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Newsletter

No. 271

April, 1981

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DEADLINE DATES: No. 272 4 May 1981
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All Newsletter Correspondence, Etc., Should be Addressed To:

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

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

I. and II. order quadrupole effects in solid state ^{127}I NMR

Dear Professor Shapiro:

Experimentally it is not easy to measure pure quadrupole resonance frequencies in the region $\nu < 10$ MHz. We had a lot of such problems when we tried to find the ^{127}I quadrupole coupling constants of some periodates, structured in the scheelite-, pseudoscheelite- or $(r_{\text{cation}} > r_{\text{anion}})$ -type. In this situation it was very helpful to use the fact that the ^{127}I NMR frequency of 40.02 MHz at the field $H_0 = 4.698$ Tesla of our Bruker FT-NMR CXP 200 allows to fulfill the condition $|e^2qQ/h| \ll |\mu_{\text{NI}} \cdot H_0|$ for the observation of I.order effects (satellites) or II.order effects (splitting of the $+1/2 \leftrightarrow -1/2$ - transition) in ^{127}I NMR powder spectra for the above mentioned low NQR coupling constants e^2qQ/h . Evidently, sufficiently high magnetic fields give a possibility to measure quadrupole coupling constants by NMR spectroscopy to orders of magnitudes, which were accessible until now only by pure NQR spectroscopy.

Fig. 1 and 2 show as an example of measured I. and II. order effects the completely unusual positive temperature dependence of the ^{127}I quadrupole coupling constants in NH_4IO_4 . The values in the region $T > 273$ K are identical with those measured by pure NQR spectroscopy. Great care has to be taken in this region because NH_4IO_4 tends to decompose explosively into NH_3 , O_2 , H_2 , I_2 and H_2O .

This unusual and strong positive temperature dependence resembles that of the ^{185}Re and ^{187}Re quadrupole coupling constants of the analogue NH_4ReO_4 , we measured earlier¹⁾. Both are not well understood until now¹⁻⁴⁾.

Another example is demonstrated in fig.3, where in a small region about $T \approx 296$ K the large II. order quadrupole splitting

Prof. B.L. Shapiro

disappears, indicating a phase transition in the pseudo-scheelite structured CsIO_4 .

These two and other examples show that measuring quadrupole effects is another area which makes highest magnetic fields desirable.

Please credit this letter to the subscription of Prof. H.P.Fritz.

Sincerely,

P.K. Burkert

P.K. Burkert

- 1) P.K. Burkert and M.F. Eckel, Z. Naturforsch. 28b, 379 (1973)
35b, 1349 (1980)
- 2) M.T. Rogers and K.V.S. Rama Rao, J.Chem.Phys. 58, 3233 (1973)
- 3) S.L. Segel, R.J.C. Brown and R.D. Heyding, J.Chem.Phys. 69,
3435 (1978)
- 4) S.L. Segel and R.J.C. Brown, J.Chem.Phys. 70, 3840 (1979)

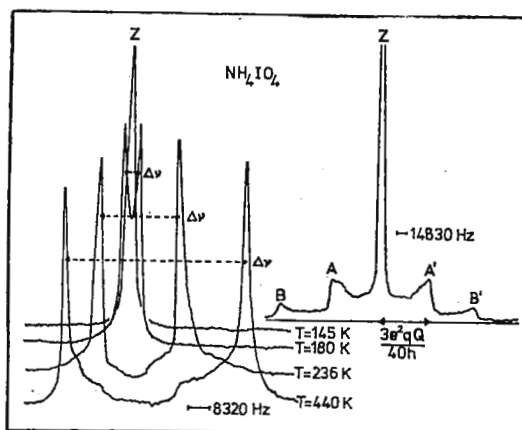


Fig.1. ^{127}I NMR signals of NH_4IO_4 with I. and II. order quadrupole effects for $T \geq 145 \text{ K}$

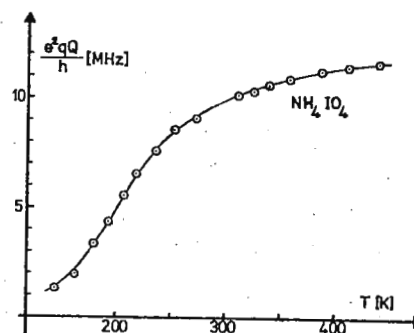


Fig.2. Anomalous temperature dependence of the ^{127}I quadrupole coupling constant in NH_4IO_4

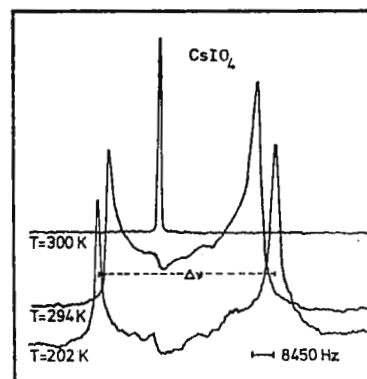


Fig.3. ^{127}I NMR signals of CsIO_4 with phase transition

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DEPARTMENT OF CHEMISTRY

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February 18, 1981

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

⁹⁵Mo NMR of Molybdenum Carbonyl Compounds'

Dear Barry,

We have been using our specifically tuned (6.5 MHz) ⁹⁵Mo probe for our JEOL PFT-100 for about a year now and have gained considerable experience searching for these sometimes elusive signals.

Natural abundance ⁹⁵Mo (15.8%; $I = \frac{5}{2}$) NMR gives signals with half widths ranging from a few Hz for MoO_4^{2-} to several hundreds of Hz for the polyoxometallates such as $[\text{Mo}_7\text{O}_{24}]^{6-}$. Many systems however have line widths in the 10 Hz range, and hence spectra can be obtained in a reasonable time at useful concentrations. The chemical shift range is large (-2200 δ to +3500 δ) which helps the identification of ⁹⁵Mo signals from similar compounds. We use as our standard aqueous 2M Na_2MoO_4 at pH 11, which is stable, gives a narrow line, and can be observed in a single pulse.

Two spectra are presented to illustrate some of the applications of ⁹⁵Mo NMR. (i) The quartet as the result of ⁹⁵Mo-³¹P coupling allows the ready identification of this coupling constant in $\text{Mo}(\text{CO})_3[\text{P}(\text{OEt})_3]_3$ whereas identification of this coupling constant from the ³¹P spectra is complicated by coupling of phosphorus to ⁹⁵Mo, ($I = \frac{5}{2}$) & ⁹⁷Mo ($I = \frac{5}{2}$). (ii) The ⁹⁵Mo spectrum of a mixture of a arene molybdenum tricarbonyl compounds with a number of different substituents in the aromatic ring shows a separate signal from each compound. The identification of the components in such a mixture is trivial from the ⁹⁵Mo spectrum compared to the complexity expected for the ¹³C or ¹H spectrum.

Please credit this contribution to the Monash University group (Dr. M. Heffernan) who are kind enough to share the newsletter with us.

Yours sincerely,

Bob

R.T.C. BROWNLEE

Max O'Connor

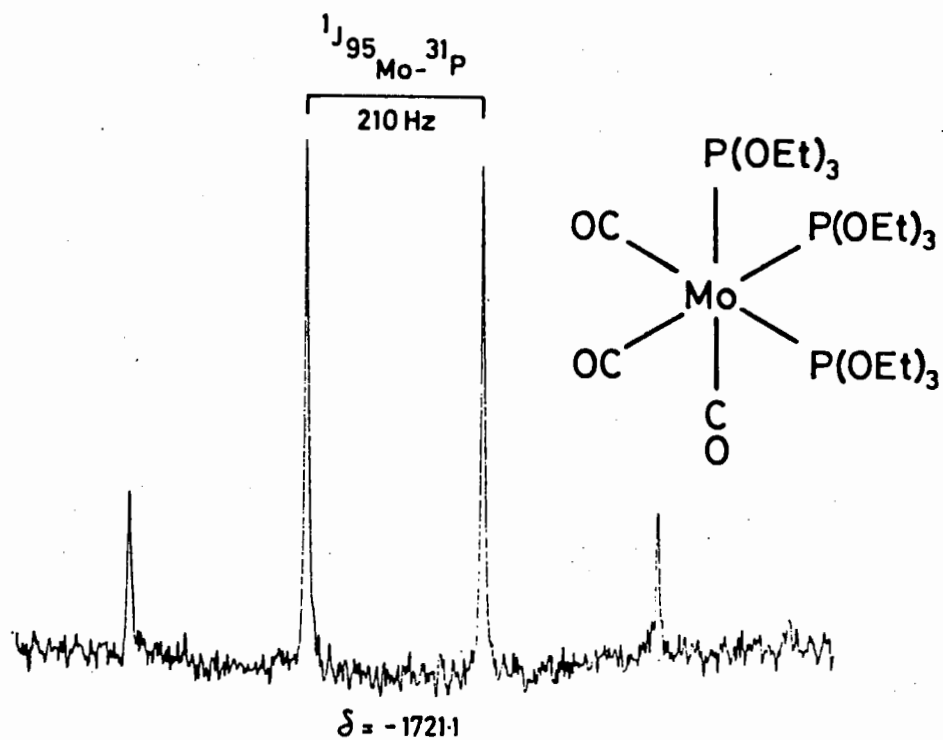
M.J. O'CONNOR

Tony Wedd

A.G. WEDD

Tony Masters

A.F. MASTERS

^{95}Mo  $(\text{xy})\text{Mo}(\text{CO})_3$

m- p- o-

$(\text{mes})\text{Mo}(\text{CO})_3$

$(\text{tol})\text{Mo}(\text{CO})_3$

^{95}Mo

The figure displays a ^{95}Mo NMR spectrum with several peaks. The x-axis is labeled $\delta(^{95}\text{Mo})$ (ppm) and ranges from -1900 to -2100. The peaks are identified as follows:

- $(\text{mes})\text{Mo}(\text{CO})_3$ at approximately -1980 ppm
- A cluster of peaks for $(\text{xy})\text{Mo}(\text{CO})_3$ between -1950 and -1980 ppm, with sub-labels m-, p-, and o-.
- $(\text{tol})\text{Mo}(\text{CO})_3$ at approximately -1960 ppm

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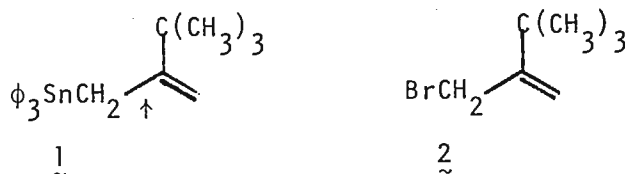
March 11, 1981

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

Dear Barry:

In response to your note here is some news from Columbus.

Hindered rotation in tin compounds: We have been interested in highly substituted allyllithium compounds which we generate by cleaving the corresponding tin compounds with butyllithium. At least one of these tin compounds, 1 (made from the bromide



2 and $\phi_3\text{SnLi}$) exhibits time-dependent NMR behavior which we ascribe to very slow interconversion among rotamers. Compound 1 is purified by distillation giving a clear liquid. This analyses correctly in every way except that the sample, in CDCl_3 , immediately on isolation, gives rise to two ^{13}C NMR spectra, in ratio 3/1, with very similar shifts. Over about two days at room temperature (25°) the lower intensity spectrum disappears. After this no amount of cooling or heating (at different rates) changes the spectrum. We can only imagine that the formation reaction generates some unstable conformer(s) which convert slowly into the most stable one by rotation about the $\text{CH}_2\text{---C=}$ single bond. Steric hindrance keeps this slow. The thermodynamically unstable conformer(s) could give $\phi_3\text{Sn}$ gauche to t-butyl; in the stable form these groups would be further apart. Similar explanations have been invoked for IR data on organotin compounds.^{1,2}

A useful non-polar NMR solvent: A non-polar ^{13}C NMR solvent with a window in the hydrocarbon region is toluene- d_5 - $\alpha\text{-C}^{12}$. Since he needed a few grams of this stuff, Dr. Rainer Stumpe, who spent a year in our lab, made it himself. Interested readers should apply for more information.

The price of isotopically enriched compounds continues to increase faster than most people's grants so it is incumbent on those of us who need these materials to develop cheap, fast, easily carried out syntheses and to share the information.

Best wishes.

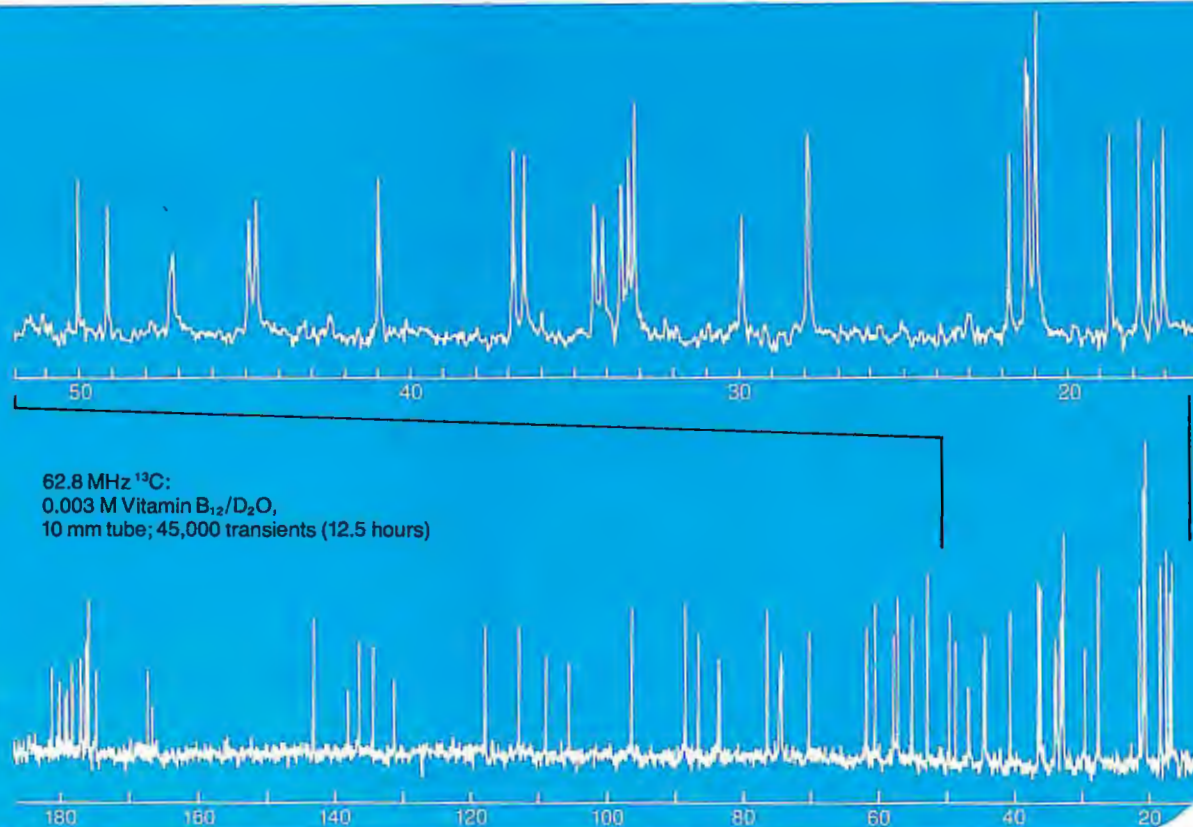
Yours sincerely,

Gideon Fraenkel

Gideon Fraenkel
Professor, Ohio State University

1. C. W. Young, J. S. Kochler and D. S. Mackinney, J. Am. Chem. Soc., 69, 1410 (1947).
2. R. A. Cummins, Amst. J. Chem., 16, 985 (1963).

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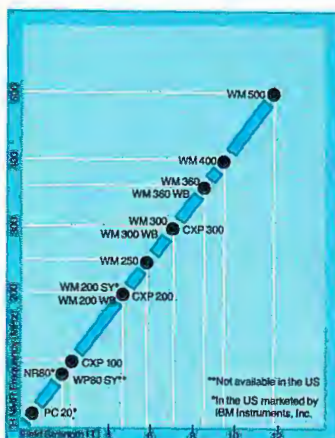
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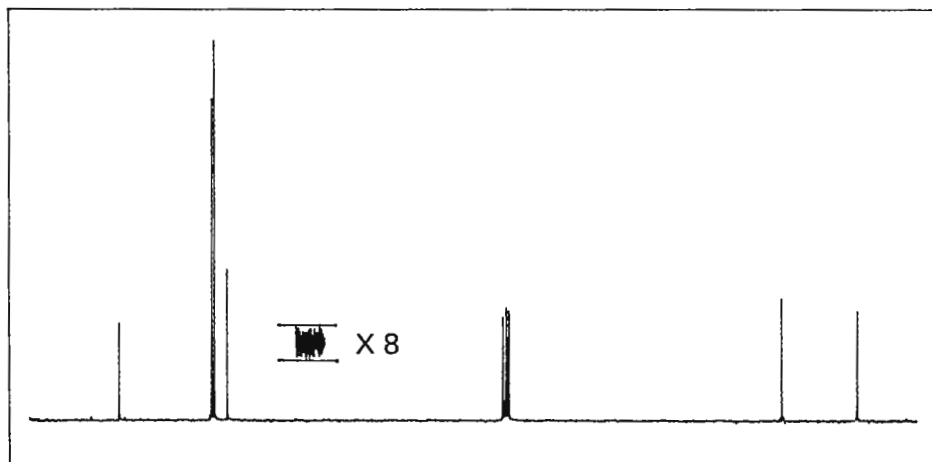
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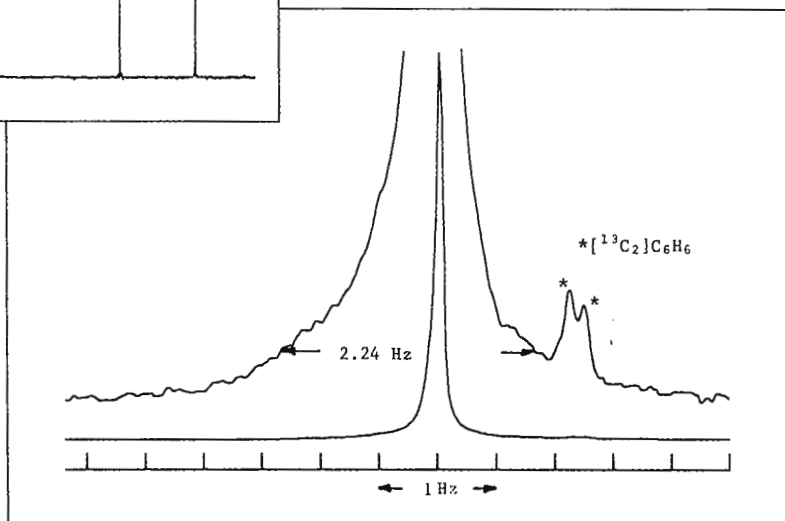


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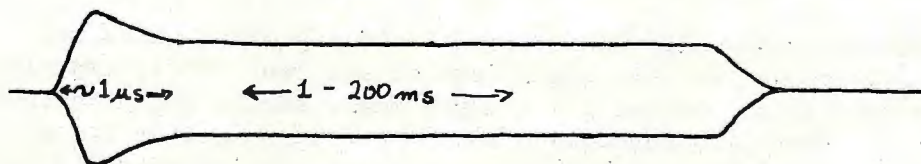
February 13, 1981

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

Dear Barry:

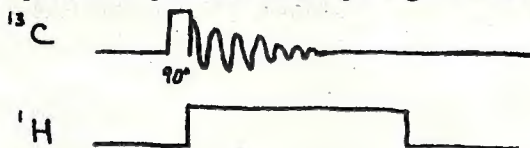
Radio Frequency Field Strengths and Rotor Impurities in Cross Polarization in Solids

Normal spin locked cross polarization NMR in solids has the advantage of being rather forgiving of the exact amplitude, time and phase of the pulses. Signal to noise may suffer, but adequate spectra can usually be obtained.¹ There are experiments where quantitation is desired and the Hartmann-Hahn condition must be carefully met and a knowledge of the amplitude of the decoupling field is desired. High Q probes and non-linear amplifiers usually give pulse envelopes which look something like:



Since estimation of γB_1 from the time of a 180° pulse ($\sim 6-15 \mu s$) is in the most nonlinear portion of the rf response it is a highly inaccurate means of determining the decoupling field which exists say 2-100ms later.

We have been using a spin tickling technique which gets around this problem. We use a liquid sample of ^{13}C enriched CH_3OH sealed in glass and inserted in a rotor. Using a very low level coherent frequency decoupling we vary the proton frequency to find the exact proton resonance. Then we offset the decoupler by 60 kHz and perform a "normal high resolution experiment" with high powered proton decoupling. i.e.:



with a low duty cycle. The Fourier transform is a quartet, the splitting of which is proportional to γB_1 . Martin, Delpuech and Martin² have described off resonance calibration of rf fields but in our particular case, the equation of interest is:

$$J_r = [(\Delta\nu + J/2)^2 + (\gamma B_1)^2]^{1/2} - [(\Delta\nu - J/2)^2 + (\gamma B_1)^2]^{1/2}$$

where $\Delta\nu$ is the decoupler offset (60 kHz in our case), J is the ^1H - ^{13}C splitting in the absence of decoupling (142 Hz for methanol) and J_r is the residual splitting. In Figure 1, we have plotted the channel separation for a 60 kHz offset, 100 μs dwell, 8K Fourier transform experiment with methanol and the rf amplitude can be easily read off the graph. An estimate of B_1 homogeneity over the sample can be made using the same equation and measuring the linewidth difference between the tickling experiment and high power on-resonance decoupling.

To measure γB_1 for the carbons, the decoupler frequency is reset, the methanol is replaced by a rotor full of adamantane and the ^{13}C rf level is adjusted for a maximum in the cross polarization signal using a contact time $\leq 1\text{ms}$. The relatively small C-H dipolar coupling in adamantane make it a good choice for setting the Hartmann-Hahn condition. The short cross polarization contact time is needed for an accurate match of the carbon and proton fields. We can see intensity differences in the amplitude of the adamantane FID with a 0.2 dB mismatch between the carbon and proton fields.

It is worth mentioning that we find it necessary to retune our probe matching circuits both when changing samples and when moving the decoupler frequency by 60 kHz. Clearly probe efficiency and rf field strengths are a function of the probe tuning and impedance match.

As an aside we would also like to reiterate a problem which was mentioned by de Wit et. al. (TAMU Newsletter, Sep. 1980), impurities in rotor materials. On our 1.4 T magic angle sample spinning instrument we use polychlorotrifluoroethylene rotors and have seen no cross polarization peaks due to impurities. On our 4.7 T instrument we have been using deuterated PMMA rotors which have enough protons to give a cross polarization signal and polyoxymethylene rotors which have impurity peaks and side bands as seen in Figure 2. These can interfere with detection of weak resonances.

Sincerely,

Bill

William L. Earl
Center for Fire Research

David

David L. VanderHart
Center for Materials Science

1. S.R. Hartmann and E.L. Hahn, Phys. Rev. 128, 2042 (1962).
2. M.L. Martin, J.-J. Delpuech and G.J. Martin, Practical NMR Spectroscopy, Heyden, London (1980) p. 209 ff.

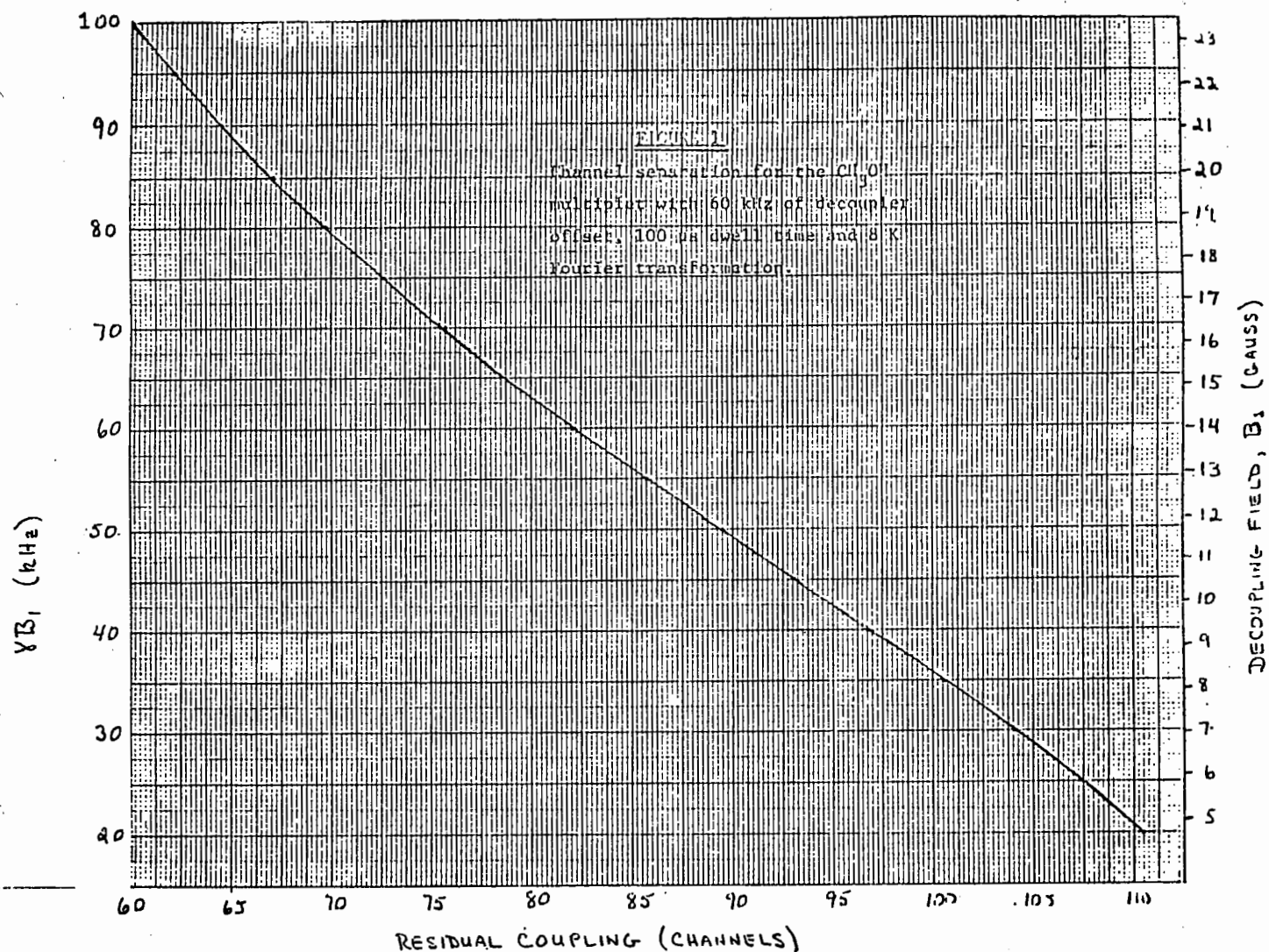
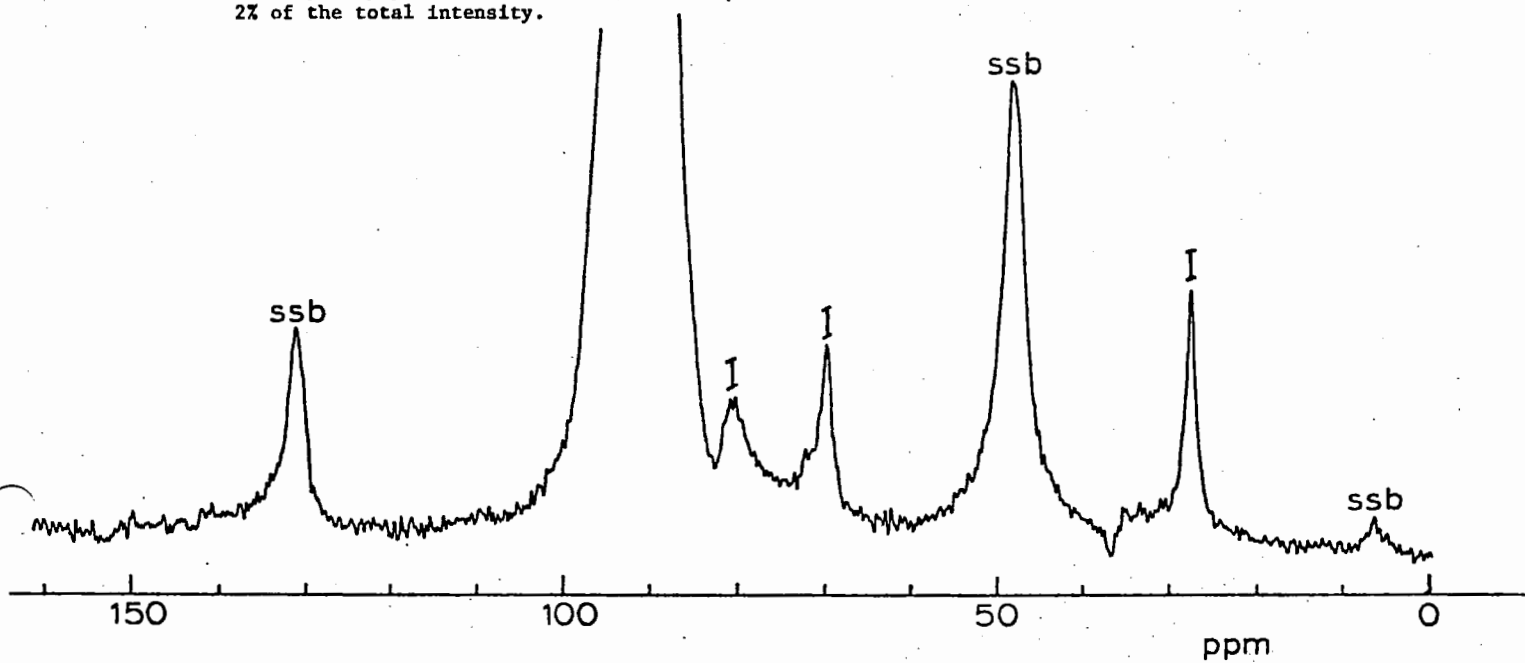


FIGURE 2
 CPMAS spectrum of polyoxymethylene (delrin) at 4.7 T.
 ssb=spinning sideband
 I = impurity
 The impurity peaks are each approximately 2% of the total intensity.



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Prof. B.L. S h a p i r o
Department of Chemistry
Texas A&M University
College Station, TX 77843

46/HÁ/81

1 March 1981

Dear Prof. Shapiro,

Our second contribution to TAMU is devoted to:

Use of Analysis of Variance for the Determination of Experimental Conditions of NMR Quantitative Measurement

The value of aromaticity (f_a) - the ratio of aromatic carbon atoms to all carbons in measured sample is an interesting characteristics of the most petrochemical products. The conditions of the measurement of quantitative ^{13}C NMR spectra can be evaluated theoretically if T_1 and NOE are known.¹ The analysis of variance can be used for the determination of reproducibility of integral intensities and by this way for checking of the experimental conditions. The Table 1 shows the results of analysis of variance of measurement of f_a of the one sample of crude oil. The parameter C_1 is a parameter characterizing experimental method of measurement (C_1 - gated decoupling with delay time 10 s, C_2 and C_3 - broad band decoupling with 10 s and 0.6 s delay times, resp.), B is a parameter of three independent measurements and parameter A means the three independent integration for each measurement were performed (replicative factor).

If the calculated F criterion is greater than the theoretical one, the difference between compared methods is signi-

ficant. It follows from the Table, that significant differences exist for all ones or C_1 and C_2 - methods, but does not exist for C_2 and C_3 - methods.

Table 1. Calculated and theoretical (in parentheses) F criterions

Comparison of:	$C_1 C_2 C_3$	$C_1 C_2$	$C_2 C_3$
Factor			
A	1.0039	1.0039	1.0039
B	0.3470(3.555)	0.5617(3.885)	1.902(3.885)
C	33.8671(3.555)	47.9316(4.451)	0.015(4.451)

The result indicate the existing influence of NOE on the measurement of f_a . The difference among independent measurements (B_1, B_2, B_3) is in the range of random errors. These statistical results can provide interesting information, even though the measurement requires a lot of time. We performed some of these statistical experiments at the end of last year during the instalation of our new FT NMR spectrometer Tesla operating for ^{13}C at 25 MHz.

Yours sincerely

Milán Hájek
Milan Hájek

Petr Trška
Petr Trška

Prague Institute of Chemical Technology

Literature

1. S.Gillet and J.J.Delpuech, J.Magn.Res. 38,433(1980)
2. System IBM 360, Scientific Subroutine Package

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Dear Professor Shapiro

Supercon Installation and Helium Recovery

At last the superconducting age has come to Marburg University. We have recently installed a Bruker WH-400 spectrometer and wish to communicate some installation details which might be useful for other people who are planning to set up a supercon.

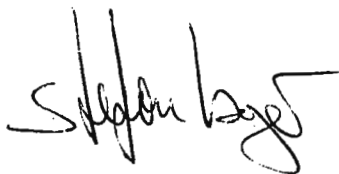
A central helium liquification system was already present in our institute with a connection to the laboratory where the supercon was to be installed. Therefore it seemed reasonable to connect the magnet to the recovery line and save the annual helium costs of about DM 4000,--. However, we measured some pressure oscillations in the recovery line which were caused by the activities of other helium users. We decided, therefore, to connect the magnet to a balloon of 2 m³, which seemed to be a good compromise between the helium diffusion rate through the balloon surface, the helium evaporation rate of the magnet, available laboratory space and cost of the balloon. The content of the balloon is transferred to the recovery line 2-3 times a week using a lab pump. This arrangement has, in our opinion, the advantage of being completely independent from all events or mishaps in the central helium liquifier system.

...

The Bruker magnet power supply B-CN-70 only has the positions "fast" and "slow" for the helium level measurement. It is said that removing the helium level probe would reduce the helium evaporation. We found it very inconvenient always having to either remove the rod or disconnect the cable after measuring the helium content. We therefore disconnected the 18 megohm-resistance on print 2 (Dwg. No. 4-3S-3308) in the power supply, which changes the position "slow" to "off". With this minor modification our magnet (Oxford coil and dewar) has a weekly evaporation rate of 12% with both cable and helium level probe always installed.

Besides some very minor starting problems, working with this 400 Mhz instrument is an extreme pleasure.

Sincerely yours



Dr. S. Berger

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If interested, you may contact Richard S. Egan, Ph.D. at (215)628-5508.



U.S. Department of Energy
Laramie Energy Technology Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

March 6, 1981

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

SUBJECT: An NMR Comparison of Shale Oils Produced by the Fischer Assay and the IGT Hytort Process

Dear Barry:

As you probably know, there is becoming an increased interest in the development of synthetic liquid fuels to replace or supplement the ever dwindling supplies of petroleum. Liquid fuels from oil shales represent an alternative to this problem. The major interest in oil shale development in the United States thus far, has focussed on the oil shales of the Green River Formation in Colorado, Utah and Wyoming. However, a substantial portion (nearly 250,000 square miles) of the Eastern United States is underlain by the Devonian Black Shales, and in principle, represents a sizeable potential resource. These shales, however, yield less than half as much liquids upon heating as do the Green River Formation oil shales, because of the lesser hydrogen contents of the Devonian shales. Therefore, processes to extract liquids or improve recovery ratios from the Devonian shales must necessarily deal with recovery techniques for hydrogen deficient materials. One such candidate process is the Institute of Gas Technologies Hytort process¹, which retorts oil shale under hydrogen pressure with the dramatic result that oil yields of Devonian shales are increased 2.5 times over those obtained by the standard Fischer assay. Characterization of the materials that are produced by the IGT process would be beneficial toward a) assessing the quality of the product oils, b) understanding the retort process and c) providing information for optimizing the process.

In this letter we report some preliminary results of our NMR studies of shale oils produced by the IGT Hytort process and shale oils produced by the Fischer assay.

Previous solid state ¹³C NMR measurements² on raw oil shales have shown that the kerogen in Kentucky oil shales is much more aromatic than Colorado oil shales; hence significant differences in the amount and type of organic material converted to liquids is expected. Thus, it is not surprising that

the carbon distribution and composition of shale oils from the two types of materials are different. The major differences between the two oils produced during Fischer assay, as shown by the spectra, are: 1) the greater carbon aromaticity of the Kentucky shale oil and 2) the higher degree of branched alkanes and/or short chain length aromatic substituents in the Kentucky shale oil. The aromatic region of the Kentucky oil shale shows a more asymmetric pattern in the aromatic region, which is probably due to a larger number of substituted aromatic carbons in this shale oil. An NMR comparison of the liquids derived from the Fischer assay and Hytort processes should reveal some of the differences attributable to the hydrogen. The ^{13}C spectra of Fischer assay and Hytort oils from Colorado and Kentucky are shown in Figure 1(a-d).

The ^{13}C NMR spectra of the Kentucky - Fischer assay and Hytort shale oils are somewhat more revealing than the analogous ones for the Colorado shale oil. The major difference is the reduction in the olefins from the Hytort process. Whether retorting these materials in the presence of H_2 prevents olefins from forming, or saturates them once formed, is not clear at this time.

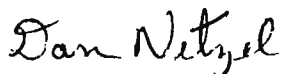
We are in the process of applying NMR to investigate this aspect of oil shale retorting.

1. Feldkirchner, H. L. and Janka, J. C. Proc. of the IGT Symposium on Synthetic Fuels from Oil Shale Dec 3-6, 1979, Atlanta, GA., p. 489.
2. Maciel, G. E., Bartuska, V. J. and Miknis, F. P., Fuel, 58, 155 (1979).

Sincerely,



F. P. Miknis

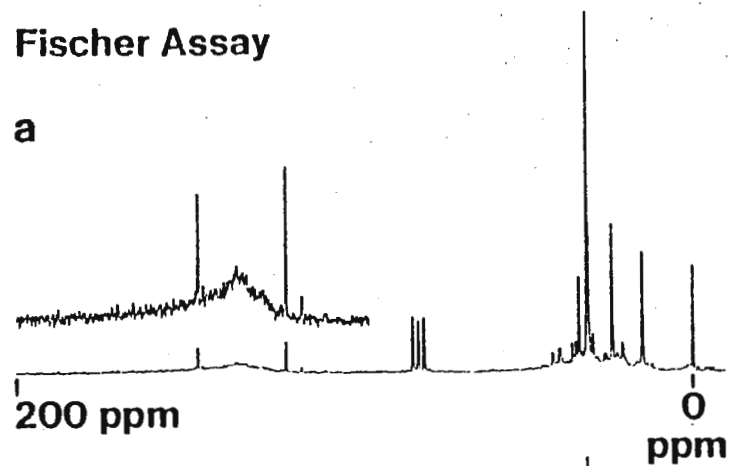


D. A. Netzel

Carbon-13 NMR

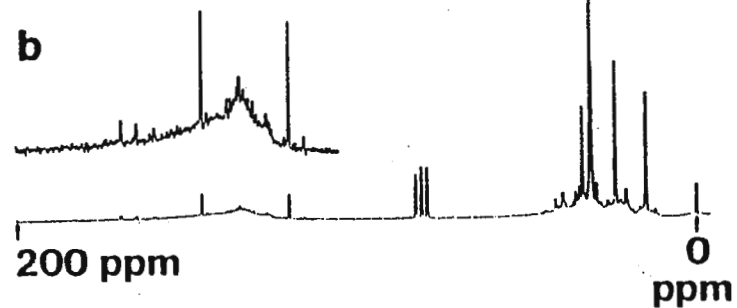
Colorado Shale Oil
Fischer Assay

a



IGT Hytort Process

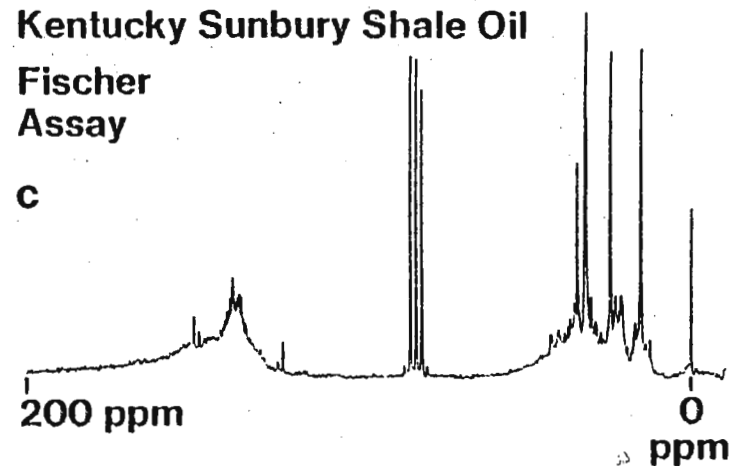
b



Carbon-13 NMR

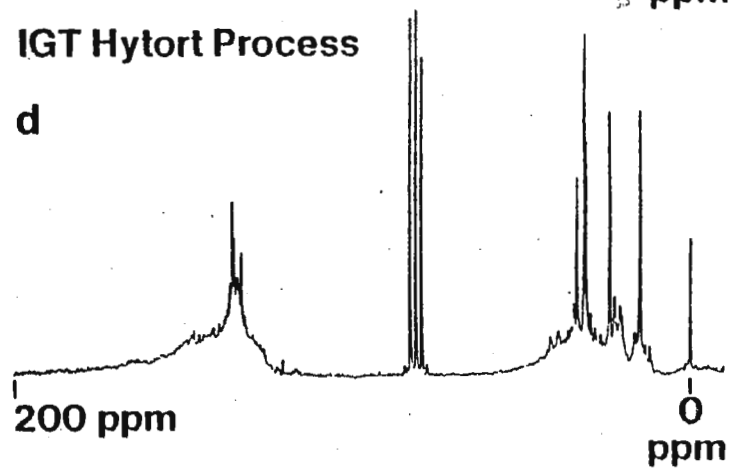
Kentucky Sunbury Shale Oil
Fischer Assay

c



IGT Hytort Process

d





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81.03.10

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

Dear Barry:

Getting 90°-pulse widths is a perennial problem facing NMR spectroscopists. This is especially annoying when one is doing relaxation experiments of samples with widely varying dielectric constants. In such cases, the pulse width can alter drastically.

The usual methods of getting pulse widths are time-consuming and tedious, at best. For instance, observing spectra intensities (after FT) for 90° pulses necessitates waiting enough time between pulses for recovery to equilibrium. Trying to null out the FID with a 180° pulse is difficult, at best, with dilute samples. Finally, the phase-error detection method has the same problem at the first-mentioned method, namely, long waits between pulses.

An alternate method I stumbled on recently while ~~playing~~ working hard on my new FX-90Q was to find the null point in the FT spectrum after applying a rapid train of 360° pulses. What is done is to apply pulses at the rate of one per second, or so. When you are near to the true 360° pulse, the spectrum nulls out. Close to the correct width gives spectra of large amplitude (but of opposite sign in intensity); as the width goes further from the correct 360° value, you encounter saturation. Thus, the method is easiest to apply when you are close to the desired pulse width; this is not true with other methods.

If the pulse width parameter can be stacked, as is the case with the FX90Q computer system, this method is very easy to do. You can find the correct width in ten minutes or so by merely stacking spectra during a coffee break (or, in Florida, an orange juice break). The only time-consuming part would be to get a preliminary phase-corrected spectrum with a small pulse width. After getting the 360° pulse, you need only divide by four to get the 90° pulse (if anyone needs help on this part, it's too late). It is assumed, of course, that your pulse generator is good enough to have the 360° pulse exactly four times as long as the 90° pulse; if this is not true, it's back to the drawing board.

Sincerely yours,

Milton D. Johnston, Jr.
Associate Professor of Chemistry

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Professor B.L. SHAPIRO
Dpt of Chemistry
Texas A & M University
COLLEGE STATION

N/réf. JJB/SL

V/réf.

TEXAS 77843

U.S.A.

PIERRE-BÉNITE, LE March 10th, 1981

Dear Professor Shapiro,

NMR Evidence for the Existence of P_4S_8

With this contribution we would like to open a subscription to the Newsletter.

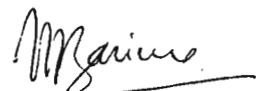
We have gained evidence by means of the FT ^{31}P nmr (80.76 MHz) that the primary product of the desulfuration of P_4S_9 by triphenylphosphine is apparently P_4S_8 , a previously unreported phosphorus sulfide bearing the same adamantanoid cage as P_4S_9 and P_4S_{10} (Fig 1).

When a 2.5 g/l P_4S_9 solution in CS_2 was allowed to react at r.t. with an equivalent amount of Ph_3P , the following signals were observed after 5 minutes (δ are downfield from external H_3PO_4) :

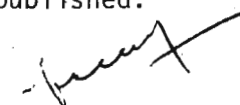
- the typical AB_3 multiplet of P_4S_9
- two equivalent singlets δ 84.6 and 110.9 ppm assigned to P_4S_7 with its unique zero $^1J_{PSP}$
- two equivalent triplets δ 13.4 and 135.4 ppm, $^2J=82.8$ Hz, indicative of an A_2X_2 system and consistent with the assumed geometry of P_4S_8
- two non attributed small singlets δ 162 and 167.2 ppm
- the signal of Ph_3PS , δ 41.9 ppm

The signals of P_4S_8 disappear completely after a week, owing probably to its dissociation to P_4S_7 and P_4S_9 .

A more detailed report will soon be published.



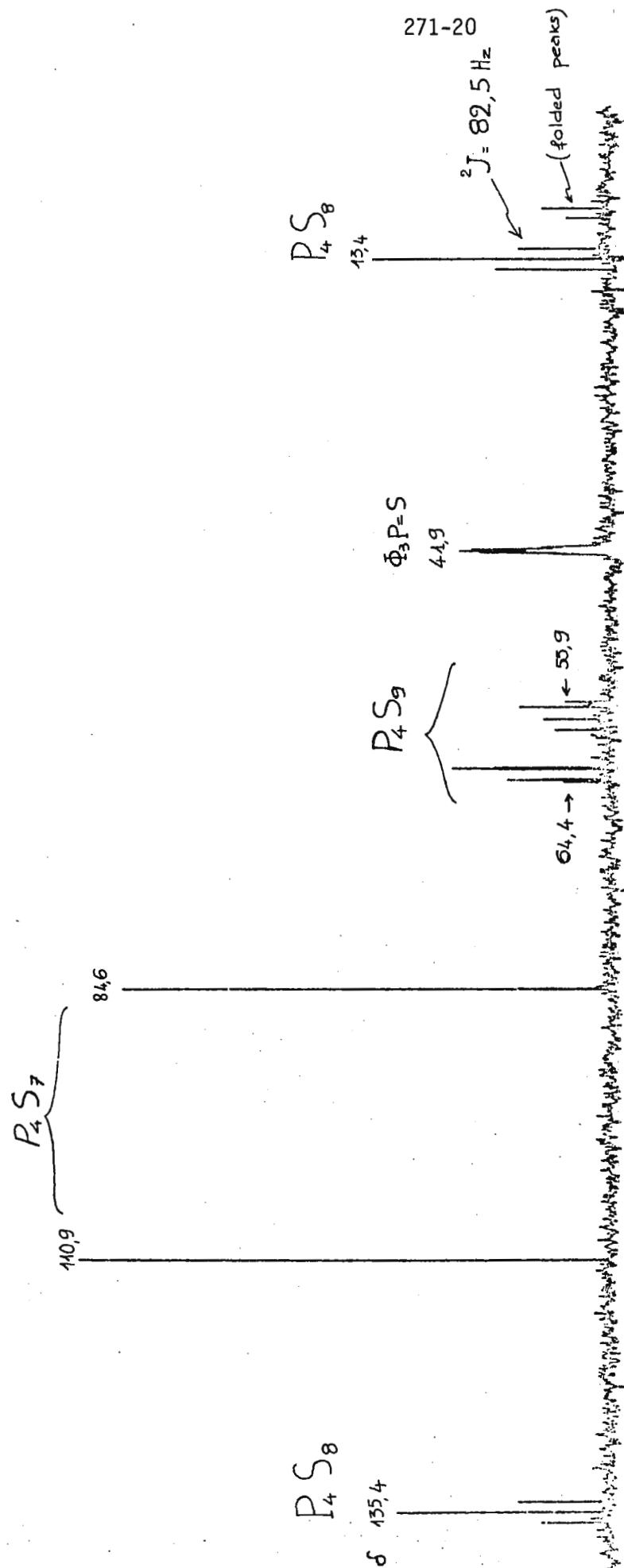
J.J. BARIEUX



M. DEMARCO

Fig. 1
 $P_4 S_9 + \Phi_3 P$ (80.76 MHz)

Conditions
 PM, 5 μ sec - PD 10 g - 16 K
 Freq 12 KHz Offset 28.07 kHz
 550 scans



Institut für Molekularbiologie und Biophysik
Prof. Dr. K. Wüthrich

HPM-Gebäude
Telefon ~~01 37 37 10~~ 01 377 44 11
Direktwahl 01 377 2473.

Postadresse:
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und Biophysik
ETH - Hönggerberg
CH-8093 Zürich

Prof. B.L. Shapiro
Dept. of Chemistry
Texas A & M University
College of Science

College Station, Texas 77843

USA

Zurich, March 10, 1981

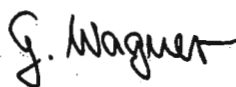
Combined COSY-NOESY Connectivity Diagram for Sequential Resonance Assignments
in Extended Polypeptide Chains.

Dear Barry,

The use of two-dimensional correlated spectroscopy (COSY) for delineation of J-coupling connectivities and 2D NOE spectroscopy (NOESY) for studies of cross relaxation networks in proteins was recently described.¹⁻³ In Fig. 1 we present a combined plot of COSY and NOESY data which was found to be particularly suitable for obtaining sequential resonance assignments in extended polypeptide chains.⁴ The plot is explained in the figure caption. The resonance assignments are based on the observation that in extended polypeptide chains the α -proton of residue i is the proton nearest to the amide proton of residue $(i+1)$.⁵

Two extensions of the experiment in Fig. 1 lead to additional information. Firstly, by analysis of the COSY peaks corresponding to amino acid side chain protons the nature of the amino acids assigned by Fig. 1 can be determined. As a consequence it is usually possible to locate the sequentially assigned residues in the amino acid sequence. Secondly, the experiment can be performed in H_2O rather than in D_2O ,³ so that its use is not restricted to polypeptide segments with slowly exchanging amide protons. In BPTI, individual assignments for a continuous segment of 20 amino acid residues were thus obtained.⁴

Sincerely yours,


G. Wagner


K. Wüthrich

1. K. Nagayama, Anil Kumar, K. Wüthrich and R.R. Ernst, J. Magn. Res. 40, 321-334 (1980).
Experimental Techniques of Two-Dimensional Correlated Spectroscopy.
2. Anil Kumar, R.R. Ernst and K. Wüthrich, Biochem. Biophys. Res. Commun. 95, 1-6 (1980).
A Two-Dimensional Nuclear Overhauser Enhancement (2D NOE) Experiment for the Elucidation of Complete Proton-Proton Cross-Relaxation Networks in Biological Macromolecules.

3. Anil Kumar, G. Wagner, R.R. Ernst and K. Wüthrich, *Biochem. Biophys. Res. Commun.* **96**, 1156-1163 (1980).
Studies of J-Connectivities and Selective ^1H - ^1H Overhauser Effects in H_2O Solutions of Biological Macromolecules by Two-Dimensional NMR Experiments.
4. G. Wagner, Anil Kumar and K. Wüthrich, *Eur. J. Biochem.* **114**, 375-384 (1980).
Systematic Application of Two-Dimensional ^1H Nuclear-Magnetic-Resonance Techniques für Studies of Proteins. 2. Combined Use of Correlated Spectroscopy and Nuclear Overhauser Spectroscopy for Sequential Assignments of Backbone Resonances and Elucidation of Polypeptide Secondary Structures.
5. A. Dubs, G. Wagner and K. Wüthrich, *Biochim. Biophys. Acta* **577**, 177-194 (1980).
Individual Assignments of Amide Proton Resonances in the Proton NMR Spectrum of the Basic Pancreatic Trypsin Inhibitor.

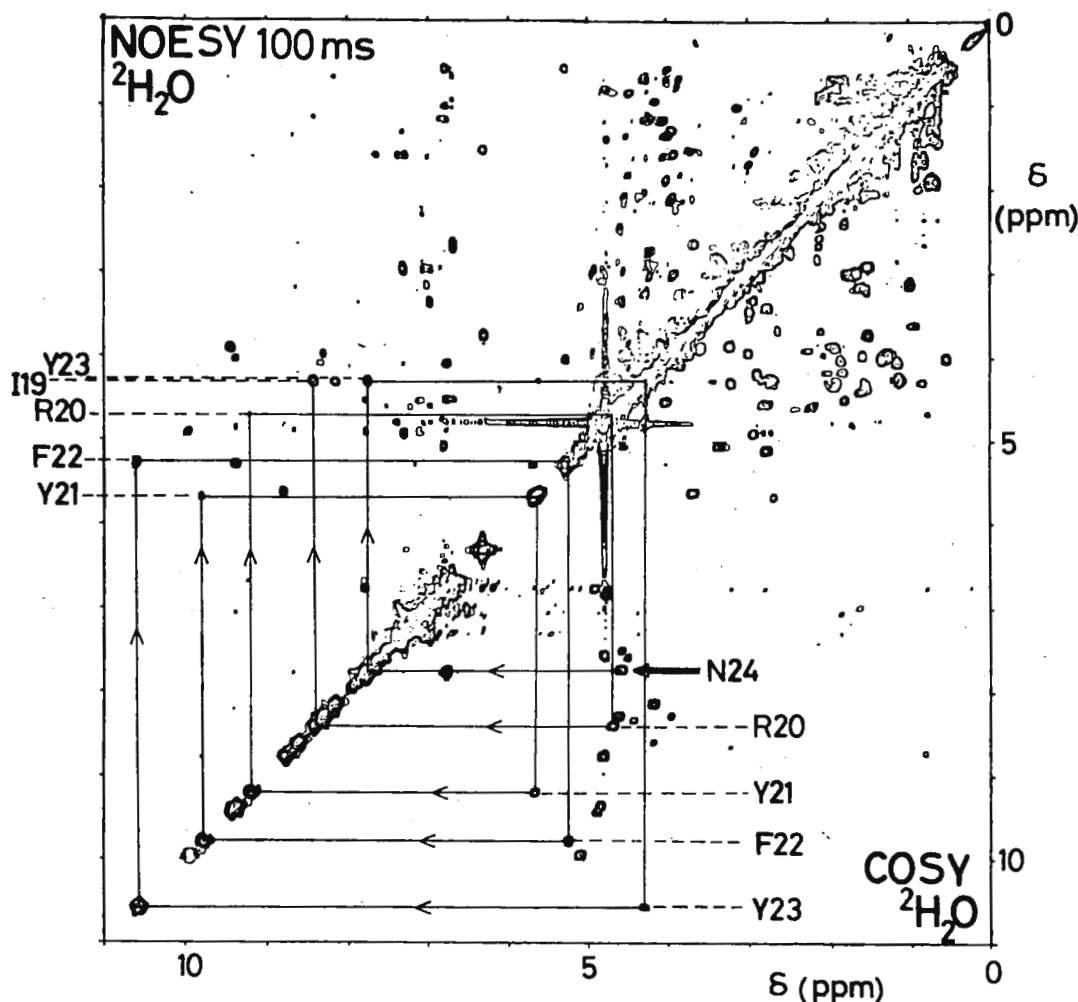


Fig. 1 Combined COSY-NOESY connectivity diagram for sequential resonance assignments in polypeptide chains. In this contour plot the upper left triangle comes from a NOESY spectrum of a D_2O solution of BPTI (basic pancreatic trypsin inhibitor, a small protein with 58 amino acid residues and a molecular weight of 6500) recorded with a mixing time of 100msec and the lower right triangle from a COSY spectrum of BPTI recorded from the same sample under identical conditions. The combination of the sequential J- and NOE-connectivities between the backbone α and amide protons of residues 24 to 19 indicated by solid lines has the shape of a spiral (" β -snail"). A β -snail is typical for extended polypeptide chains such as the individual strands in β -sheets.⁴

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NMR Applications Laboratory

Tel. (042) 23 25 75

Telex 78 841



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

Zug, March 12, 1981

Dear Dr. Shapiro:

* C * O * S * M * I * C *

For quite a while now we have been intrigued by the thought that Ray Freeman's and Ad Bax' "INADEQUATE" pulse sequence might in fact be quite ADEQUATE for directly arriving at the full structure (the carbon backbone, to be precise) of an unknown via an analysis of the satellites representing one-bond carbon-carbon couplings.

Our program "COSMIC" ("Computer-Originated Structure Models from "Inadequate"-derived Coupling data"), written in PASCAL for our XL-200 datasystem, analyses the ^{13}C satellite frequencies taken from an "INADEQUATE" spectrum plus the ^{13}C chemical shifts from a conventional noise-decoupled spectrum, establishes all pairs of matching satellites, checks for strong coupling effects, determines secondary isotope shifts and prints a list of all carbon-carbon bonds found. Reconstructing the connectivity graph and filling in the hetero atoms (if any) is all that is left for the chemist to do.

In our most challenging case tried so far, the computer gave us the full carbon connectivity matrix and hence the full two-dimensional structure of 5 α -andro-stane! (With the preliminary and unrefined version of COSMIC we are presently using, some operator intervention is required to help the computer with ambiguities in cases as complex as this one, where COSMIC has to evaluate close to 10'000 possible satellite combinations).

As a side benefit, we have measured lots of carbon-carbon coupling constants and isotope shifts that will eventually provide a wealth of additional structural information. We will just have to learn to interpret these data.

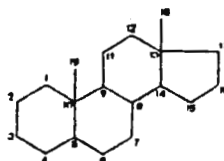
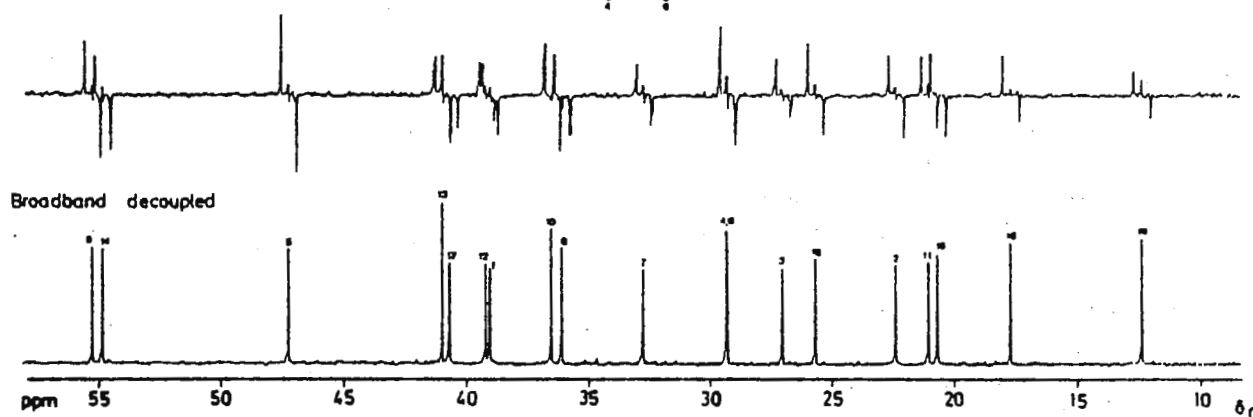
A full paper describing the details of COSMIC and discussing applications is in preparation.

Sincerely yours,

Toni Wirthlin

René Richarz

Willi Ammann

5 α -Androstane

Bottom trace: Conventional ^{13}C spectrum, δ (ppm) from TMS.
Top trace: "INADEQUATE" spectrum. The experiment was optimized for JCC = 34 Hz, N=0. 7140 transients were completed.

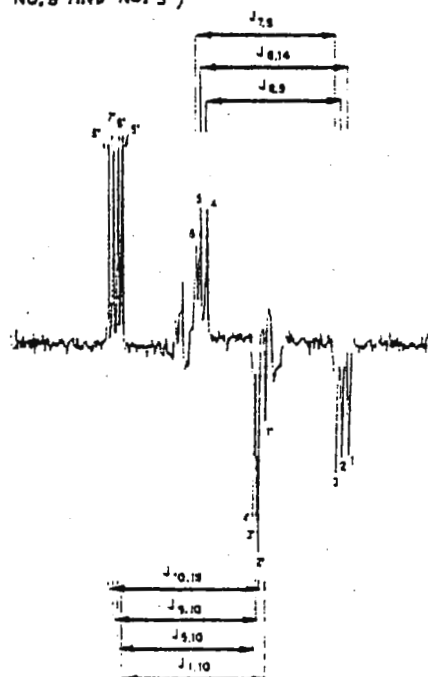
[illegible]

Fig.3. Data input (only partially represented, corresponding to partial spectrum shown in Fig.2) and result of the "COSMIC" analysis. The signal numbering system (from low field to high field in the conventional ^{13}C spectrum) has to be differentiated clearly from the standard numbering and nomenclature.



19 March 1981

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

The Release of Serotonin (5-HT) from its Storage Complex

*Roche Products Limited · PO Box 8 · Welwyn Garden City · Hertfordshire AL7 3AY
Telephone Welwyn Garden 28128 Telex 262098 ROCHEW*

Dear Barry

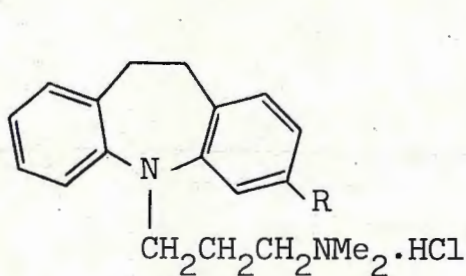
After our first "final ultimatum" from your office in some fifteen years, we hope that this contribution is acceptable, to forestall expulsion from the Newsletter.

Previous studies¹ on tricyclic antidepressants such as imipramine (I) have demonstrated that they form stable complexes in solution with biogenic amines such as serotonin (5-HT) (IV). The formation of these complexes is characterised by large, upfield shifts in the ¹H n.m.r. spectrum, indicating that the complex is formed between the aromatic ring of the 5-HT and the side chain ⁺NHMe₂ group of the antidepressant. It is known from other studies that adenosine triphosphate (ATP) (V) forms strong complexes with 5-HT².

These studies may have some significance in the mechanism of action of these drugs. While it is a commonly held view that the action of the tricyclics is to block the re-uptake of 5-HT at the brain synapse, the alternative theory that 5-HT is held in a storage form with ATP at the presynaptic vesicle is well supported.

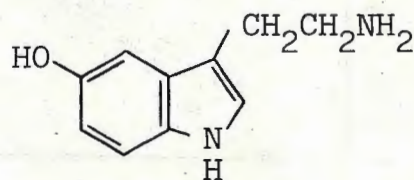
Further experiments were carried out with 1:1 complexes of ATP:5-HT (0.1M) in aqueous solution. Addition of a tricyclic antidepressant to this solution caused a shift of the 5-HT resonances to low field, particularly the ring protons.

We interpret this as reflecting the release of 5-HT from its complex. Similar observations were made for each of three different tricyclic antidepressants (I), (II) and (III), measuring the shifts for H-2 and H-6 of the 5-HT ring (Figure). It appears that in addition to the well-known inhibition of re-uptake it is possible that tricyclic antidepressants may also act by triggering the release of 5-HT from storage vesicles to the presynaptic cleft.

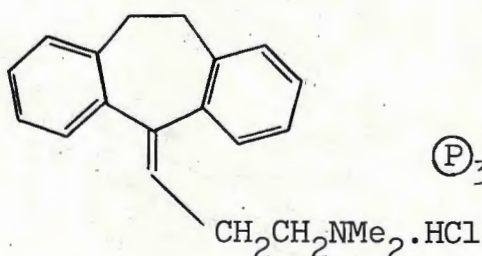


(I) R = H

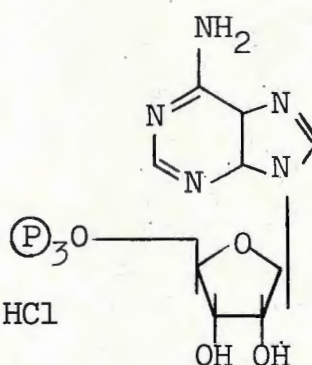
(II) R = Cl



(IV)



(III)



(V)

With best wishes.

Sincerely,

Tom *Whitcombe*
Dr W A Thomas and I W A Whitcombe
Physical Methods Department

1. K. Lewtas, Ph. D. Thesis, University of Liverpool, 1979
2. T. Nogrady et. al. Mol. Pharmac. 1972, 8, 565
3. T. Nogrady et. al. Mol. Pharmac. 1975, 11, 795

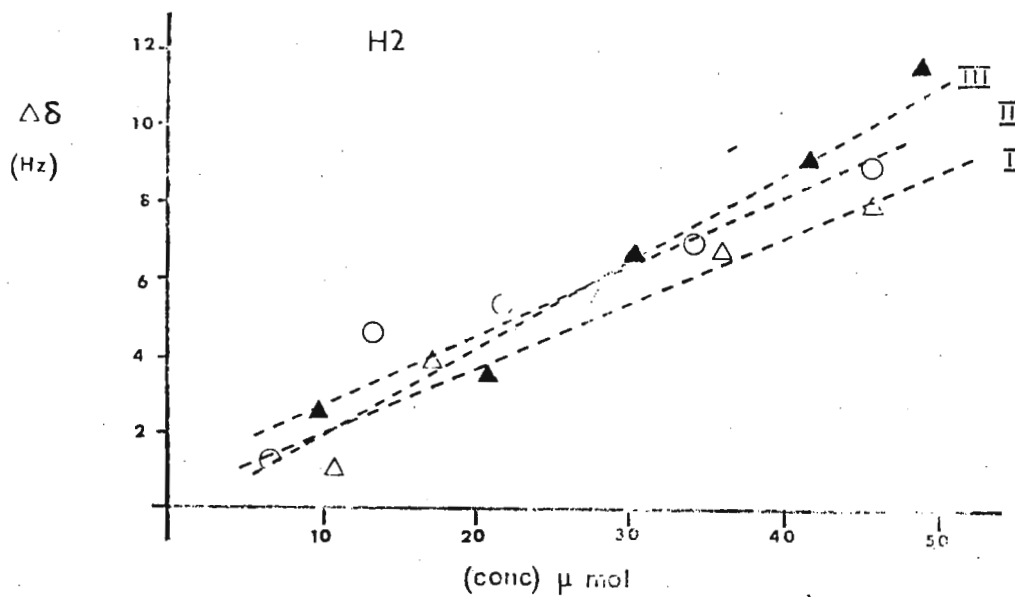
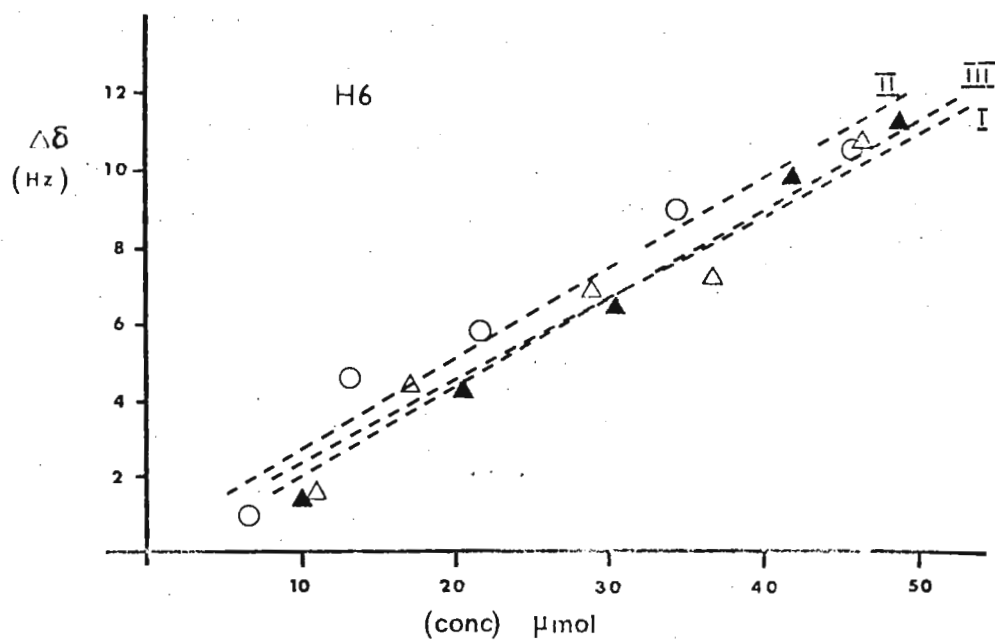


Figure:- Plot of shift ($\Delta\delta$) of H6 and H2 protons of 5-HT on addition of tricyclic antidepressant (I), (II) (III) to a 1:1 ATP/5-HT complex.

Signal Noise $\times 2.5 \times 2^{\text{VA}}$ = Varian XL-200

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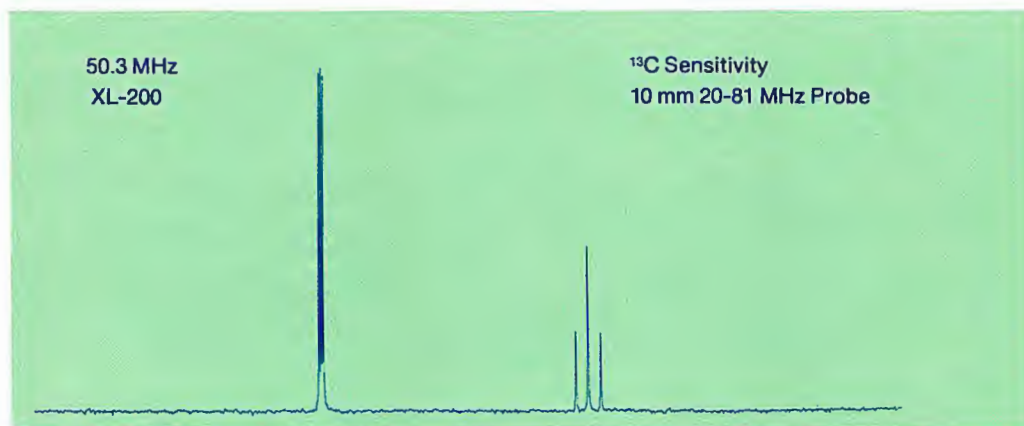
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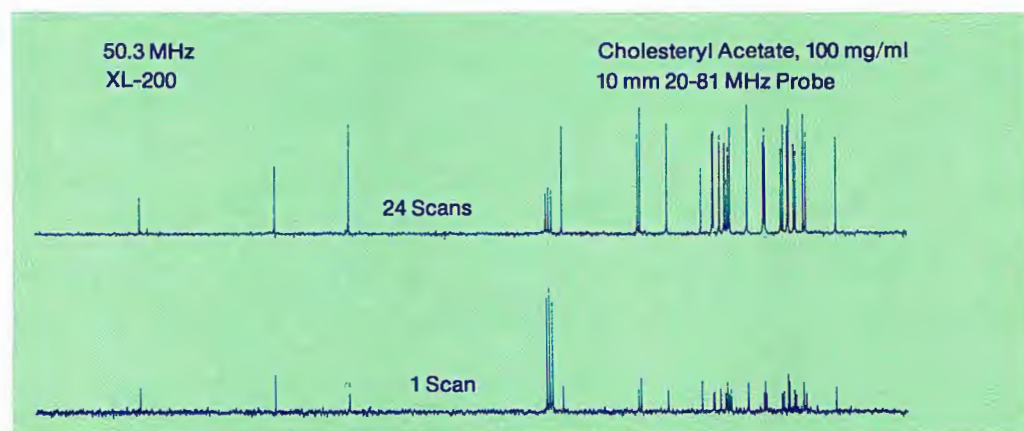
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Palo Alto 415-493-4000
Ext. 3047



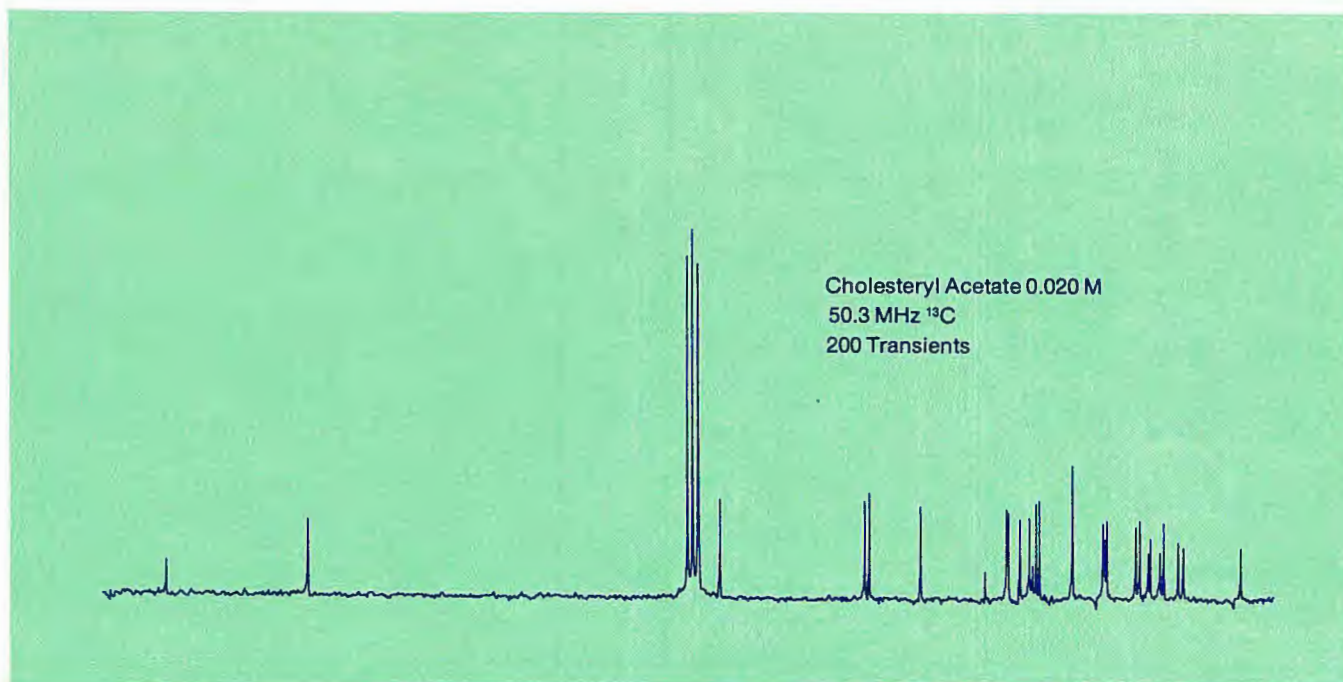
^{13}C Sensitivity Test: Single transient following 90° pulse on 60% C_6D_6 /40% dioxane using the 10 mm 20-81 MHz broadband probe.



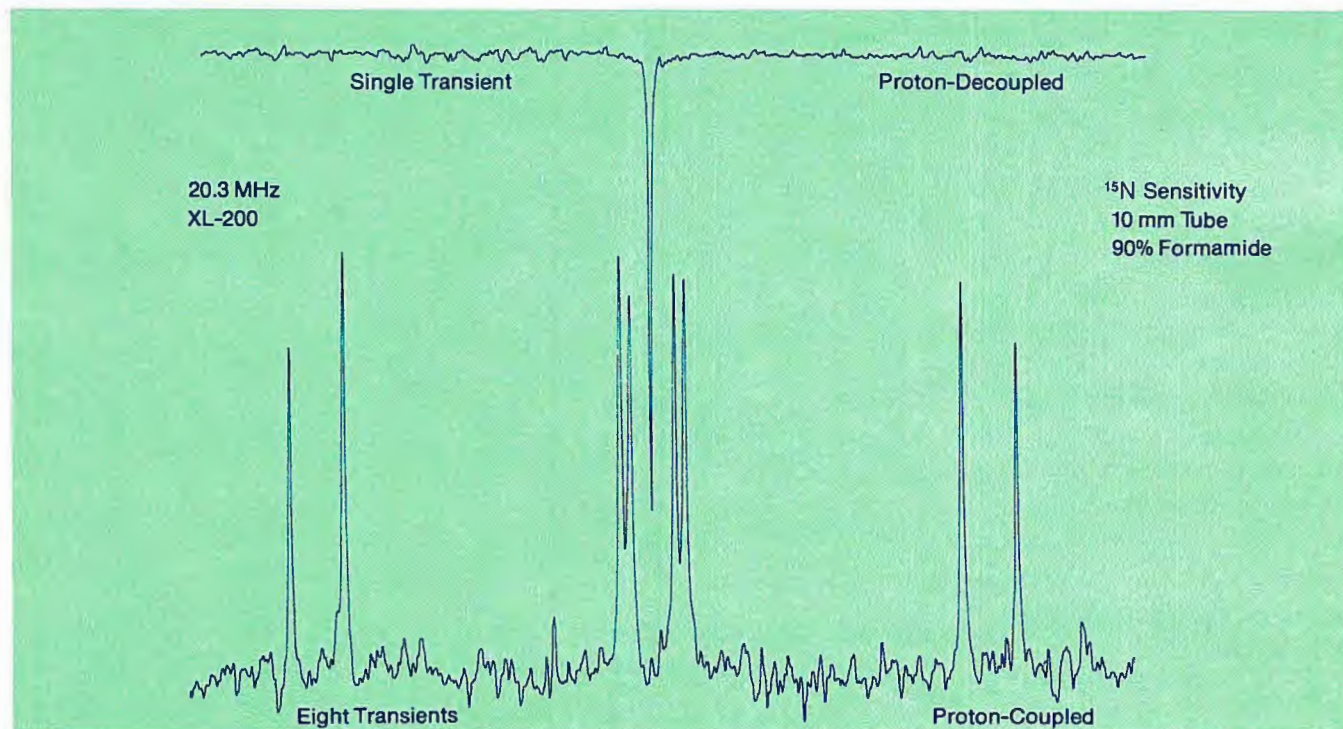
^{13}C Sensitivity Test: Cholesteryl acetate, 100 mg/ml, 10 mm broadband probe. Transients accumulated using 90° pulses every 2.28 seconds with 0.5 Hz line-broadening.

**Additional spectra appear
on the following page**





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



¹⁵N Sensitivity Test: 90% Formamide in dms0-d₆, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.

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March 22, 1981

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

Dear Professor Shapiro:

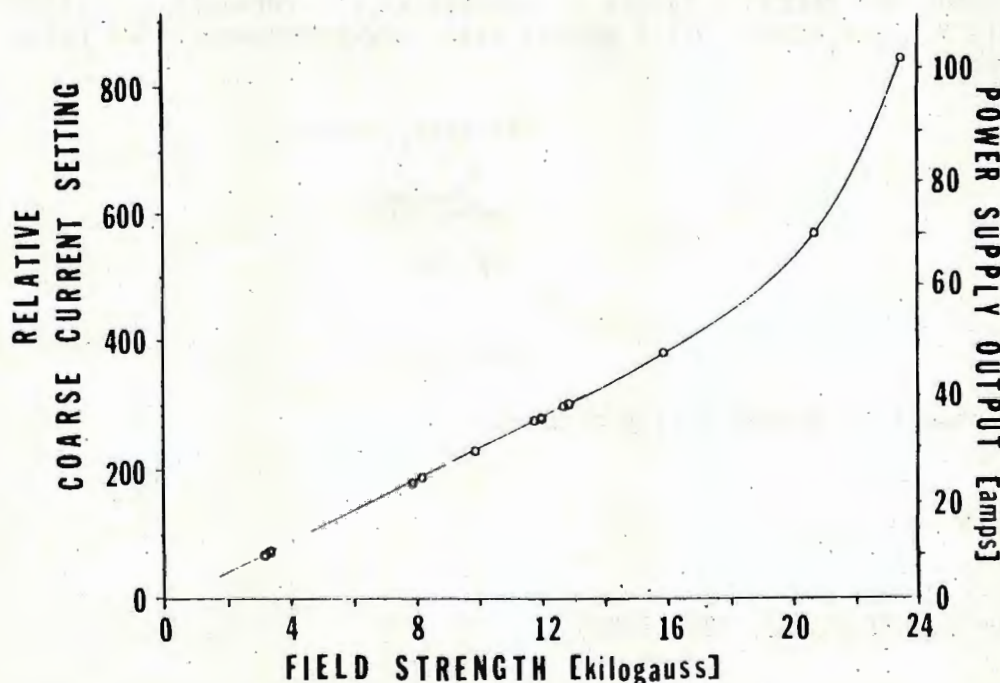
Current vs. Field Strength Curve For Varian 15-Inch Magnet

We have run experiments on a number of nuclei at field strengths from 3 to 23.5 kilogauss using a Varian low impedance 15-inch magnet. Since there are a number of similar magnets in use with various consoles such as the Varian XL-100-15, Nicolet TT-23, Bruker SXP, and Varian HA-100D-15 we thought that this curve might be of interest to other readers. It was determined empirically by observing the resonances of eleven different nuclei at 13.56 MHz plus protons at 100 MHz. The power supply output values are expected to be similar from one system to another, but the relative coarse current settings will likely be shifted from one system to another because of resistor values and tolerances being different.

Sincerely,

Ronald E. Block

Ronald E. Block, Ph.D.
Associate Scientist



A non-profit institution for medical research and education--supported by tax exempt contributions

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Varian / 611 Hansen Way / Palo Alto / California 94303 / U.S.A.

Tel. (415) 493-4000

Telex 34-8476



March 13, 1981

Dr. Barry L. Shapiro
Editor, TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77848

"New Level of 10 mm N-15 Sensitivity"

Dear Barry:

Nitrogen NMR of the spin - 1/2 variety usually requires large sample tubes and sufficient sample material to obtain natural abundance spectral information. In order to reduce run times and conserve precious sample material, we have developed a 10 mm fixed frequency ^{15}N probe which makes natural abundance ^{15}N studies routine. Figure 1 illustrates the probe's performance on the standard 90% Formamide sensitivity test. Here the decoupled spectrum represents one 90° pulse with NOE. The coupled spectrum is the accumulation of 8 transients with NOE. These results are about a factor of two better than the results recently reported by Jakobsen, Dagaard and Ellis for an 18 mm fixed frequency probe (TAMU 269-22). Figure 2a demonstrates the probe performance on 0.10 M (114 mg/ml) Gramicidin-S using 90° pulses and a 2 sec repetition rate (total run time 4.0 hours). Figure 2b shows the spectrum obtained on the above sample in 10 minutes using refocused INEPT¹. Figure 2c represents an overnight run (15.1 hours) on 0.010 M Gramicidin-S (11.4 mg/ml) using the refocused INEPT pulse sequence.

Sincerely yours,

Toby Zens

Please credit to Howard Hill's account.

/bry
Enclosure

¹G. Morris, JACS, 102, 428 (1980)

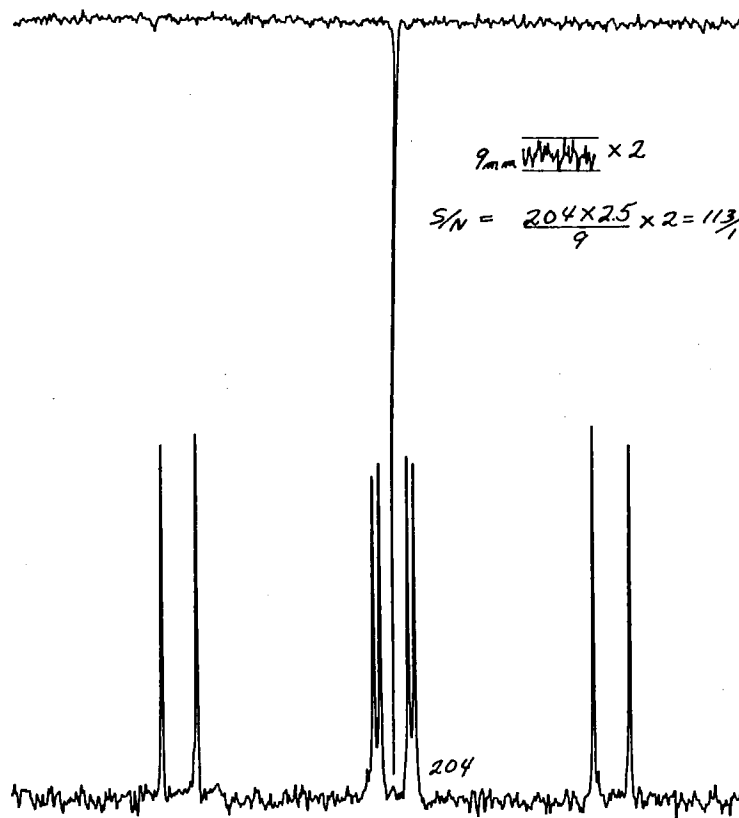


FIGURE 1

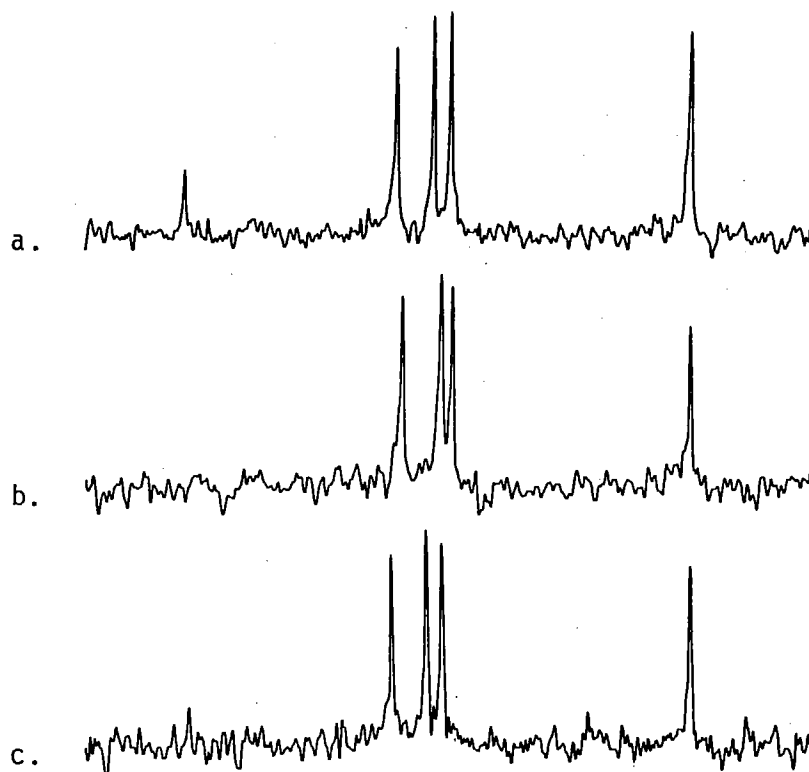


FIGURE 2

CHIMIE ORGANIQUE PHYSIQUE

E.R.A. n° 315 - C.N.R.S.

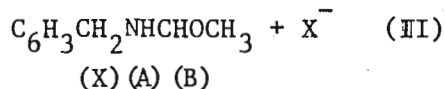
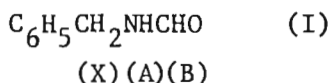
March, 17 th 1981

Selective population inversion of satellites of satellites

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

Dear Barry,

Although the method of selective population transfer (1) is not very appropriate as a general procedure of sensitivity enhancement it remains a powerful and versatile technique for spectral identification and the determination of relative signs of coupling constants. For example, it allows the accurate measurement of small $J^{15}\text{N H}$ coupling constants in the amide structure (I) and in the corresponding iminium salt (II)



Thus selective inversion of a non-degenerate transition in the ^{15}N satellite spectrum of proton H_A may introduce specific polarizations in poorly resolved ^{15}N multiplets. These polarizations lead to narrow positive and negative components in a given submultiplet resulting from the coupling constant $^2\text{JNCH}_\text{X}$ and a value of 0.6 Hz is thus accurately determined in compound I.

As shown in the figure it is also possible, in a compound (I) enriched at a level of only 30 % in ^{15}N , to selectively invert a transition in an unobservable multiplet which corresponds to the ^{15}N satellite spectrum of transitions which are themselves ^{13}C satellite transitions of proton H_B . Thus by inverting the two low frequency components of the $2 \times 2 \times 2$ proton multiplet associated with the coupling constants $^1\text{J}(\text{C}_\text{B} \text{H}_\text{B})$, $^2\text{J}^{(15}\text{N} \text{H}_\text{B})$ and $^3\text{J}(\text{H}_\text{A} \text{H}_\text{B})$ ($= 2\text{Hz}$), polarizations are observed in the ^{15}N satellite transitions of the carbon spectrum. Denoting the ^{13}C transitions of the species which contains both the ^{15}N and the ^{13}C isotopes 1 to 16 from high to low frequencies, we observe negative polarization of the quadruplet 13-14-15-16 produced by the $^2\text{J}(\text{C}_\text{B} \text{H}_\text{A}) = ^3\text{J}(\text{C}_\text{B} \text{H}_\text{X})$ ($= 4 \text{Hz}$) coupling constants and associated with a given spin state of ^{15}N . The progressively connected quadruplet 5-6-7-8 is positively polarized. This result corroborates the fact that $^2\text{J}(\text{N H}_\text{B})$ and $^1\text{J}(\text{C-N})$ have the same sign.

Similarly proton transitions which are ^{125}Te satellite transitions of a ^{13}C satellite spectrum can be selectively inverted at the natural abundance level of both the ^{125}Te and ^{13}C isotopes (0.08 %). These experiments enable the determination of the relative signs of various ^{125}Te - ^{13}C coupling constants in tellurophenes (2).

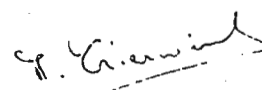
Yours sincerely,



M.L. MARTIN



H. MARTINEAU

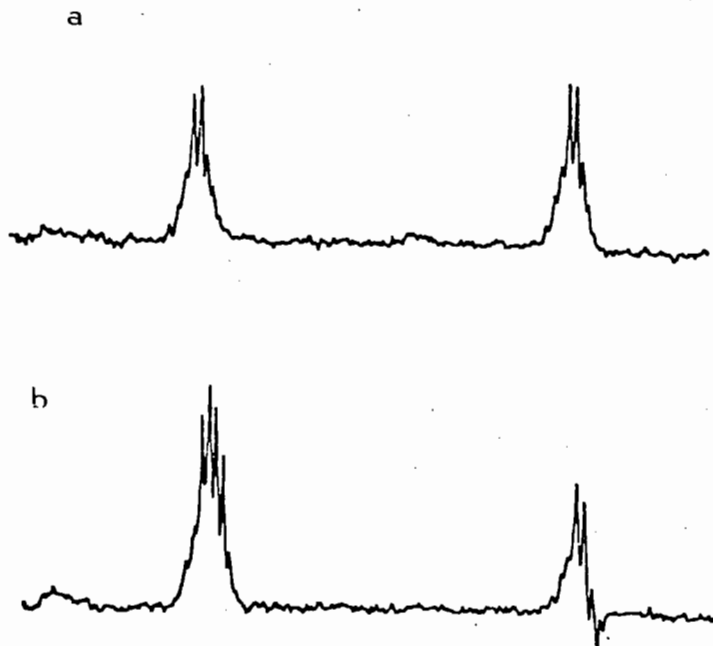


M. TRIERWEILER

- (1) K.G.R. PACHLER and P.L. WESSELS, J. Magn. Res., 12, 337 (1973).
(2) M.L. MARTIN, M. TRIERWEILER, V. GALASSO, F. FRINGUELLI and A. TATICCHI,
J. Magn. Res., 42, 155 (1981).

Figure Legend

- a) Normal ^{13}C spectrum of carbon C_B of compound I enriched in ^{15}N at a level of about 30 %. The ^{13}C spectrum of the labelled compound gives rise to 2 x 4 multiplets with 15 % intensity, on both sides of each of the two main quadruplets resulting from the species which contains the ^{14}N isotope.
b) Same spectrum as a) but exhibiting selective population transfer in the satellite ^{15}N spectrum of C_B .





PURDUE UNIVERSITY

SCHOOL OF SCIENCE
at INDIANAPOLISPHYSICS DEPARTMENT
1201 East 38th Street
Indianapolis, Indiana 46205
(317) 923-1321

March 18, 1981

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

TITLE: Strong coupling effects in rapidly exchanging weakly coupled spin systems

Dear Barry:

While testing our recently published (J. Mag. Res. 41, 463 (1980)) method for simulating NMR lineshapes for the $ABC \rightleftharpoons A'B' + C'$ exchange problem (applicable to the ^{31}P NMR of phosphoryl transfer enzyme reactions) we noticed some unusual intensity effects for rates large enough to make all exchanges fast. Using an exchange rate of 10^7 s^{-1} and the spectral parameters (NMR operating frequency = 40.3 MHz):

$$\omega_A = 11.0 \text{ ppm}, \omega_{A'} = 10.4 \text{ ppm}, \omega_B = 4.4 \text{ ppm}, \omega_C = 4.8 \text{ ppm}, \omega_{C'} = 2.9 \text{ ppm},$$

$$J_{AB} = J_{BC} = 15.0 \text{ Hz}, J_{AC} = 0, J_{A'B'} = 18.2 \text{ Hz}; [ABC]/[A'B'] = 0.8, [AB] = [C];$$

$$(T_{2A})^{-1} = 8\pi^{-1}, (T_{2B})^{-1} = (T_{2C})^{-1} = (T_{2A'})^{-1} = (T_{2C'})^{-1} = 10\pi \text{ s}^{-1}, (T_{2B'})^{-1} = 30\pi \text{ s}^{-1};$$

and varying ω_B between 14 ppm and 24 ppm, the spectra shown in Fig. 1 are obtained. Note that the intensity pattern of the $(A + A')$ and $(B + B')$ resonances is exactly like that of a strongly coupled two spin system (in Fig. 1a the exchange averaged chemical shifts of A and B nuclei are equal to each other). We felt that the "average A" and "average B" nuclei are strongly coupled under fast exchange although the individual AB and A'B' pairs are weakly coupled (J_{BC} is "washed out" of the spectrum). In order to verify this contention we resimulated the spectra by turning off the off-diagonal elements involving J_{AB} and $J_{A'B'}$ in the calculation and obtained the spectra in Fig. 2. The intensity pattern in Fig. 2 is exactly that for a coupled two spin system which is incorrectly treated by ignoring the off-diagonal elements, thus verifying the above interpretation of the spectra in Fig. 1. Therefore, two weakly coupled spin systems in fast exchange can give rise to a spectrum with strong coupling features. Although this might sound somewhat unusual the explanation for the observation is straightforward in terms of the effect of the off-diagonal elements of spin-spin coupling in the presence and absence of exchange. We welcome comments from TAMU readers whether this feature was noticed earlier by other people, or better yet if there is an experimental example for it.

Sincerely yours,

K. V. Vasavada

J. I. Kaplan

B. D. Nageswara Rao

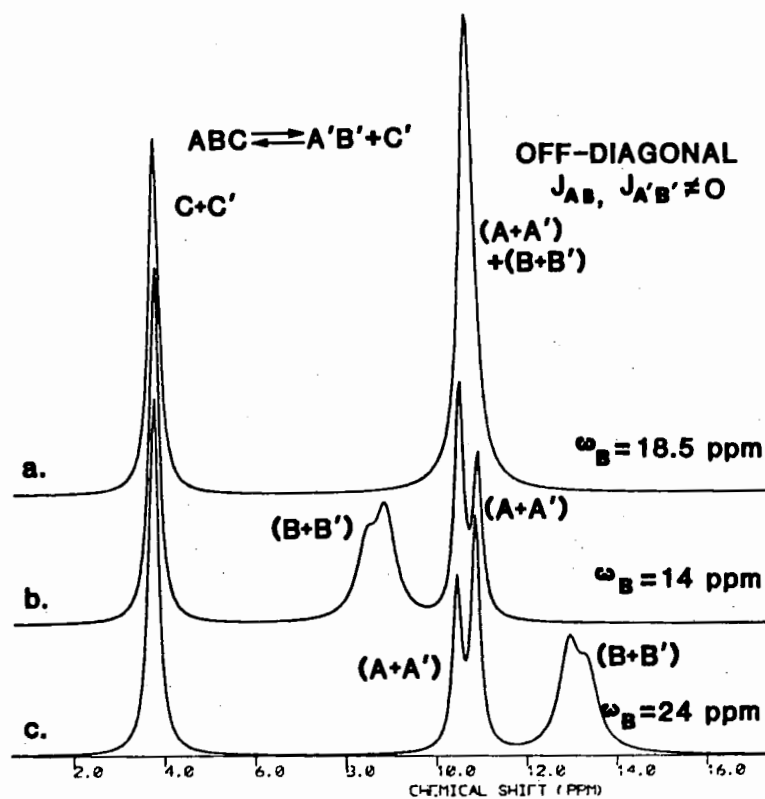


Figure 1

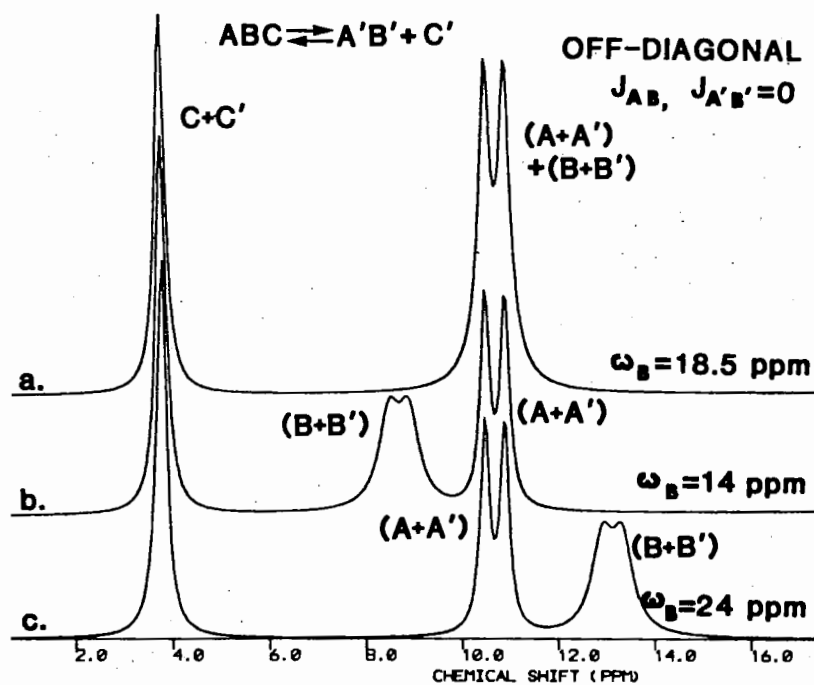


Figure 2



UNIVERSITY OF STOCKHOLM

ARRHENIUS LABORATORY

Physical Chemistry

Dr. Bernard Shapiro

Department of Chemistry

Texas A & M University

College Station, Texas 77840

March 23, 1981

Title: Internal rotation of CH_3 and CD_3 groups

Dear Professor Shapiro,

We have recently completed a variable temperature ^{13}C T_1 study of the internal methyl rotation in 1-methylnaphthalene (1-MN) and a similar ^2H T_1 study of its perdeuterated analogue (1-MN- d_{10}). The purpose of the investigation has been to find whether the isotope effects would conform to the predictions of absolute rate theory model proposed for some time ago¹.

The measurements were made for 2M solutions in deuteriochloroform using a XL 100 spectrometer. After demonstrating the full NOE in the ^{13}C spectra, assuming the CH distances (1.08Å for the ring carbons and 1.09Å for the CH_3 group) and the deuterium quadrupole coupling constants (193 kHz for the ring deuterons, 165 kHz for the CD_3 deuterons) the effective correlation times for different sites in the two molecules were evaluated.

If the overall motion of the molecule is treated as isotropic small step rotational diffusion, the average ring τ_c^{eff} gives the corresponding diffusion constant D. τ_c^{eff} for the methyl group is related to D and the rate, R_i , of random jumps between the three equivalent equilibrium positions, by the equation derived by Woessner²:

$$\tau_c^{\text{eff}} = \frac{A}{6D} + \frac{B + C}{6D + \frac{3}{2}R_i}$$

For tetrahedral methyl groups, $A = 1/9$ and $B+C = 8/9$.

Following the procedure applied previously to ^{13}C data³, we plot the D and R_i values versus $1/T$ in the figure. We note that the rotational diffusion constants in 1-MN and 1-MN- d_{10} are identical at a given temperature. On the other hand, the R_i values for the CH_3 group are a factor of more than two larger than the R_i values

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S-104 05 STOCKHOLM
Sweden

Street address
Bergiusvägen 65
Frescati
Tel. 15 01 60 (exchange)

for the CD_3 group. The activation energies for R_1 are $9.0 \pm 0.2 \text{ kJ mole}^{-1}$ (CH_3) and $9.3 \pm 0.2 \text{ kJ mole}^{-1}$ (CD_3) (error limits of 1σ). According to calculations¹, the activation energy for the CH_3 group should be about 0.2 kJ mole^{-1} lower than for the CD_3 group and the E_a 's should provide a reasonable approximation to the threefold barrier, V_3 . The combined ^{13}C and ^2H experiments agree qualitatively with the former prediction (we cannot claim the quantitative agreement because of experimental uncertainties) and we hope therefore that we also can trust that the V_3 value in 1-MN is about $9\text{--}9.5 \text{ kJ mole}^{-1}$.

Yours sincerely,



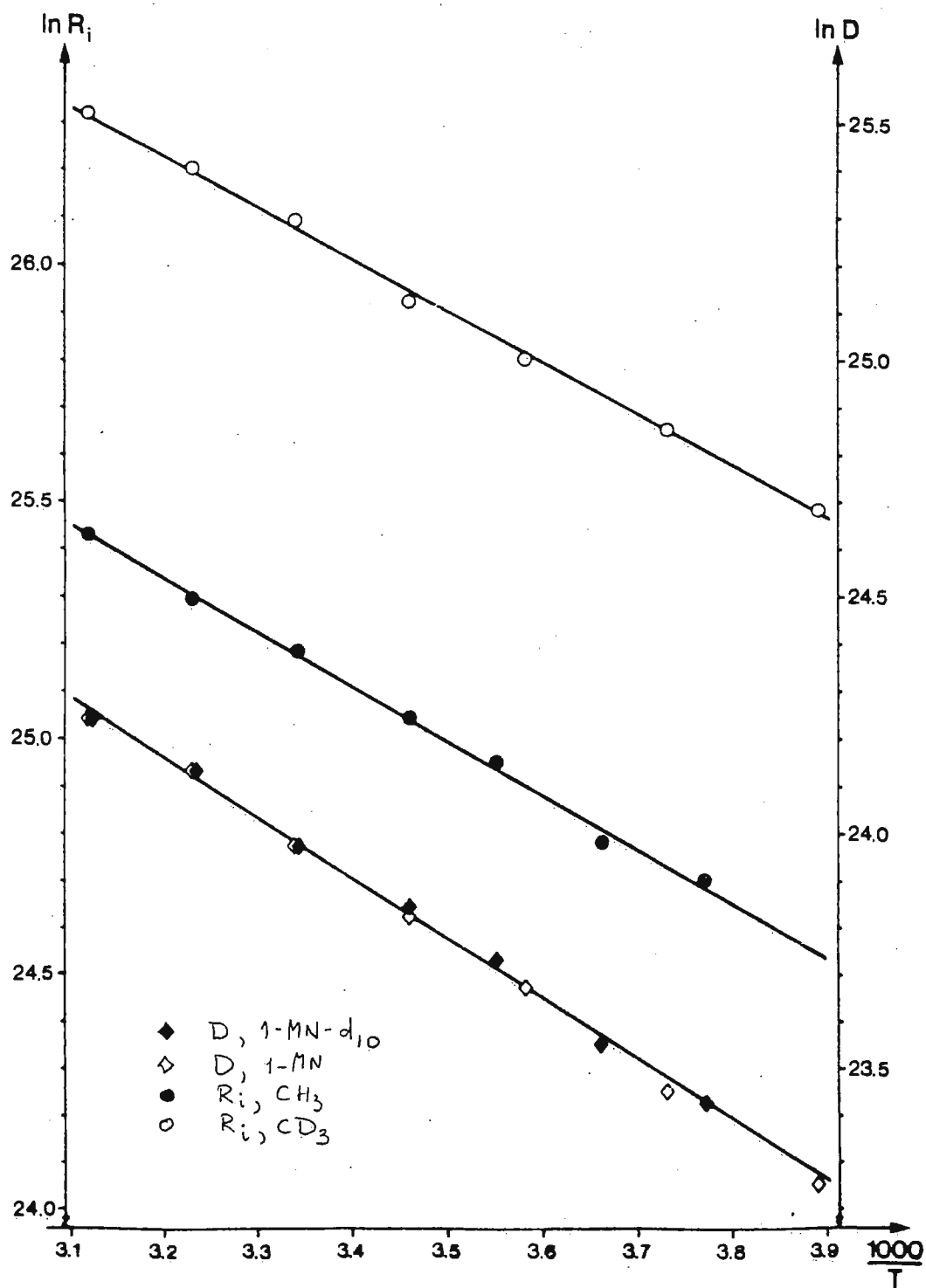
Anders Ericsson



Jozef Kowalewski

References:

1. J. Kowalewski and T. Liljefors
Chem. Phys. Lett., 64, 170 (1979).
2. D.E. Woessner
J. Chem. Phys. 36, 1 (1962).
3. A. Ericsson, J. Kowalewski, T. Liljefors and P. Stilbs
J. Magn. Res., 38, 9 (1980).



Dr. Klaus Roth

19.3.1981

Freie Universität Berlin,
FB 21, WE 02, Takustraße 3, 1000 Berlin 33Prof. B. L. Shapiro
Dep. of Chemistry
Texas A&M University
College Station, TX 77843
USA

Dear Prof. Shapiro,

Optimal Parameters in the Convolution Difference Technique

In the Convolution Difference Technique the resolution enhancement is obtained by subtracting a portion k of the original fid multiplied by a function $\exp(-n/T_2)$ from the unmodified fid. This results in a frequency domain spectrum of the type

$$J(\nu)_{\omega} = \frac{1}{\pi w_0} \left[\frac{1}{1 + 2 \left(\frac{\nu}{w_0} \right)^2} - k \frac{1+n}{(1+n)^2 + 2 \left(\frac{\nu}{w_0} \right)^2} \right]$$

where w_0 is the width of the original line.

In using this technique it is important to realise that the reduction in linewidth is accompanied by a decrease in S/N ratio and some baseline distortion. In order to predict the influence of the various parameters on to the final sensitivity, resolution and line distortion Dr. Barry Kimber from the National Institute for Medical Research, London and I have investigated these effects in a short paper which we have submitted to J. Magn. Reson. Preprints are available upon request.

Yours sincerely,



(Dr. K. Roth)



UNIVERSITY OF SOUTH FLORIDA

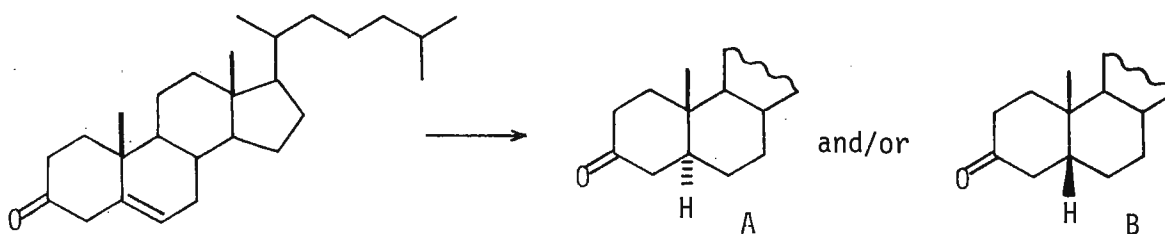
TAMPA • ST. PETERSBURG • FORT MYERS • SARASOTA

DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620813:974-2144
SUNCOM: 574-2144

17 March 1981

Dear Barry:

In our continuing studies with lanthanide shift reagents we have encountered an example which clearly illustrates the importance of using a chemically reasonable model. Consider the following hypothetical reduction of cholestenone which could yield either (or both) of the stereoisomers A and B.



If only a single isomer were obtained from such a reaction, the verification of a stereochemical assignment by spectroscopic methods could be quite difficult.

We have studied these two stereoisomers with $\text{Eu}(\text{fod})_3$ in CCl_4 , and our results indicate that "traditional" methods for carrying out structure correlations with shift reagents are inadequate. While cholestanone affords a satisfactory fit only for structure A, coprostanone gives a good agreement factor for both stereoisomeric possibilities.

Table. Comparison of Experimental and Predicted LIS for Cholestanone and Coprostanone.

Compound	Agreement Factor (C-O-Eu angle)	
	Structure A	Structure B
Cholestanone	0.03 (175°)	0.15 (150°)
Coprostanone	0.03 (139°)	0.03 (177°)

Only when the geometry of the complex is restricted so that the carbon-oxygen-europium bond angle is approximately linear is the problem resolved. When this condition is satisfied, coprostanone affords a satisfactory agreement factor only with structure B. Indeed, inspection of the table shows that the "optimum" fit of coprostanone to structure A corresponds to a complex having a C-O-Eu bond angle of 139°. We reject such a bond angle for an unhindered ketone as chemically unreasonable (J. Am. Chem. Soc., 102, 6591 [1980]). While traditional methods of fitting the LIS data would have yielded the correct assignment of isomer A for cholestanone, they would not have permitted a choice between stereoisomers A and B for coprostanone.

Best regards,

Douglas J. Raber

Title: LIS OF KETONES

DEPARTMENT OF BIOCHEMISTRY

THE UNIVERSITY OF ALBERTA
EDMONTON, CANADA T6G 2H7

PHONE: (403) 432-5460

March 23, 1981

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

Dear Barry: "RELAXATION OF PROTEIN BOUND PHOSPHORUS NUCLEI"

We have been studying the ^{31}P NMR of the ATP bound to G-actin. By nitrating Tyr-69 with TNM, we have been able to increase the concentration of G-actin in solution without incurring polymerization. This modification has no observable effects on the ^{31}P NMR spectrum, indicating that the modified Tyr (69) is likely quite far from the ATP binding site of G-actin. We determined T_1 and T_2 values for the bound ATP resonances at 36.4, 81.0, 109.3 and 162.0 MHz in order to sort out the effects of chemical shift anisotropy (CSA) and dipole-dipole (D-D) relaxation. In the non-extreme narrowing limit ($\omega^2 \tau_c^2 \gg 1$), the contribution of CSA to $1/T_2$ is proportional to ω^2 (Equation 1) while the contribution of DD is independent of ω^2 (Equation 2 for ^{31}P - ^{31}P DD interaction and Equation 3 for ^{31}P - ^1H DD interactions). For $\omega^2 \tau_c^2 \gg 1$, the contribution of CSA to $1/T_1$ is independent of ω^2 (Equation 4), while the DD contribution is inversely proportional to ω^2 (Equation 5 for ^{31}P - ^{31}P interactions and Equation 6 for ^{31}P - ^1H interactions).

$$1/T_{2\text{CSA}} = 4/45 \omega_P^2 (\Delta\sigma)^2 (1 + \eta^2/3) \tau_c \quad (1)$$

$$1/T_{2\text{DD}}^{\text{PP}} = 9/20 \frac{\gamma_P^4 \hbar^2}{r_{\text{PP}}^6} \tau_c \quad (2)$$

$$1/T_{2\text{DD}}^{\text{HP}} = 1/5 \frac{\gamma_H^2 \gamma_P^2 \hbar^2}{r_{\text{HP}}^6} \tau_c \quad (3)$$

$$1/T_{1\text{CSA}} = 2/15 \omega_P^2 (\Delta\sigma)^2 (1 + \eta^2/3) 1/\tau_c \quad (4)$$

$$1/T_{1DD}^{PP} = 3/5 \frac{\gamma_P^4 \hbar^2}{r_{PP}^6 \tau_c \omega_P^2} \quad (5)$$

$$1/T_{1DD}^{HP} \approx \frac{0.4 \gamma_P^2 \gamma_H^2 \hbar^2}{r_{HP}^6 \tau_c \omega_P^2} \quad (6)$$

The observed values of $1/T_2$ for the α , β and γ phosphates of ATP bound to nitrated G-actin are plotted versus ω^2 in Figure 1, and the observed values of $1/T_1$ are plotted versus $1/\omega^2$ in Figure 2. Figure 1 shows that at high magnetic field strength, CSA dominates T_2 relaxation processes accounting for about 90% of the linewidth of all three phosphates of protein bound ATP at 162 MHz. Figure 2 shows that CSA also dominates T_1 relaxation processes, accounting for about 80% of the $1/T_1$ relaxation rate at 162 MHz. With the experimentally determined $1/T_{2CSA}$ and $1/T_{1CSA}$ terms, equations (1) and (4) can be combined to solve for τ_c or $(\Delta\sigma)(1 + \eta^2/3)^{1/2}$. The τ_c values determined were 40, 44 and 41 nsec for the α , β and γ phosphates of protein-bound ATP, while the theoretical τ_c for a macromolecule the size of G-actin is 36 nsec. This indicates that each phosphate in the ATP is firmly bound to the protein. The values determined for $(\Delta\sigma)(1 + \eta^2/3)^{1/2}$ were 260, 260 and 240 ppm for the α , β and γ phosphates; these values are higher than would be expected from model compounds and likely reflect some interaction of the protein with the bound ATP increasing the anisotropy of electron density around the ^{31}P nuclei.

The effects of chemical exchange between free and protein-bound ATP on these T_1 and T_2 values has been considered. Published values of the dissociation rate constant of ATP from G-actin range from 10^{-5} to 10^{-3} sec^{-1} , indicating that we are probably in the very slow exchange limit for both T_1 and T_2 processes. We also considered the effects of cross-relaxation between ^{31}P and ^1H nuclei, since our spectra were taken in the absence of ^1H decoupling. In the non-extreme narrowing limit, the calculated value of σ is very low, since the W_0 and W_2 terms roughly cancel. The ratio of ρ/σ is about 112, indicating that cross-relaxation of ^{31}P nuclei with ^1H nuclei is negligible in the non-extreme narrowing limit.

Best regards,

And Brauer

Dr. Manfred Brauer and

Brian

B.D. Sykes,
Professor of Biochemistry

Fig. 1

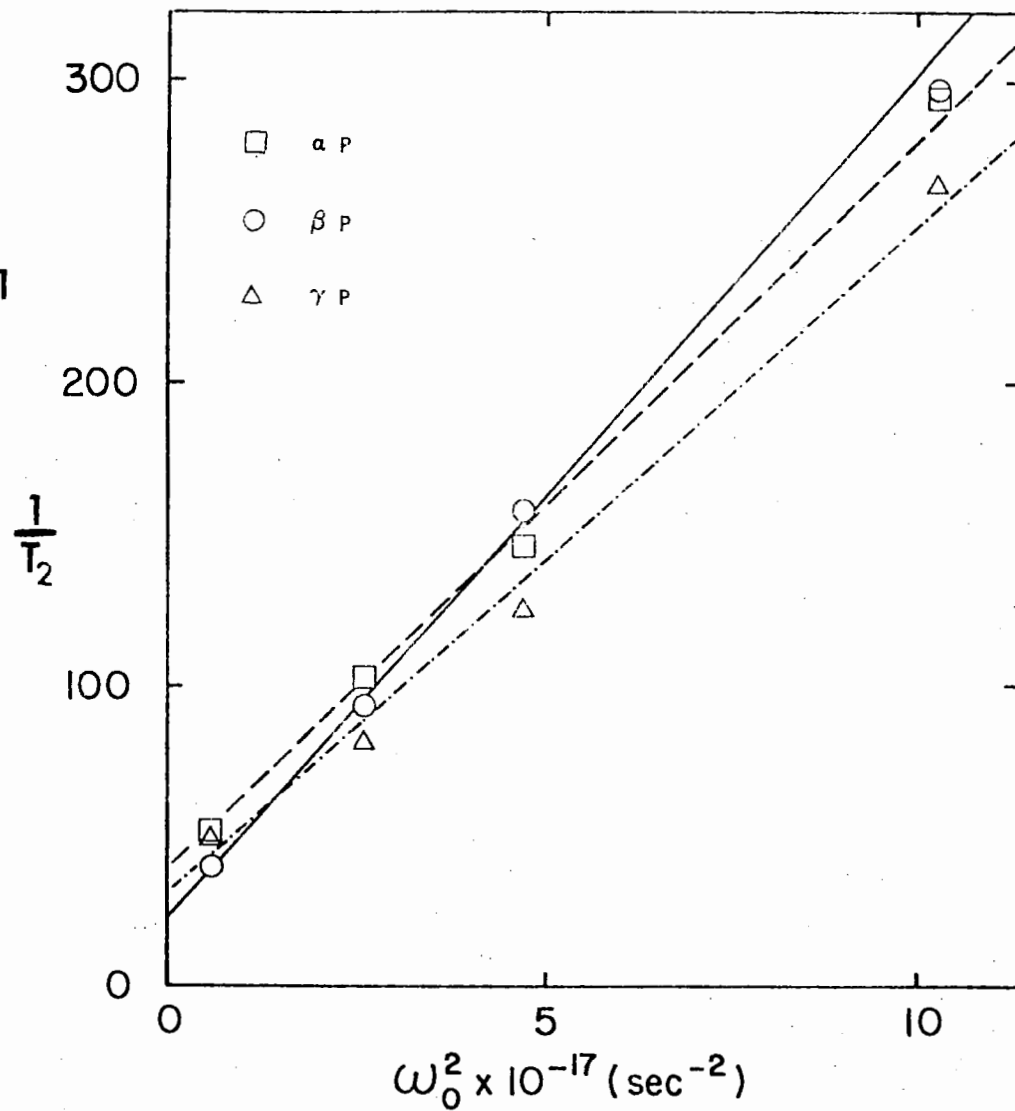
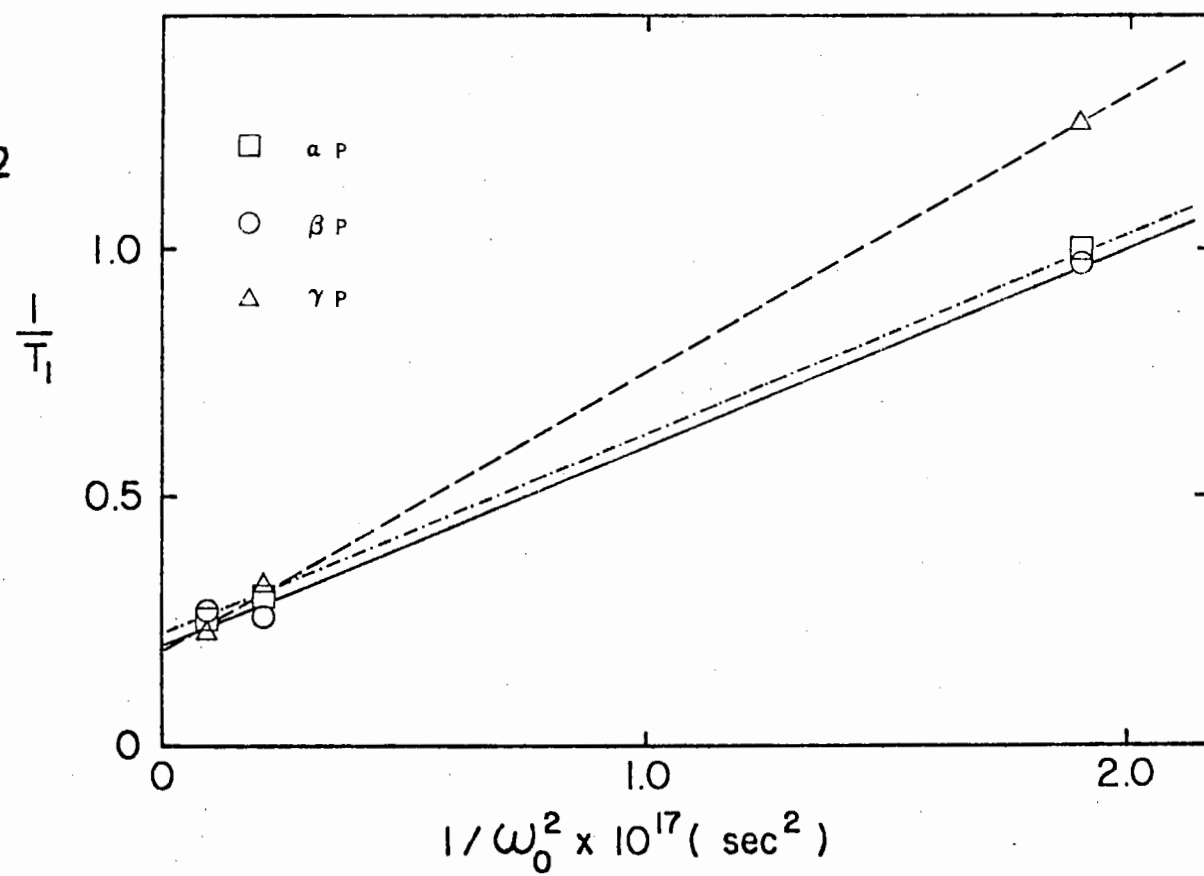


Fig. 2





CORPORATE
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DEVELOPMENT

GENERAL ELECTRIC COMPANY, RESEARCH AND DEVELOPMENT CENTER, P.O. BOX 8
SCHENECTADY, NEW YORK 12301, Phone (518) 385-2211

March 24, 1981

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

Re: ^{13}C NMR of Brominated Poly(phenylene oxide) (Br-PPO)

Dear Barry,

In the past year we have used ^{13}C NMR extensively to characterize a variety of brominated poly(phenylene oxide)s. The degree of bromination can be easily determined from integration of the resonances labeled A, B and C in the Figure. The three spectra correspond to samples which were 50%, 70% and 100% brominated (a, b and c) where 100% bromination in our terminology is one bromine atom per PPO ring. Assignments are given for the Br-PPO homopolymer (C). All spectra were obtained under quantitative conditions. The resultant analyses were found to be consistent with gravimetric determinations. The data for a series of mono- and dibrominated PPO's will be published shortly.

Sincerely,

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

A handwritten signature in cursive script, appearing to read "P. E. Donahue".

E. A. Williams P. E. Donahue
Chemical & Structural Analysis Branch
INORGANIC MATERIALS & STRUCTURES LAB

/ldr

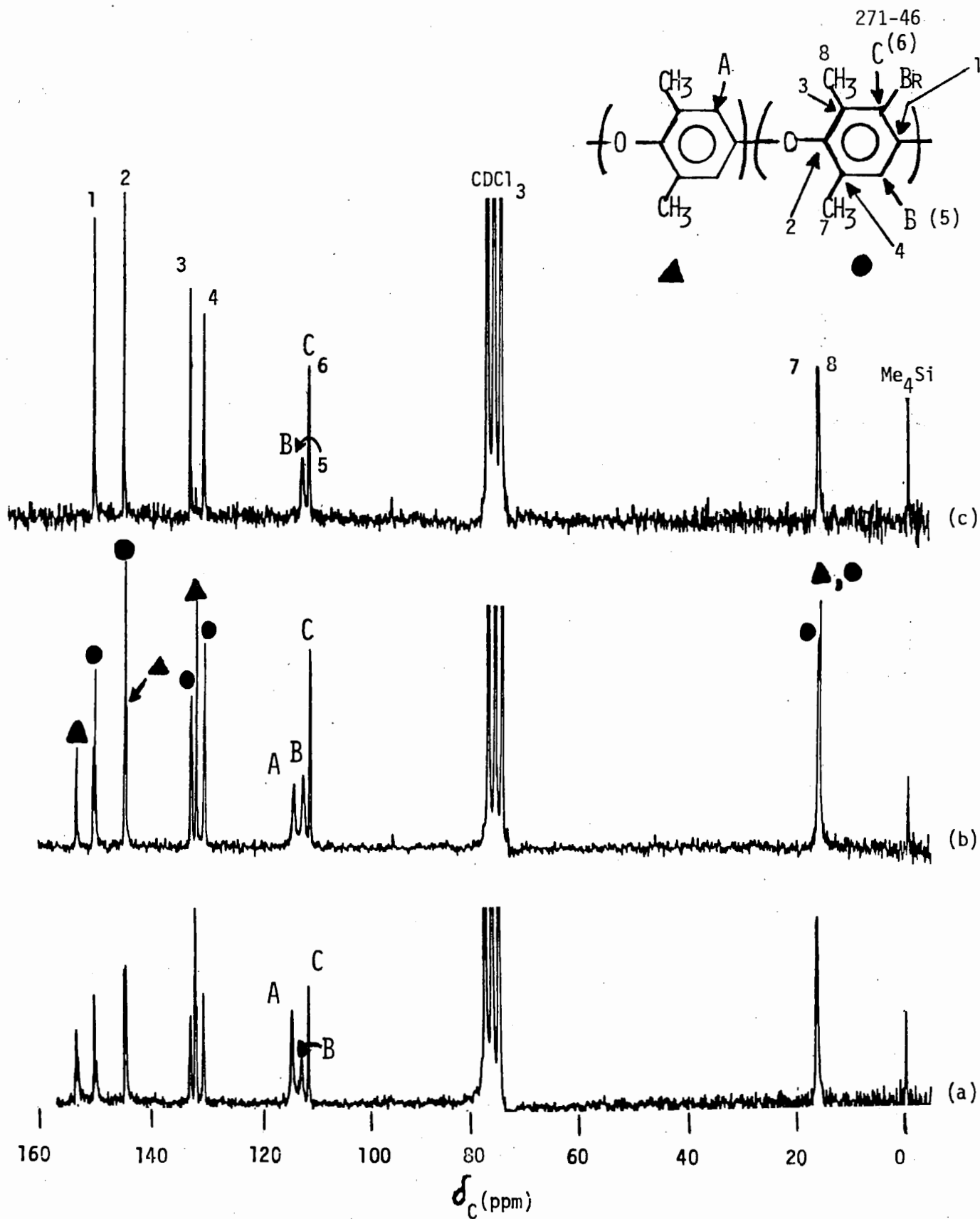


Figure. ^{13}C NMR spectra of (a) 50% brominated PP0, (b) 70% brominated PP0 and (c) 100% brominated PP0 (one bromine per ring).



INSTITUTE

P.O. BOX 21, CRANFORD, NEW JERSEY 07016
201/272-8820 EXT. 247

March 16, 1981

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

Dear Barry:

The JEOL INSTITUTE is a non-profit, educational function that has been recently formed to teach short but comprehensive courses in NMR. These courses are of interest to both analytical and research scientists dealing with NMR spectroscopy in all its forms. The first course that we have formulated has been given twice, and has received outstanding critiques by the attendees. In view of these excellent responses, we plan to expand the number and nature of the courses given, and would appreciate your disseminating this information to the NMR community via the Texas A&M Newsletter.

In addition to my duties as Director of the JEOL INSTITUTE, I teach the first three sessions of the course presently in our curriculum. There are two other sessions in the same course, and these are taught by Dr. Thomas C. Farrar and Dr. John S. Waugh.

It should be emphasized that although the JEOL INSTITUTE is associated with JEOL USA INC., it is a wholly independent and non-profit organization. Instrument references from other manufacturers are treated equally and without bias. The sole responsibility of the JEOL INSTITUTE is educational in its nature.

The first session of this course deals with the physics and basic concepts of a wide variety of NMR phenomena. The signals generated by these experiments are traced through block diagrams of the instrument, through the computer, and finally to the recorder. This is a three-day session, and is designed to give in-depth concepts of the best techniques to employ so that the maximum information can be obtained from the instrument. It includes T_1 and NOE measurements, decoupling techniques, and their applications for structure determinations. In addition, this session also serves as an excellent preparation for more advance training in trouble-shooting, or for making simple modifications to perform experiments not originally planned by the instrument manufacturers.

The second session is taught by Dr. Thomas C. Farrar and deals with analysis of dynamic systems. Topics such as T_1 -rho and spin-echoes are covered as well as some applications of these techniques in determining molecular motions.

The third session is taught by Dr. John S. Waugh and reviews the basic ideas and concepts involved with magic angle spinning, cross-polarization, two-dimensional spectroscopy and NMR imaging.

Separate courses are being planned for the future which will give considerably more details concerning the exact experimental techniques required to actually obtain 2-D spectra, spectra of solids, etc. In addition, courses in interpretation of spectra are also being considered.

The next course is scheduled for the first week of June 1981 (June 1-5, 1981). Further details may be obtained by writing:

JEOL INSTITUTE
P.O. BOX 21
CRANFORD, NEW JERSEY 07016

Sincerely yours,


Daniel D. Traficante

BOSTON COLLEGE

CHESTNUT HILL, MASSACHUSETTS 02167

(617) 969-0100

March 11, 1981

DEPARTMENT OF CHEMISTRY

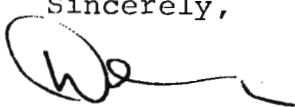
Professor B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

Equipment Needed

Recently some of the shim coils in our aged A-60A died, rendering it nonfunctional. We thus need a new left pole cap, but the price of a new replacement part is prohibitive. Consequently, I'd like to ask any of your readers who may have retired an A-60A and are cannibalizing it, to contact me if a pole cap were available at a reasonable price.

Sincerely,


Dennis J. Sardella
Associate Professor
(617) 969-0100 ext. 3612



McMASTER UNIVERSITY

Department of Chemistry

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

Telephone: 525-9140

March 24, 1981

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

Title: $^{91}\text{Zr}\{-^1\text{H}\}\{-^1\text{B}\}$ spectrum of $\text{Zr}(\text{BH}_4)_4$

Dear Dr. Shapiro:

Until a short time ago, zirconium-91 NMR received little attention¹. Recently it became desirable to decouple protons and boron-11 from the ^{91}Zr spectrum of $\text{Zr}(\text{BH}_4)_4$, both separately and simultaneously. Principles for retuning the decoupling coil are well known² and the method adopted here was to remove all tuning elements from inside the probe and mount new single tuned and double tuned networks inside small brass boxes which could then be attached separately, via two BNC connectors, to the base of the probe. One BNC connector is the one originally for the proton decoupling input and the other is a new one mounted at the hole vacated by a variable capacitor of the original tuning network. It should be noted that some capacitors have "tinned copper clad steel" leads and therefore should not be used. Hanging the capacitor on a string in the magnet gap while observing a lock signal is a good test for suitability.

A General Radio 1164-A frequency synthesizer (locked to a 5 MHz source from the spectrometer) and an RF Communications Inc. type 805 amplifier were used to decouple boron-11 at 28.875 MHz. A bandpass filter was required at the output of the amplifier and also a reject filter (28.875 MHz) was needed at the input to the signal amplifier. Facility for proton decoupling was already available with the Bruker WH90.

The results of these modifications appear in the accompanying figure. A fuller account will be forthcoming.

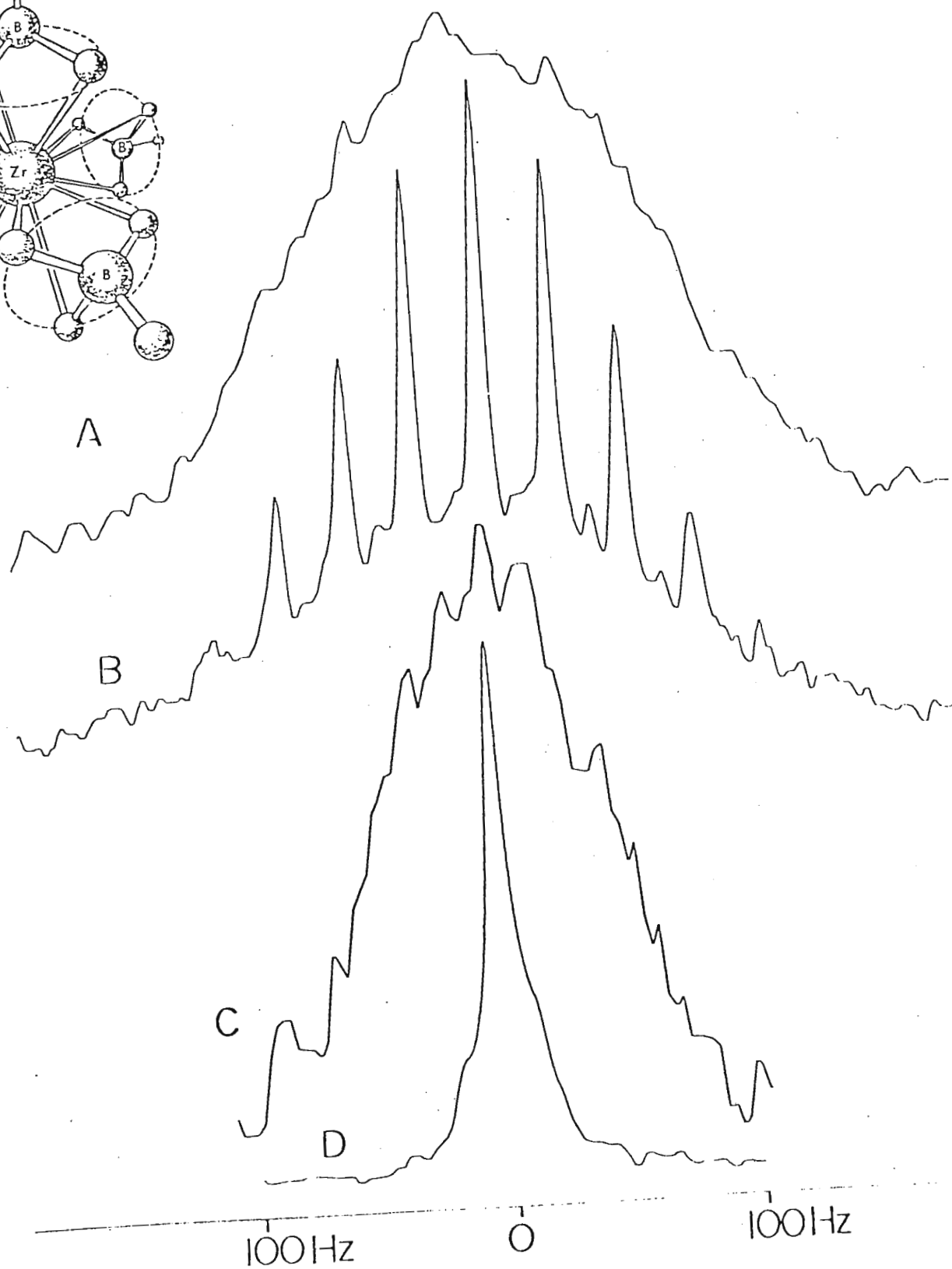
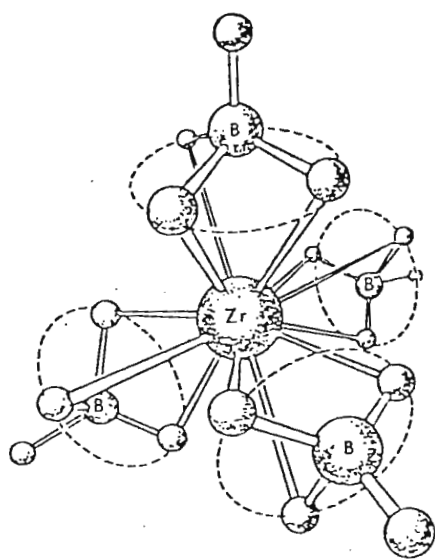
Yours sincerely,

J.I.A. Thompson *Nguyen Hao* *Brian Sayer* *Michael J. McGlinchey*

/ks
 enclosure

J.I.A. Thompson, B. Sayer, Nguyen Hao,
 and M.J. McGlinchey.

1. B.G. Sayer, Nguyen Hao, G. Denes, D.G. Bickley and M.J. McGlinchey, *Inorganica Chimica Acta*, 48, 51, 1981.
2. Hoult, D.I.; *Progr. NMR Spectroscopy*, 1978, 12, 41.



The ^{91}Zr NMR spectrum of $\text{Zr}(\text{BH}_4)_4$ at 25°C : A, fully coupled; B, ^{11}B decoupled; C, ^1H decoupled; D, ^1H and ^{11}B decoupled.

271-51

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Villeurbanne, le 17 Mars 1981

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

Cher Monsieur SHAPIRO,

Title : "GERM"

Le congrès 1981 du Groupe d'Etude en Résonance Magnétique Nucléaire (GERM) s'est tenu à Pont-à-Mousson les 11, 12 et 13 Mars 1981. Le Comité d'organisation 1981 (D. BESSERE, A. BRIGUET, J. COURTIEU, M.Y. MARTIN, J.J. MOULINES, J. PARELLO, W. VON PHILIPSBORN, P. SERVOZ-GAVIN) vous prie de publier le programme de cette réunion où une centaine de participants étaient présents.

Pour 1982, la réunion du GERM s'effectuera conjointement avec celle du comité homologue allemand et elle se tiendra toujours à Pont-à-Mousson, les 10, 11 et 12 Mars. Le comité d'organisation 1982 effectuera sans doute un rappel de cette manifestation grâce aux pages du TAMU NMR Newsletters.

Veillez croire, Cher Monsieur SHAPIRO, en nos sentiments les meilleurs.



A. BRIGUET

P.S. Pouvez-vous attribuer cette contribution au Laboratoire de Spectroscopie Hertzienne (J. DELMAU, J.C. DUPLAN, A. BRIGUET) ?

PONT à MOUSSON, 11 au 13 Mars 1981

PROGRAMME

Mardi 10 Mars au soir - Accueil des participants - Dîner à partir de 20h30

Mercredi 11 Mars

8h30 - 9h30	S. FORSEN (Lund) <i>"N.M.R. of magnesium, calcium and cadmium ; biological applications."</i>
9h.30 - 10h30	O. LUTZ (Tübingen) <i>"N.M.R. of 3A and 3B group elements and of vanadium and copper."</i>
10h30	Pause
11h00 - 12h00	C. BREVARD (Wissembourg) <i>"R.M.N. des noyaux de faible rapport gyromagnétique ; cas de l'argent, du tungstène et du molybdène."</i>
12h30	Déjeuner
16h15 - 18h15	Tables rondes TR1 & TR2
18h30 - 19h30	J-Y. LALLEMAND (Paris) <i>"Philosophie de l'emploi et de l'adaptation des calculateurs."</i>
20h00	Dîner

Jeudi 12 Mars

8h30 - 9h30	I-D. CAMPBELL (Oxford) <i>"N.M.R. experimental techniques for the investigation of biomolecules"</i>
9h30 - 10h30	J. PARELLO (Montpellier) <i>"Structure et dynamique de protéines."</i>
10h30	Pause
11h00 - 12h00	G. WEIL (Strasbourg) <i>"R.M.N. des macromolécules synthétiques."</i>
12h30	Déjeuner
16h15 - 18h15	Tables rondes TR3 & TR4
18h30 - 19h30	B. LAMOTTE (Grenoble) <i>"R.M.N. in vivo"</i>
20h30	Dîner

Vendredi 13 Mars 1981

8h30 - 9h30	M. CHARVOLIN (Orsay) "R.M.N. des milieux hétérogènes non biologiques."
9h30 - 10h30	J. TABONY (Grenoble) "Surfaces et molécules adsorbées."
10h30	Pause
11h00 - 12h00	A. BRIGUET "Imagerie R.M.N."
12h30	Déjeuner

Dispersion des participants.

TABLES RONDES

TR1	: Milieux hétérogènes Modérateur : J. COURTIEU (Orsay)
TR2	: Techniques expérimentales dans les milieux biologiques. Modérateur : J. PARELLO (Montpellier)
TR3	: Sur l'utilisation et l'adaptation des calculateurs. Modérateur : W. VON PHILIPSBORN (Zurich)
TR4	: Polymères. Modérateur : D. BESSERE (Clermont-Ferrand)



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March 4, 1981

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

"Positions Available - Post Doctoral Fellowship,
NMR Spectroscopist/Natural Products Chemist"

Dear Dr. Shapiro:

I have two openings for research scientists in our Corporate Research Laboratories in Manhattan, New York.

A post doctoral fellowship position for 1 to 2 years. Suitable candidate should have working experience in the isolation of natural products by chemical and chromatographic methods, and a strong background in structure elucidation using high field NMR spectroscopy.

We are also looking for an NMR spectroscopist/natural products chemist, an experienced Ph.D. with a proven track-record in the isolation and identification of natural products. The successful candidate will be familiar with all useful chromatographic and spectroscopic techniques and will be expert in the use of ^1H and ^{13}C NMR instrumentation.

Interested candidates should send to me a complete resume, including the names of two people to whom reference may be made on their behalf.

Sincerely,


William D. Rosenberger
Personnel Manager

WDR:dp



March 9, 1981

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

"An Accustomed Level of 10 mm C-13 Sensitivity"

Dear Prof. Shapiro,

We were somewhat puzzled to read of Dr. Toby Zens' enthusiastic introduction of a 'new generation' of probes from our worthy competition (TAMU 269-49). Our puzzlement centres mainly around what it is, exactly, that is new.

We enclose a couple of spectra recorded as part of day to day operations in Mississauga. The only unusual treatment was to use Dr. Zens' 3.5 Hz line broadening in the ASTM test. Normally, and so as not to mislead customers, we employ (natural linewidth notwithstanding) a line broadening equal to data point resolution achievable with a given sweepwidth and data table size. The spectra were obtained on our 18 month old WM-250 using our 10 mm ^{17}O - ^{31}P broadband probe.

We should perhaps welcome Dr. Zens to the new generation. Would that we had been able to do so in 1979!

Sincerely yours,

Martin Smith

Charles Rodger

Alex Bain

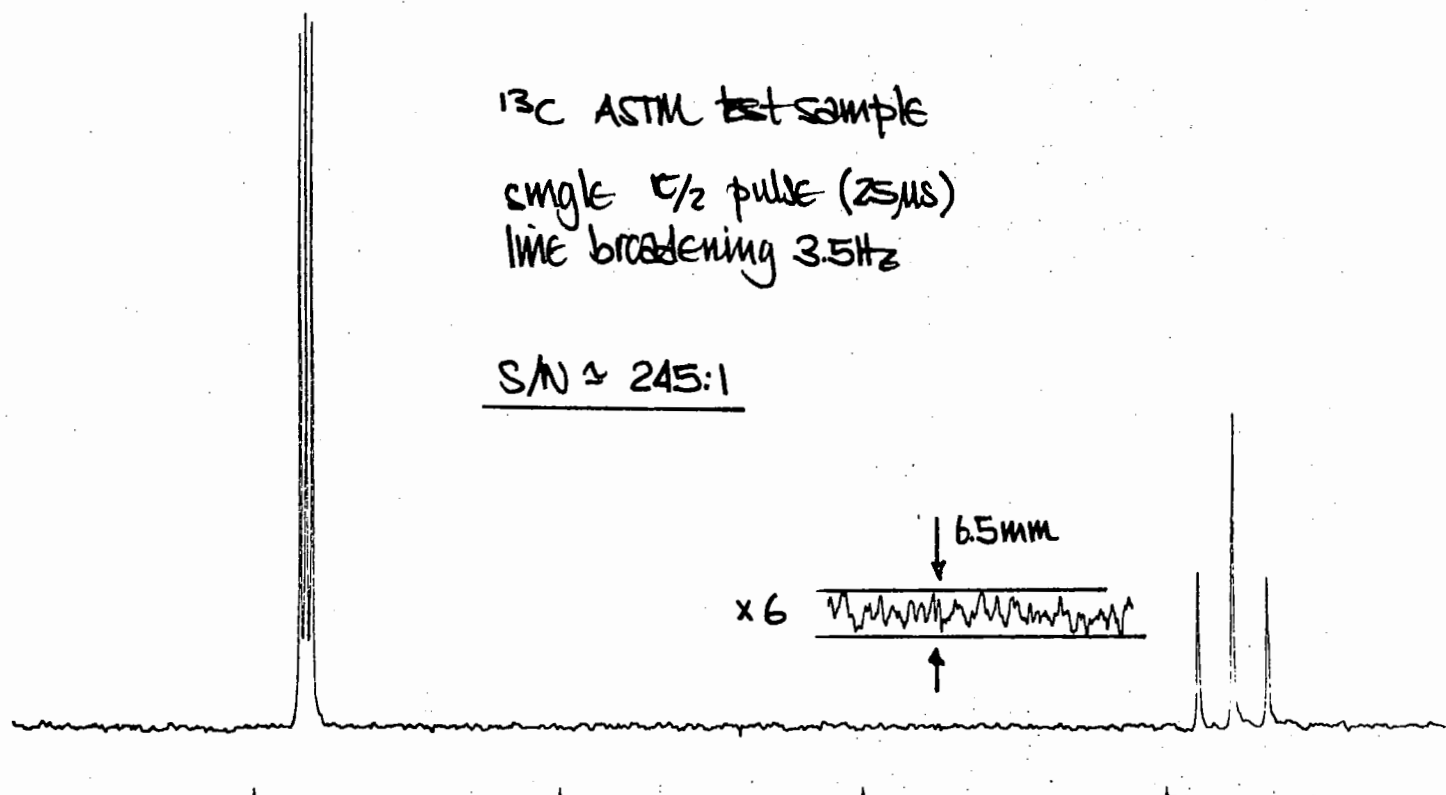
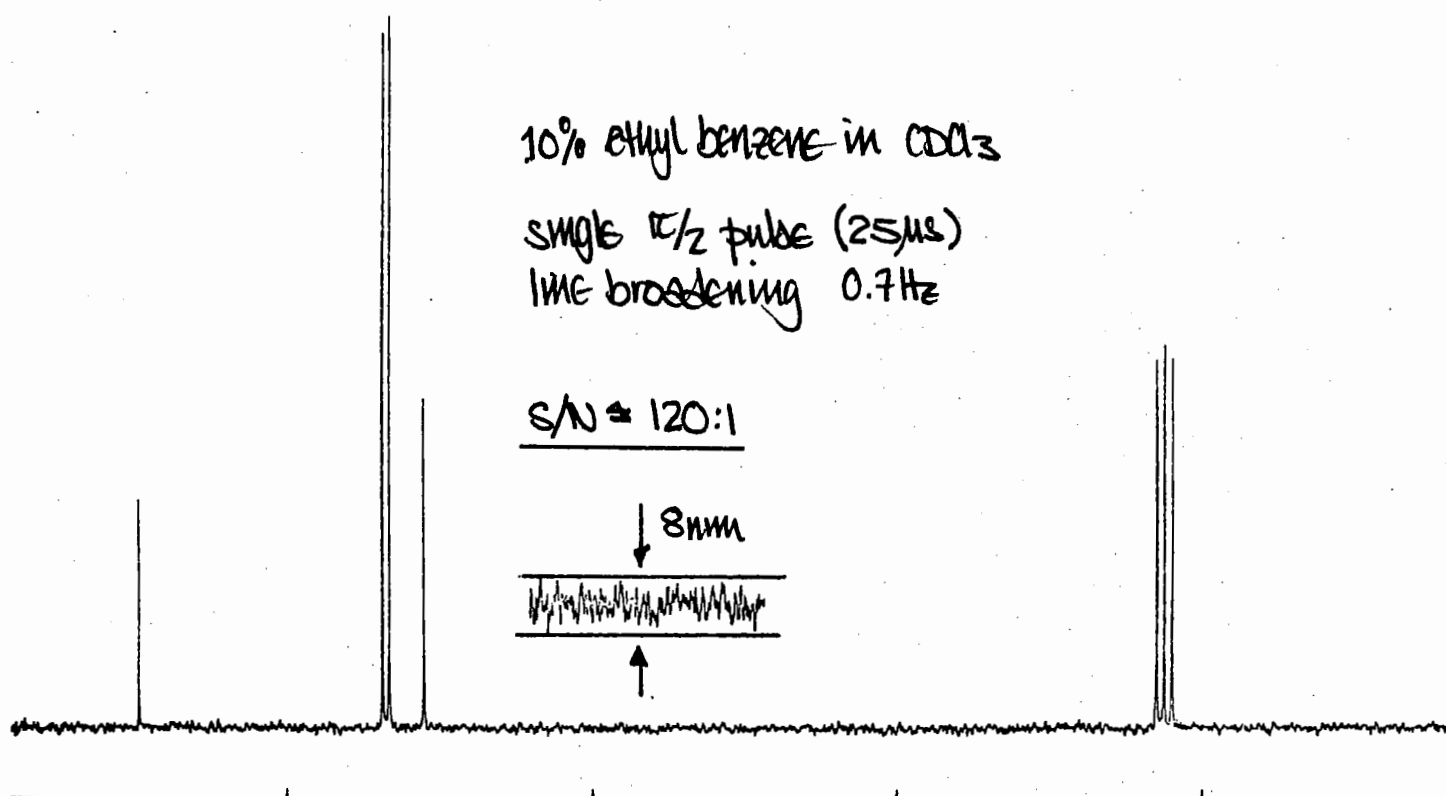
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WM250 : 62.8 MHz ^{13}C spectra (10 mm broadband probe)



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THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.
Department of Chemistry

24 March, 1981

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

Dear Barry,

LONG-RANGE COUPLING IN ESTERS

Nearly 13 years ago, Dr (now Professor) S.M. Verma and I reported (1) several proton-proton coupling constants of up to 0.9 Hz through four or five bonds including the central C-O-C bonds of esters, and suggested that the couplings could all be ascribed to transmission through planar-W or extended-W σ -bond systems, the function of the ester group being to maintain the necessary degree of planarity.

I have recently had a senior undergraduate student, Mr Dennis O'Shea, make calculations of coupling constants on various conformations of simple esters by my current DEC20 descendant of the QCPE program, FINITE.

Dennis began with various ab initio geometries of methyl formate (2) and showed that minor local variations were not significant but changes of configuration about the O-C bond and of Me-group conformation certainly were. In particular, for the Z-configuration (Me group cis to carbonyl O) with the Me group staggered about the O-C bond, the four-bond planar-W formyl-methyl H-H coupling as calculated by the INDO approximation is 2.62 ± 0.02 Hz, only slightly smaller than three times the observed 0.9 Hz, and the CNDO/2 value (2.31 Hz) is only a little smaller again. Neither the Z eclipsed-Me conformation, nor either conformation for the E-configuration give values remotely near the above, so we believe the earlier experimental conclusions and the argument that σ - π interactions are not significant in these long-range couplings have now been substantiated theoretically.

For methyl acetate, the Z-configuration with both Me groups staggered about the O-C bond gave 5J (planar, extended-W) values of 0.58 Hz (INDO) or 0.43 Hz (CNDO/2), both considerably smaller than three times the observed value (0.25 Hz). No other conformations for the Z-configuration gave values remotely near these, but some conformations for the E-configuration gave values in the range, -0.25 to -0.87 Hz; the E-configuration may, however, be discounted in view of its much higher energy (15-22 kJ/mol).

Yours sincerely,

Noel V. Riggs
Noel V. Riggs

1. N.V. Riggs and S.M. Verma, Tetrahedron Lett., 1968, 3767.
2. I.G. John and L. Radom, J. Mol. Struct., 1977, 36, 133.

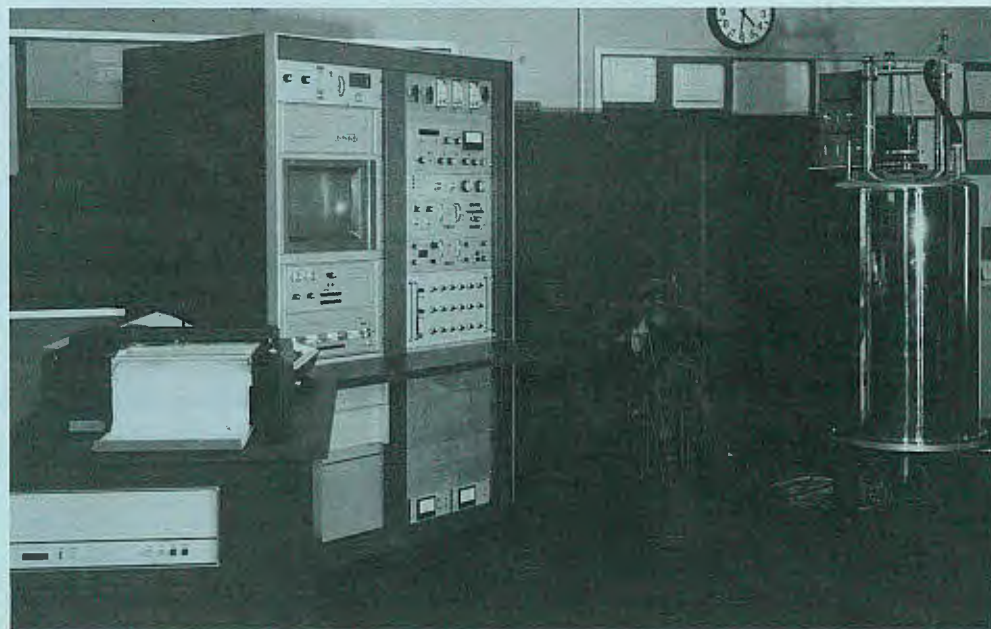
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