar containing an immersed heating element. The flow rate, and hence the minimum sample temperature attainable, is adjusted by varying the current through the element. Temperature maintenance is achieved by means of the standard Varian controller, except that the sensor/heater unit is mounted in a short length of vacuum-insulated glass tubing connected to the bottom of the probe. The normal position occupied by the heater/sensor device is taken by a thermocouple which records the temperature just below the sample. Unattended operation is facilitated by the use of some fail-safe devices. A pressure relief valve on the dewar will cope with any blockage in the transfer lines. Any drop in flow through the probe is also sensed by a device at the exit port on the probe. Should the flow of cold air drop, then a relay is activated which switches off the heating element in the dewar, the heating element in the temperature controller, the proton decoupler transmitter, and halts further acquisition. While this device functions satisfactorily, we intend to replace it with a device which senses any change (of more than a predetermined, variable amount) in the output of the thermocouple placed below the sample.

Dry air for the sample spinner is obtained from regular compressed air which is passed through a bank of old preparative g.l.c. columns packed with molecular sieves. These columns are mounted in the original g.l.c. oven (Megachrom) so that regeneration of the sieves may be readily achieved by back-flushing with dry nitrogen while holding the temperature of the oven at about 180°C. This arrangement will supply dry air for up to 20 hours before regeneration is necessary.

Yours sincerely

Handwritten signature of J. W. Blunt.

J. W. Blunt

Handwritten signature of T. K. Ridley.

T. K. Ridley



TEXAS CHRISTIAN UNIVERSITY
Fort Worth, Texas 76129
817-926-2461

Department of Chemistry

August 17, 1978

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

Boric Acid: A Regio-
and Stereoselective
Nonparamagnetic Shift
Reagent

Dear Barry:

Recently we were faced with the problem of making C-13 assignments in a diterpene characterized with both 1,2- and 1,3-diol functions at opposite extremes of the molecule. Reasonably a lanthanide shift reagent would cause all the carbons to move making assignment by this means doubtful. From the dim recesses of the mind came the recollection that boric acid formed esters with vicinal diols, and so some was added to the terpene in pyridine solution. A number of chemical shifts were altered which, when coupled with a variety of other data, allowed the assignments to be made. Let it also be noted at this point that 1,3-diols capable of cis or syn geometry also form borate esters.

Below you see a stick representation of the C-13 spectrum of the mixture of cis and trans 1,3-cyclohexanediols sold by Aldrich in pyridine solution. Boric acid was added in two increments with the effects noted. Clearly the cis isomer was selectively esterified thus allowing its line assignments.

The chemical shift effects of borate ester formation resemble those of acetylation as evidenced by the data for 1,3-butanediol. For the cyclic diol

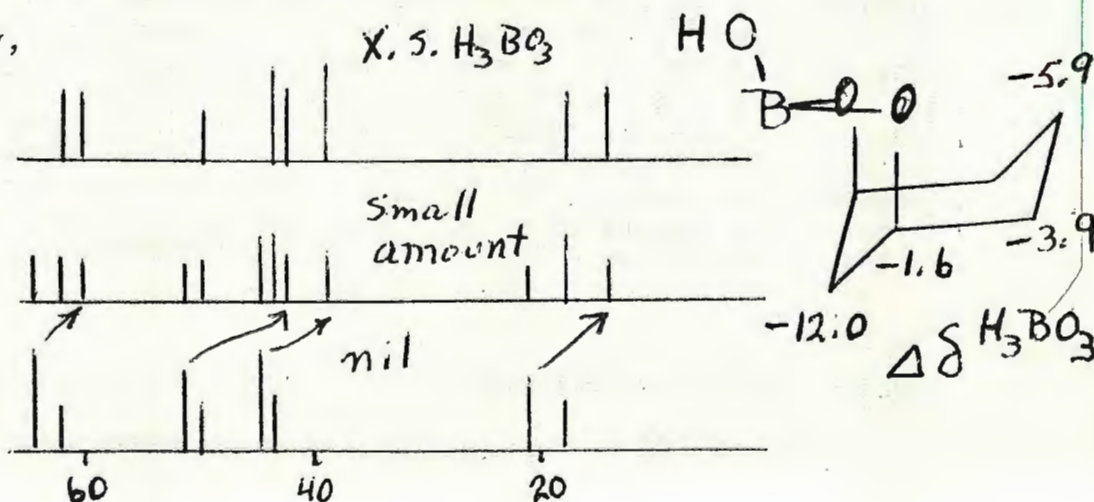
CH ₂	-	CH ₂	-	CH	-	CH ₃	
OH				OH			
0.7	-5.7			1.8	-3.4	$\Delta\delta^{OAc}$	
1.4	-8.0			2.3	-1.0	$\Delta\delta^{H_3BO_3}$	

Additional 1,3 γ interactions are added at carbon-5 when the diol is converted from its preferred diequatorial form.

Yours sincerely,

Bill
W. B. Smith
Chairman

bw





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August 24, 1978

TELEX NO. 13-8840

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

PG SPECTROSCOPY; OR PROLIFIC PULSE PROGRAMMING

Dear Professor Shapiro,

While pulsing away one day (in the background) on our FX-90Q system, we decided to see what we could do with the PG-200 pulse programmer. Hence, we began experimenting with some fancy pulse sequence programs (other than the pre-canned SINGLE, DOUBLE, T_1 -rho and Carr-Purcell-Meiboom-Gill sequences). Since the instruction set is quite straightforward, a program could be generated through software in minutes from a simple pulse sequence diagram. The commands are load loop counters, jump conditional or unconditional, load hardware output register, timing interval, and a macro instruction for data acquisition. The hardware register has 13 outputs for individual devices. Two are unassigned and are available for user expansion; three are assignable through the program to pre-connected hardware (homospoil and spin lock level for example). Thus, the optional spin-locking unit gave us an attenuator for the observe output level which could be controlled directly by the PG-200. Connection of one line to an unassigned hardware register output also gave us an RF phase shift control for the 1H irradiation channel.

In a very short time, we had produced sequences to do transient NOE¹ by pre-irradiation, pre-saturation for eliminating ^{13}C solvent peaks, cross-polarization², and selective excitation³.

An example of the selective excitation is given in Figure 1. The compound is ethylcrotonate in deuterated benzene/acetone. Spectrum A is the coupled ^{13}C using gated decoupling. Spectra B through G are individual carbons selectively excited by setting PI*** (pulse interval) at $1/f$, where f is the frequency from the RF carrier. This is the center of the spectral width using DQD*. Note in Spectrum G, one line of the d_6 acetone multiplet is excited also since it is exactly the same frequency from center as the carbonyl carbon. In Spectrum E, the one methyl carbon happens to be exactly at the third harmonic of the vinyl carbon (hence the lower intensity). For this sequence, we did not even

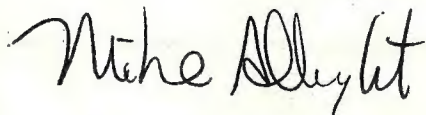
*Digital Quadrature Detection



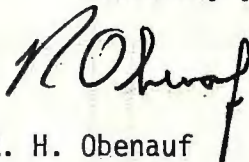
"Bringing the Scientist Tomorrow's Capabilities Today."

need the attenuator since the pulse width has 0.1 usec setability. The second loop counter eliminated the need for an external modulator and since PI*** was one of the 18 autostack parameters, the whole series of spectra were run unattended. In conclusion, the standard foreground/background configuration and 5 minutes were all that was necessary to set up a selective excitation sequence which then could be run in the unattended background mode for all carbons in a spectrum.

Sincerely yours,



M. J. Albright



R. H. Obenauf



K. Goto

MJA/nc

Enclosures

REFERENCES:

1. J. Kowalewski and A. Ericsson, TAMN-NMR Newsletter, 232, 44 (1978)
J. Schaefer, "The Carbon-13 NMR Analysis of Synthetic High Polymers", p. 190, in "Topics in Carbon-13 NMR Spectroscopy", Vol. 1, ed. G.C. Levy, Wiley, New York, 1974.
2. M. Mehring, "NMR Basic Principles and Progress", Vol.11, "High Resolution NMR Spectroscopy in Solids", Springer Verlag, Berlin, 1976.
3. G. A. Morris and R. Freeman, J. Magn. Resonance, 29, 433 (1978).

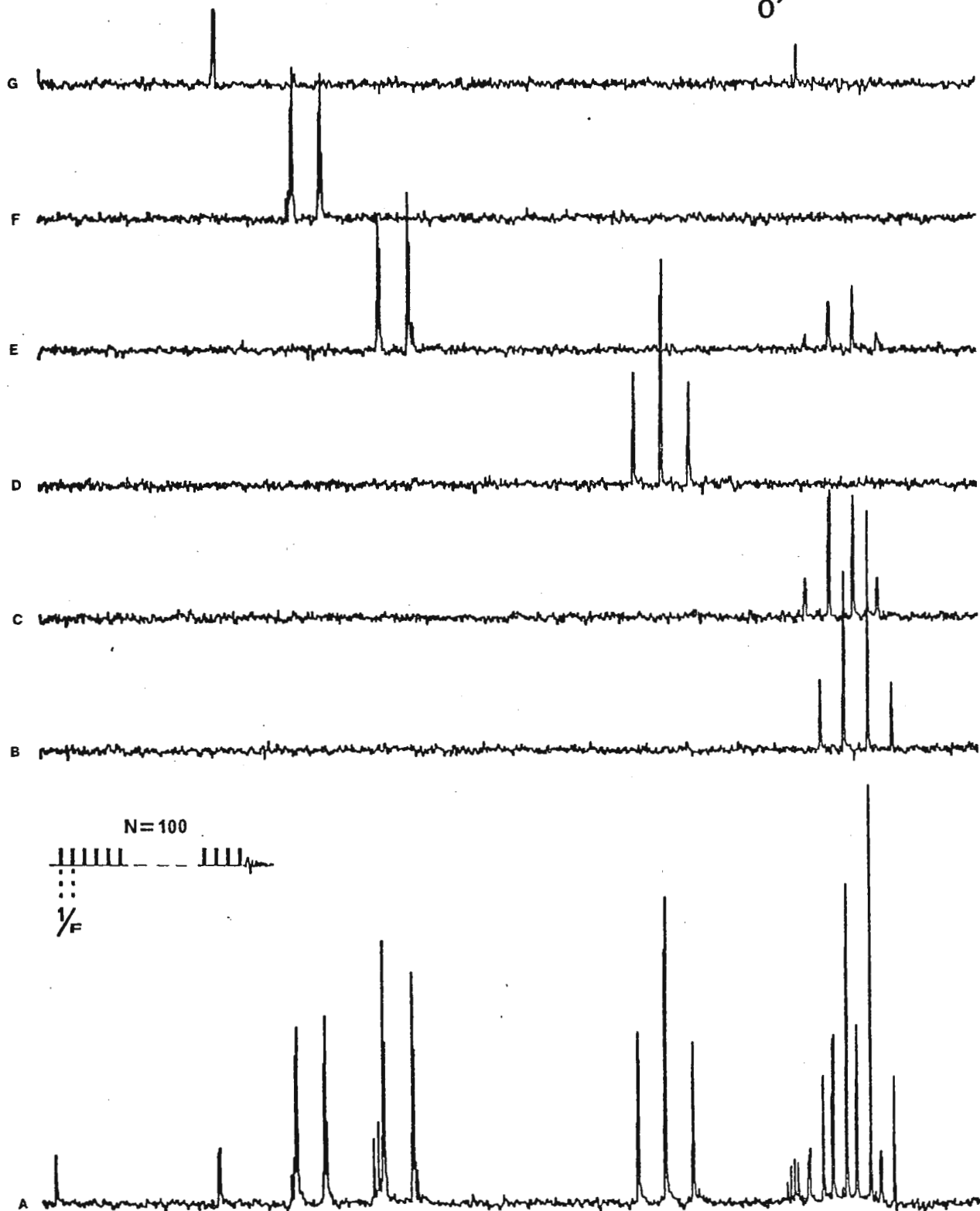
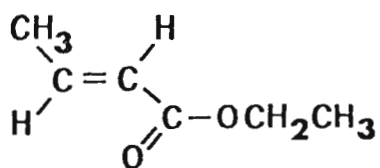


FIG 1

TEXAS A&M UNIVERSITY

COLLEGE OF SCIENCE

COLLEGE STATION, TEXAS 77843

Department of
CHEMISTRY

En Quête des Temps de Recherche Perdus.

The current issue (#240) marks the completion of twenty unbroken years of existence of this Newsletter. Because this is not a completely trivial period of time, perhaps the event ought not to go completely unmarked. Hence the historical remarks which follow.

The Newsletter was started in October of 1958 by Aksel A. Bothner-By and myself, at what was then Mellon Institute (now part of Carnegie-Mellon University) in Pittsburgh, PA. This original incarnation of the Newsletter was named Monthly Ecumenical Letters from Laboratories Of NMR, with the not surprising and semi-pronouncable abbreviation MELLONMR in fact surviving long after the official name of the Newsletter had changed. For your amusement, the first issue of MELLONMR is reproduced without change as pages 50 - 59 of this, the 240th consecutive monthly issue.

At the end of issue #1 is the original mailing list, a non-systematic creature of Aksel's and my then limited acquaintance. While I would hesitate to advance a moral or conclusion to the observation, you may note that the following are still subscriber/participants in the Newsletter after 20 years: Herb Gutowsky, Paul Lauterbur, Charlie Reilly, Jack Roberts and Jim Shoolery, in addition of course to Aksel Bothner-By and myself. (Is it not remarkable that none of the seven of us has aged during a 20-year span!) Inspection of the mailing list for issues #2 and #3 turns up several more names of those who are today still getting the Newsletter. Perhaps I will dig up the occasional letter from the early years for inclusion in future issues of the Newsletter so that we can think fondly or in stupefied amazement at what passed for news years ago.

From October 1958 through January 1964, (issues #1-#64) the entire cost of the Newsletter was born by Mellon Institute, through Aksel Bothner-By's persuasiveness with management and his willingness to commit the necessary funds from his departmental budget. I personally feel that it is appropriate we remember this substantial act of generosity which enabled the launching and firm foundation of this 20-year enterprise.

MELLONMR #1 contains some items of mild interest: you will find, for instance, that the philosophy and policies under which the Newsletter operates today are (except for financial matters!) quite indistinguishable from those originally concocted. This fact, together with the self-regulating nature of the Newsletter mailing list suggests that few changes are in order for the future.

Issue #1 also contains the first of several discussions of the problem of standards and referencing of NMR spectra, a topic which even today continues to charm (?) the likes of Ted Becker, Wallace Brey, Jack Roberts and - when forced! - myself. Plus ça change,.....

Less obvious in issue #1 is the pain and artistry involved in producing the then-superb 60 mc [sic] spectra of isobutylene. These spectra represented almost state-of-the-art quality obtainable from a commercial spectrometer, and were obtained on one of the very first, very new Varian HR-60 spectrometers. This wonderful machine with its remarkable spectral dispersion was unadorned with such modern frivolities as controlled temperature cooling water for the magnet, shim coils, or field/frequency locking. (What the magnet did have, however, was protection from room air currents, in the form of a lavender vinyl shower curtain adorned by many swans; this optimal design due to Christine Bothner-By.) Field homogeneity was changed - occasionally improved - by use of a long-handled wrench manipulated by an 8-foot long pipe. Sweeps were routinely calibrated by the imposition of audio sidebands, and couplings measured by graphical interpolation or wiggle beats. Not knowing any better, one didn't mind these laborious procedures, for we were very happy with the remarkable 60 mc dispersion, and truly ecstatic at having finally been emancipated from the ancient torture devices of the Sanborn and the equally infamous G-10 recorders. The term "good old days" did not apply to all aspects of NMR spectroscopy.

In January of 1964 an excellent opportunity at the Illinois Institute of Technology enticed me to move my family and the Newsletter to Chicago. (I think that on any given day, at least two of my three girls have already started to forgive me.) Thus the totally unpronounceable new name of IITNMRN ran from issue #65 through #119. For the first 3½ years of IITNMRN, the entire expense of the Newsletter was born by the Illinois Institute of Technology, until the Newsletter had grown to such a size and mailing list that it was no longer reasonable or practical to rely on IIT's generosity. The back cover of the August 1967 issue (#107) contains a substantial list of corporations and universities in this country and abroad who answered the call for support for the Newsletter, and who continued to provide all necessary funds so that the Newsletter could be mailed to participant/recipients without charge. This meta-stable financial posture continued until ca. October 1969, at which time the paid subscription system was established.

Subscription income has always been, and continues to be, much less than is needed to cover the costs of producing and mailing the Newsletter. We have continued to be dependent on the goodwill and generosity of our Sponsors, Contributors and Advertisers. Let me urge those who value the Newsletter to note the list of Sponsors and Contributors which is printed in each month's issue, and to say a kind word to them from time to time. Likewise, please notice those who advertise in the Newsletter and

tell them (better yet - show them) that their efforts and financial support are appreciated. We have lost advertisers in the past for want of feedback to them from the readership they are trying to reach. In the face of continually rising production and mailing costs, we still need a few more advertisers to put the Newsletter into a really healthy financial posture. Your efforts along these lines will really be appreciated. Please note that most of our advertisers have been with us on a regular, monthly basis since the inception of advertising in the July 1972 issue (#166), and we all owe them an especial debt of gratitude.

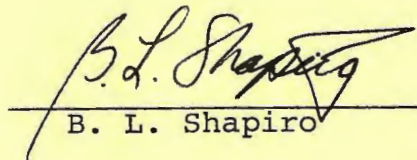
Although it is always dangerous and possibly unjust to single out one particular individual (i.e., non-corporate) Sponsor, I can not help but note for all that Professor Robert Kosfeld of the TH of Aachen, Germany has been a long-standing, exceptionally generous Sponsor of the Newsletter. Those of us who have had the pleasure of visiting Professor and Mrs. Kosfeld and members of his group in Aachen will not be surprised at this outstanding contribution to the general welfare of the NMR community.

Over the years, the Newsletter mailing list has grown in a rather slow but steady manner. Despite financial pressures to do otherwise, we have stuck quite faithfully to the policy of requiring participation in the Newsletter by sending in technical contributions as a criterion for receiving the Newsletter. Without this very infrequently suspended policy, and the unfortunately non-trivial financial part of the subscription, growth and the present size of the mailing list would have been much greater. At present, we send out approximately 275 copies per month, and a survey of a few years ago indicates that each copy is read by approximately six individuals. Our present mailing list includes subscriber/participants in 31 states of the U.S.A., 7 Canadian provinces, and a total of 22 countries.

The nature of the contributions to the Newsletter has continued over the years to range over a broad spectrum, which we feel is very healthy. We will continue the policy of letting anything reasonable appear in the Newsletter - new developments in theory and practice, new hardware and software, data, notices of forthcoming meetings, positions available and wanted, etc. [By "anything reasonable" our veteran readers will understand items other than reports of new instances of non-equivalent methylene protons, or how to clean magnet cooling coils.] Until Wes Andersen and John Waugh defected from the mailing list, and before age and status stodgified the written efforts of the likes of Ray Freeman, Paul Lauterbur and Alex Pines, we could even count on the occasional contribution of a humorous (intentionally so) nature. Surely there are others who can come up with the occasional letter strictly pour s'amuser - I would hate to think that we have nothing more entertaining to look forward to than the next locker-room-type acronym.

Since August of 1968, you have been receiving the TAMU NMR Newsletter. The Newsletter is now completely self-supporting, i.e., all costs are born by funds raised by subscriptions, Sponsorships and Contributorships, and Advertising. Since 1971, the smooth operation of the Newsletter has been due in major part to the competence, financial accumen and patience of my highly valued assistant, Mrs. Loretta M. King. Mrs. King handles almost all of the operations aspects of the Newsletter, and is capable with such diverse tasks as handling printers, seeing that your Newsletter is mailed with attractive stamps, arranging for advertising and billing, and she has even managed to somehow cope with the Byzantine mysteries of State bureaucracies and the Italian postal system!

Although we feel that by now the Newsletter has settled into a fairly adequate routine - aside from the ever-present problem of finances - we are always open to suggestions for the improvement of any aspect of the Newsletter. Please do not hesitate to write or call if you have an idea, or a lead for a new Advertiser, etc. With your guidance and support, we look forward to continuing the Newsletter indefinitely.


B. L. Shapiro

11 September 1978

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 1

Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

Introduction

This is No. 1 of a proposed monthly letter designed to expedite the exchange of information and ideas among laboratories engaged in research on the application of N-M-R to problems in organic chemistry. We hope that you will be interested in receiving this letter and in being a regular contributor to its contents. We feel that the effectiveness with which its purpose is accomplished depends directly on the informality and small size of the undertaking; to this end we suggest that distribution be limited to those who contribute with some regularity. It is understood that appearance of material in this letter will be construed in no way to constitute official publication. Material appearing in this letter is to be solely for the readers' personal use, and quotation of results is to be made only by direct arrangement with the originators of the work.

Subject Matter

We hope that you will feel free to submit any material whatsoever, whether complete or fragmentary. Data already in hand is, of course, welcome. Among subjects which you might consider appropriate are:

2.

- (1) Reproductions of spectra or parts of spectra.
- (2) Measurements and calculations on same.
- (3) Theoretical considerations and interpretations.
- (4) Novel experimental methods and techniques.
- (5) Complete or partial mysteries.
- (6) Comments on material appearing in earlier letters.
- (7) Requests for help in locating sources of odd or rare compounds.

We intend to exercise no editorial function, but will simply assemble and reproduce sufficient copies of what is submitted to furnish the contributors with one copy each.

Practical Considerations

The reproductions of submitted material will be made by the Xerox process, which requires only that (1) material be submitted in an 8 1/2" x 11" format with a 1 1/2" left-hand margin, and (2) no blue ink be used - heavy black lines and writing are best. As this is essentially a photographic process, the originals of any material submitted can be returned, and actual spectra pasted to 8 1/2" x 11" paper, etc., will produce quite well.

We would like to suggest further that (1) the contributors use a minimum number of pages to present their material adequately, and (2) an identification of the origin of the submitted material appear on each page.

3.

Material received by B. Shapiro by the 25th of each month will be included in the next letter, which will be sent out as soon as compilation, reproduction, collation and mailing can be completed.

It is with considerable trepidation that we approach the subject of standardization of spectra. Nevertheless we are compelled to settle on some convention so that submitted spectra and measurements will be readily interpretable by all participants without resort to an IBM 704, witchcraft or much tedious arithmetic.

After considering the numerous systems which have been used in the literature and discussed and suggested at various meetings, public and private, we have come to the conclusion that the best scheme for reporting chemical shifts is a combination of that suggested by Reilly et al and that suggested by Tiers. The system we suggest is as follows:

- (A) Both an internal and an external reference should be used.
- (B) The internal reference of choice is tetramethylsilane (obtainable from either Anderson Laboratories, Inc., Weston, Michigan, or Peninsular ChemResearch Inc., 1103 N.W. Fifth Avenue, P.O. Box 3597, Gainesville, Fla.).
- (C) The position of tetramethylsilane as an internal reference is assigned the chemical shift number, $\delta = + 10.00$.
- (D) Chemical shifts will be quoted in parts per million (ppm), increasing positive values of δ corresponding to resonances occurring at increasing applied magnetic fields (i.e. to increasing shieldings).

4.

This is a rather arbitrary set of rules, and some amplification and explanation is probably in order. Firstly, to define terms: by internal reference, we mean a substance added directly to the sample whose spectrum is being taken, so that the spectrum is actually recorded on a liquid mixture; by an external reference, we mean a substance whose spectrum is recorded simultaneously with that of the sample, but which is not physically mixed with it -- perhaps contained in a sealed capillary added to the N-M-R sample tube, or contained in an annular space in a specially constructed cell.

We suggest running the chemical shift scale from the internal reference, because this usually gives a more nearly consistent scale of chemical shifts than external referencing. It is not perfect, however, and no satisfactory theory has as yet been developed which would allow one to correct exactly for specific solvent effects. It is not outside the realm of possibility that such a theory will be developed, and it seems quite possible that the deduction of and/or the application of such a theory may be based on a knowledge of absolute (i.e. externally referenced) line positions. For this reason, it would seem highly desirable that both internal and external reference substances be used in standardizing N-M-R spectra. Whatever practice is followed, it is clear that the spectra will have the greater potential value the more completely are the conditions described under which they are obtained. For example, as a minimum requirement, the following should also be specified:

5.

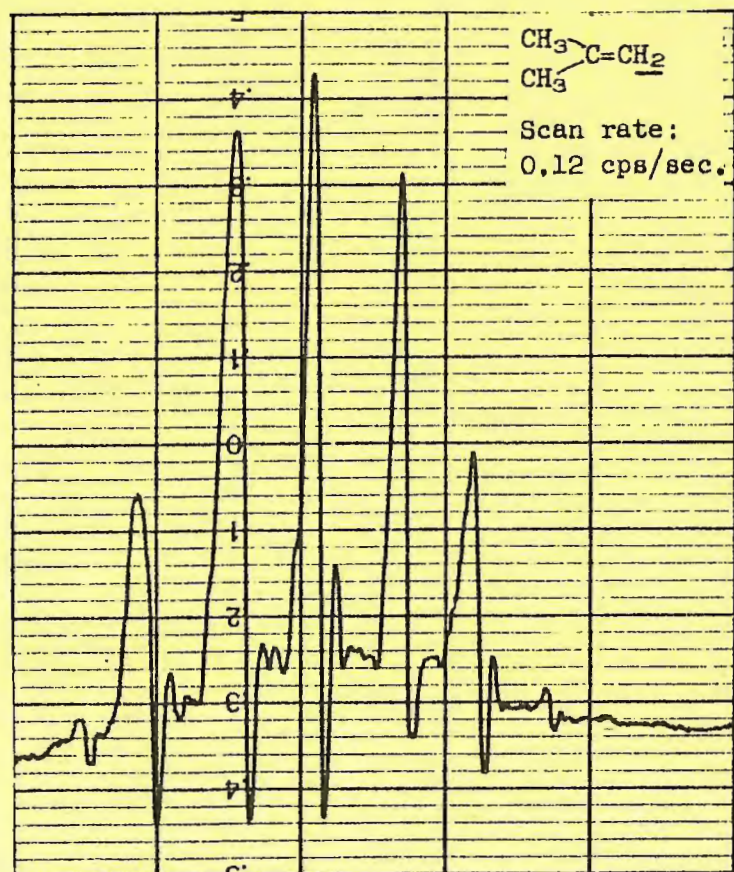
- (1) R.F. oscillator frequency
 - (2) Solute and internal reference concentrations
 - (3) Details of source + preparation of sample (e.g. whether or not dried, distilled, degassed, etc.)
 - (4) Temperature of the sample
 - (5) Any unusual conditions
-

We are very much looking forward to hearing from you. We hope for your contributions, but will also welcome any comments, criticisms, or suggestions on the operation of this newsletter. Appended is the current mailing list for this letter -- if you have any suggestions for additions (or deletions!?), we will be happy to receive them.

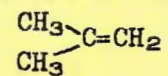
A. A. Bothner-By

B. L. Shapiro

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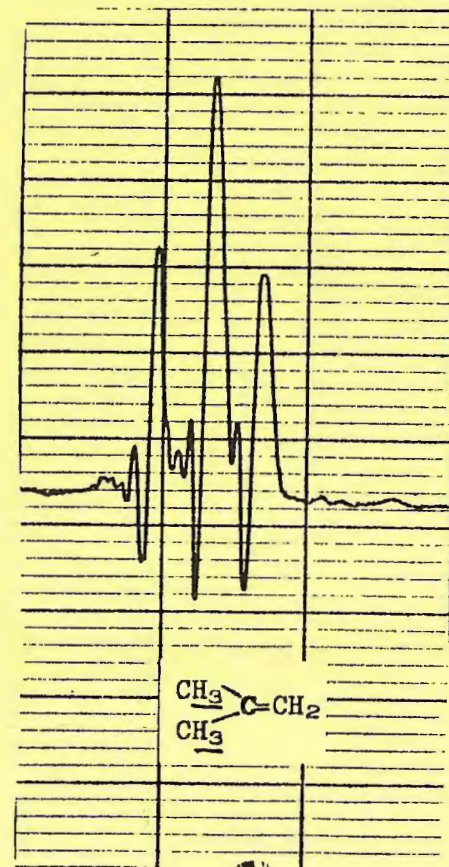
Isobutylene



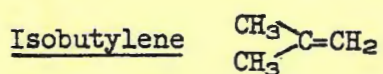
Neat, degassed

See data on
following page.

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7.



(Phillips Petroleum Co. Pure Grade)

CCl_4 solution: $\text{Me}_2\text{C}=\text{CH}_2$ 10%

Me_4Si 1%

External reference: CHCl_3

Both the sample solution and the CHCl_3 capillary were degassed.

Resonances observed at 60 mc.

Temperature: 24°C .

$$\delta_{\text{Me}} = 8.30 \pm 0.01$$

$$\delta_{\text{CH}_2} = 5.40 \pm 0.01$$

The external CHCl_3 resonance signal appears at 7.42 ppm from the line of Me_4Si .

$\delta_{\text{Me}} - \delta_{\text{CH}_2} = 2.90$ In the neat liquid, the Me- CH_2 separation is 2.96 ppm.

$J = 1.20 \pm 0.03$ cps. (apparently, the same for cis and trans hydrogens.)

13 October 1958

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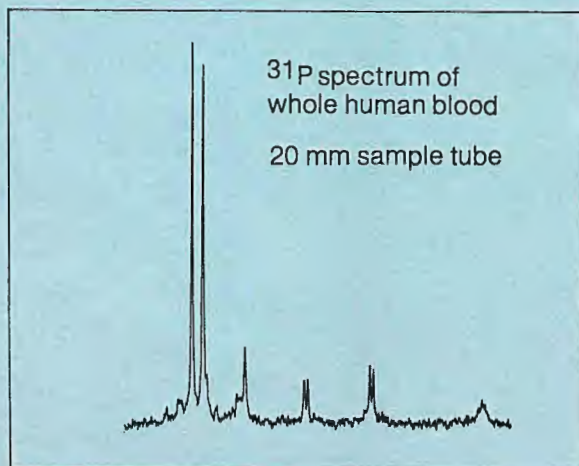
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