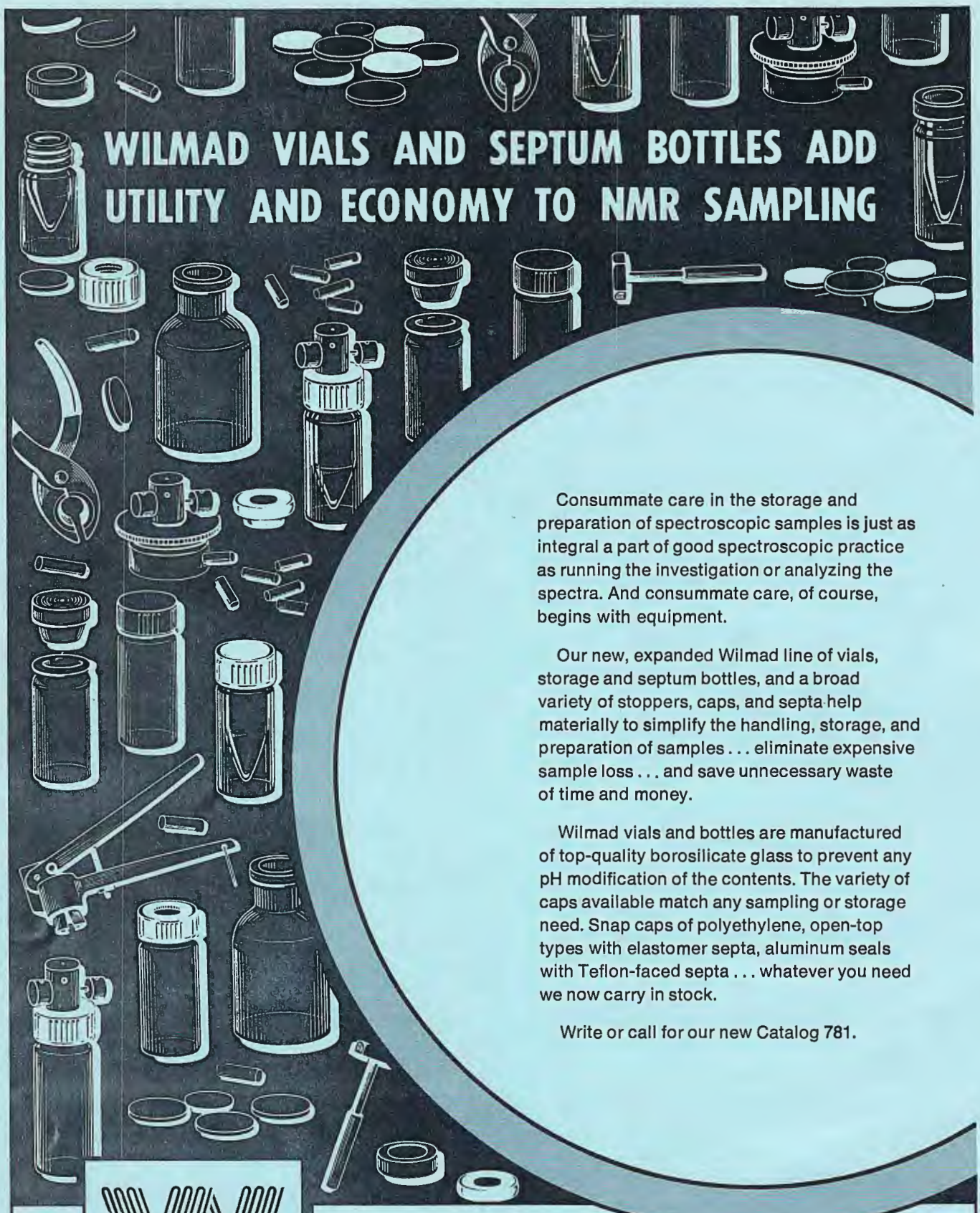
Texas A&M University
N-M-R Newsletter

No. 238

July, 1978



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DEADLINE DATES: No. 239: 7 August 1978
No. 240: 4 September 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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 238

238-1

UNIVERSITY OF GRONINGEN DEPARTMENT OF PHYSICAL CHEMISTRY
ZERNIKELAAN, PADDEPOEL, GRONINGEN, THE NETHERLANDS

Tel.: 050 - 117087

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

GRONINGEN, May 17, 1978

"Laser Photo-CIDNP in Proteins: A Novel Surface Probe".

Dear Barry,

Here is some news from our national NMR facility at Groningen. During the last year we have been working on a new method, which combines the glamour of laser beams with that of a 360 MHz spectrometer. We believe that this "photo-CIDNP method" holds promise for the study of protein structure in solution.

A solution of a protein containing a small amount of a dye (usually a flavin) is irradiated by an Argon laser in the probe of the Bruker HX-360. Alternating "light" and "dark" FID's are taken, which can be subtracted to yield the pure CIDNP spectrum. Polarization is generated in a cyclic photoreaction of the dye with certain surface residues (Tyr, His, and Trp) of the native protein. As an example I have included some CIDNP spectra of ribonuclease (collaboration with J.A. Lenstra and B. Bolscher). Fig. 1 shows the light, dark, and difference spectra of RNase A. Enhanced absorption is observed for His 119 (active site!) and emission for two tyrosines. Fig. 2a shows a blow-up of the aromatic region of RNase A with the resolution enhanced by digital filtering. Connections have been made by spin-decoupling for three tyrosines (Y1, Y2, and Y3). It can be seen in the photo-CIDNP spectrum of Fig. 2b that Y1 and Y2 are polarized in RNase A and, interestingly, in Fig. 2c that a third tyrosine Y3 shows up for RNase S. Y3 must be Tyr 25 rendered accessible to the dye by the cut in the subtilisin loop. Fig. 2d shows the result of binding the inhibitor 2'-CMP to RNase A. The lines due to His 119 are completely suppressed showing that access to this active site residue is blocked by inhibitor binding.

By comparison with nitrated RNases we have assigned the tyrosines Y1 and Y2 to Tyr 76 and Tyr 115, respectively.

Although the general usefulness of the method in studies of protein structure remains to be established, we have had a lot of excitement with these experiments.

Best regards,

Yours sincerely,

Robert

Robert Kaptein

P.S. Please credit this contribution to the account of Dr. W.D. Weringa

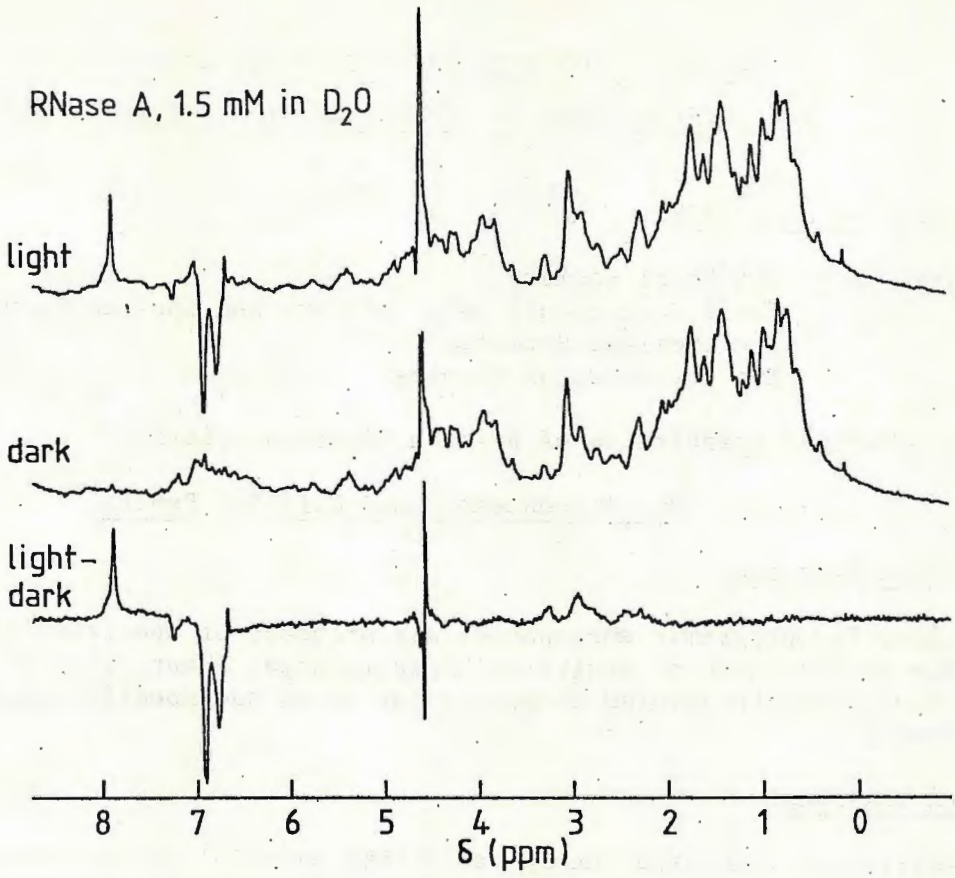
RNase A, 1.5 mM in D_2O
light
dark
light-
dark
8
7
6
5
4
3
2
1
0
δ (ppm)

Fig. 1

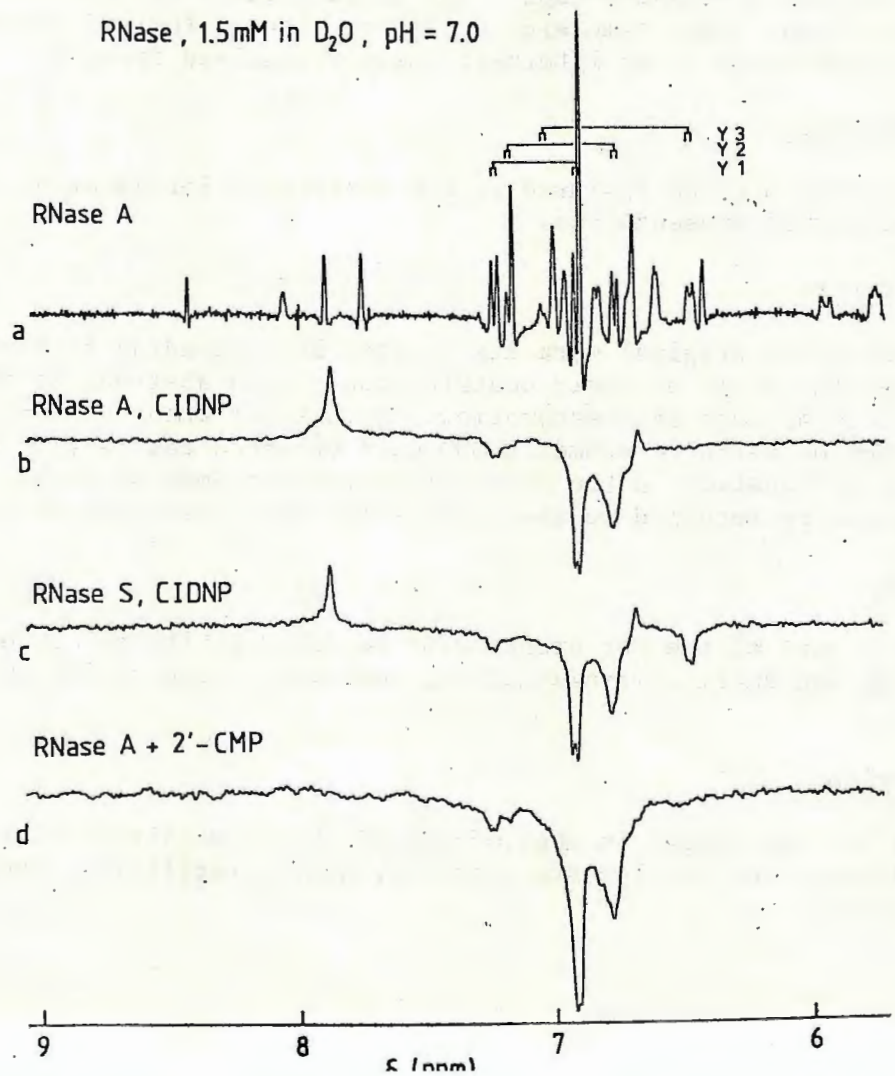
RNase , 1.5mM in D_2O , pH = 7.0
Y 3
Y 2
Y 1
RNase A
a
RNase A, CIDNP
b
RNase S, CIDNP
c
RNase A + 2'-CMP
d
9
8
7
6

Fig. 2

XXI COLLOQUIUM SPECTROSCOPICUM INTERNATIONALE

8th INTERNATIONAL CONFERENCE ON ATOMIC SPECTROSCOPY

CAMBRIDGE 1-6 July 1979

Sponsored by:- The Royal Society
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The Institute of Physics

Organised by the Association of British Spectroscopists

2nd Announcement and Call for Papers

Scientific Programme

The scientific programme encompasses all branches of spectroscopy with particular emphasis on the theme of analytical spectroscopy. There will be one, two, and three days symposia devoted to particular areas and specific applications of spectroscopy.

Lecture Sessions

The provisional timetable incorporates five parallel lecture sessions arranged to minimise overlap of related topics and to facilitate the movement of delegates between sessions. Each symposium will open with an invited lecture on a topic of special significance by an internationally recognised speaker.

Poster Sessions

Poster sessions will be featured at the conference for material which is better suited to this manner of presentation.

Call for Papers

Papers describing original work are invited and intending authors should submit to the Secretariat the title of their contribution and an abstract of 50 words by 4 September 1978, in the language of presentation. Authors of accepted papers will receive special typing paper on which to submit a 300 word extended abstract in English, French or German for publication in the Official Conference Book of Abstracts. These typed sheets should be returned to the Secretariat not later than 15 January 1979.

Exhibition

An integral part of the Conference will be the Exhibition. Several large halls will house large and small instrumentation, equipment, accessories and books throughout the week.

Accommodation

Delegates will be housed in the colleges of the University. These are all within walking distance of the lecture theatres, dining facilities, social headquarters and exhibition.

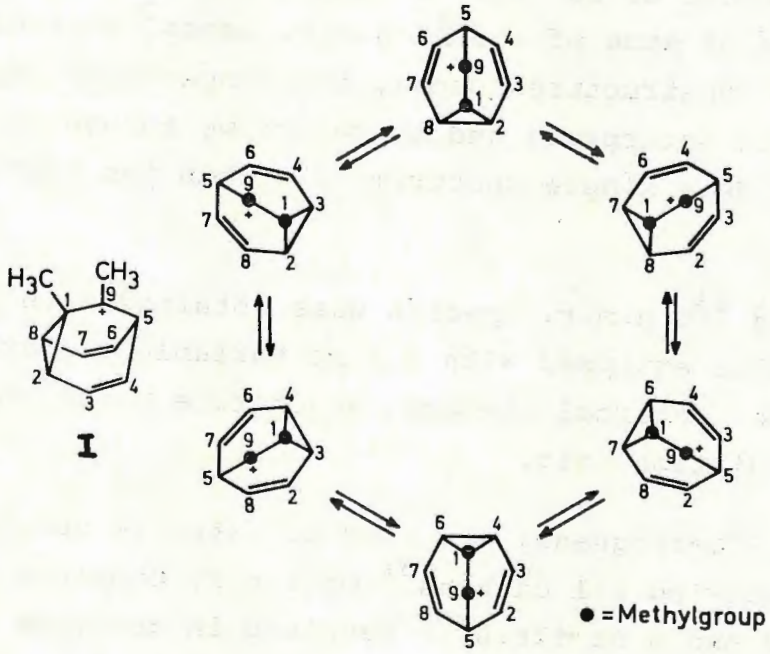
Social Programme

There will be a full social and ladies programme every day.

Further Details

All who contact the Secretariat will receive in due coarse further information on all aspects of the conference. Contact: Association of British Spectroscopists, P.O. Box 109, Cambridge CB1 2HY, United Kingdom.

CONT'D. FROM P. 238-5



With best regards,

Yours sincerely

Per Ahlberg and Carin Engdahl

UNIVERSITY OF UPPSALA
INSTITUTE OF CHEMISTRY
Docent Per Ahlberg and
F.K. Carin Engdahl

Uppsala

1978-06-06

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

Dear Dr. Shapiro,

We wish to communicate results on the subject: "Transfer of ^{13}C Spin Saturation by the Degenerate Rearrangements of Carbocations."[1)]

In particular we wish to report the behaviour of the unstable 1,9-dimethylbarbaralyl cation (I) which undergoes degenerate rearrangements at ca -130 ^{o}C as shown by band shape temperature dependence of some of its ^{1}H n.m.r. bands.[2)] However, due to its broad and nonstructured bands, the temperature dependence is not easy to interprete and therefore we turned to ^{13}C n.m.r. which yields a simple spectrum of I when the protons are decoupled.

The ^{1}H and ^{13}C n.m.r. spectra were obtained with a JEOL FX 100 spectrometer equipped with a 5 mm variable temperature $^{1}H/^{13}C$ dual probe, external Li-lock, quadrature phase detection and a multiirradiation unit.

An extra ^{13}C-frequency was used to saturate selected carbons while observing all carbons[3)] of ion I. Complete saturation of carbons 2 and 8 at -128.0 ^{o}C resulted in decrease of the signal from carbons 3 and 7 to ca. half the size it had before saturation. The singlett from carbons 4 and 6 was only slightly diminished. Similarly complete saturation of carbons 4 and 6 resulted in substantial decrease of the 3,7-singlett but the 2,8-signal was only slightly saturated. Complete saturation of carbons 3,7 created a intensity drop of the 2,8- and 4,6-singletts to about half their size before saturation.

Mailing address
Box 531
S-751 21 UPPSALA 1, Sweden

Telephone
018 - 13 94 60

Furthermore we found that no other carbons of ion I are exchanging rapidly with the six carbons 2,3,4,6,7 and 8 and the methylgroups and carbons 1,5 and 9 did not exchange rapidly with each other.

In conclusion we found that the phenomenological mechanism shown below must operate. In this mechanism the bridge consisting of carbons 1,5 and 9 is rotating stepwise around the "pseudo ring" made up by carbons 2,3,4,6,7 and 8.

The ^{13}C relaxation times (T_1) were measured and by use of these and the results above the rearrangement rates were obtained according to B.E. Mann.[4] The relaxation times were very short, ca. 0.06 s at -128.0 ^{o}C. This made it possible to use short repetition times. Acceptable spectra were obtained in less than 10 min. of samples being ca. 0.2 M in carbocation. The dilute ionic superacid solutions were prepared in our recently reported ion generation apparatus.[5]

The above illustrates the usefulness of transfer of ^{13}C spin saturation in the study of degenerate rearrangements of carbocations, a field in which this technique doesn't seem to have been used previously.

This letter has kindly been requested by Dr. P. Stilbs at the Institute of Physical Chemistry and we therefore wish that you credit this contribution to his subscription.

References

1. C. Engdahl and P. Ahlberg, in preparation.

2. P. Ahlberg, Chem. Scr. (1972) 2, 231.

3. P. Ahlberg, Chem. Scr. (1976) 9, 47.

4. B.E. Mann, J. Magn. Reson. (1975) 21, 17; ibid. (1977) 25, 91 and Prog. in NMR Spectroscopy (1977) 11, 95.

5. P. Ahlberg and C. Engdahl, Chem. Scr. (1977) 11, 95.

Cont'd. bottom of p. 238-4.

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LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918
69621 VILLEURBANNE – FRANCE

TÉL. (78) 52.07.04

Professor J. DELMAU

MICROPROCESSOR INTERFACING BETWEEN A TELETYPE AND THE C 1024 TIME AVERAGING COMPUTER

Dear Professor B.L. SHAPIRO,

An interface has been built in order to extract numerical values of memorized signals from the C 1024 Time Averaging Computer (C.A.T.) and present them to a teletype. The main operating signals are address, readout of channel contents with or without reset. The output of each channel is directly available on the CAT but interfacing must be provided for matching CAT logical levels to TTL levels. Since contents of memories are given in a pure binary mode it is necessary to convert them to decimal and then to format for teleptype printing. Microprocessor use provides an elegant solution to perform such functions[1].

I - C 1024 Signals

The contents of channels are available as seventeen bits of pure binary but it is easier to use only sixteen. In this case, each of the binary coded signals can be addressed to the microprocessor input through a multiplexor controlled by the microprocessor using two successive readout of eight bits (Figures 1, a and b). Three successive readings would be needed for all seventeen bits. Address advance is provided by the leading edge of TTL signals. As shown on Figure 1b the content of each memory is available during 750 μs, then output levels return to zero. Address advance of the CAT and multiplexing operations are achieved through a unique TTL sequence generation which is provided by programming the microprocessor. Reset of channel address is executed by a positive TTL level. Memories readout be either : non destructive readout (NDRO) or destructive readout.

II - Microprocessor and programs

As it can be seen from the preceeding section three operating signals C_0, C_1, C_2 must be employed : C_0 to monitor the advance of the CAT and the simultaneous multiplexer channel choice, C_1 to control the NDRO, and C_2 to reset channels addresses. These sequences are generated by a 8080 microprocessor which is also connected to a teletype.

Flow charts and readout program are available on request.

Sincerely,

C. LAPRAY A. BRIGUET J. DELMAU J.C. DUPLAN G. TETU

1 W. BANKS and J.C. MAJITHIA, IEEE Transactions on Instrumentation and Measurement, 25, 245 (1976)

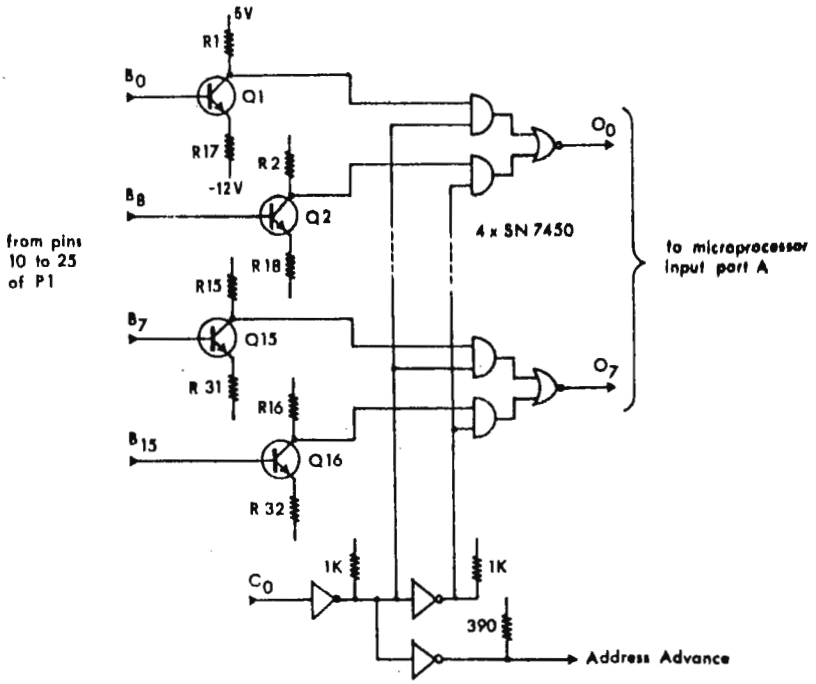


Fig. 1b

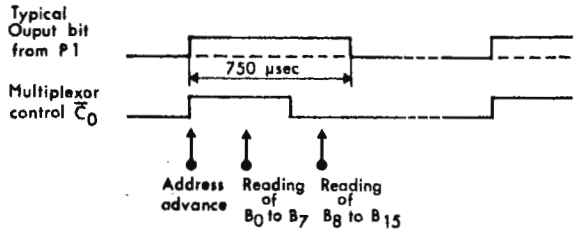


Fig. 1a) Control signals C_1, C_2 for the CAT are shifted from TTL levels to (-3V, OV) logical C 1024's levels, through transistors Q_{17} and Q18 (2N 2907). The logical output levels (-12V, OV) of bits from pins 10 to 25 of P_1 are shifted to TTL levels through transistors Q_1 to Q_{16} (2N 2222). Then the 16 bits output is sent to input A of the microprocessor as two height bits input words through a multiplexor consisting of four SN 7450 integrated circuits.

Fig. 1b) This figure shows how to read successively these two words in order to get properly the data from C 1024's channels.

The control multiplexor signal C_0 is also used as the address advance control.

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

Department of Chemistry

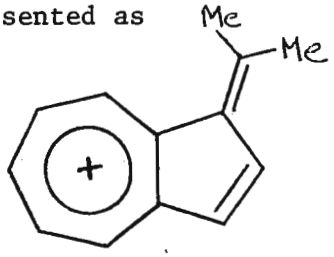
June 6, 1978

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

Dear Barry:

Charge Dispersal in 1-Substituted Azulenes

In our studies of substituent-induced ^{13}C chemical shifts (SCS) in 1-substituted azulenes, we found carbons in the (unsubstituted) seven-membered ring to shift downfield with increasing electron demand, while carbons 2 and 3 in the (substituted) five-membered ring exhibit random fluctuations. If the SCS are indicative of electron density redistribution or withdrawal, this pattern of SCS suggests development of tropylium ion character in the seven-membered ring, with the five-membered ring acting, in effect, as a conduit for electron flow. To investigate this point further, we looked at the 2-(1-azulenyl)-propyl cation, thinking it might be best represented as



1

Although we have not yet obtained really satisfactory spectra, its proton spectrum (-38°C in CD_3CN) clearly shows two nonequivalent methyl groups. Based on the average methyl proton shift, we estimate a charge of +0.25 at the exocyclic carbon (as compared to +0.5 in αα-dimethylbenzyl). This compares well with the value of +0.30 we find in 1-azulenylmethyl by CNDO calculations.

Three further interesting points emerging from our CNDO calculations are:

1. the barrier to rotation of the exocyclic CH_2 is calculated to be 48.3 kcal/mole-close to that expected for a double bond;

2. there is strong alternation of π-bond orders in the five-membered ring (i.e., pronounced butadienic character);

3. positive charge develops primarily at carbons 5,7 and 10, and, to a lesser extent, carbons 3 and 9.

All of the above considerations suggest the π-structure of the ion is best approximated as a heptatrienyl cation (rather than a tropylium ion) attached to the 1,3-positions of a butadiene π-system.

This work was done by Shahla Sadigh-Esfandiary as part of her M.S. thesis.

Sincerely,

Dennis J. Sardella
Associate Professor

DJS/bl

CONT'D. FROM P. 238-11

comes ADAM, Another Double fourier transform Applications Module, (designed for double FT processing on a 1080).

AMOS is presently fully operational while ADAM is in its final stages of debugging and is expected to be operational by early July. Object and/or source tapes for either of these programs are available on request.

Prophetically yours,

Dan Terpstra
Research Assistant

George C. Levy
Professor

Department of Chemistry
The Florida State University
Tallahassee, Florida 32306

June 13, 1978

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

A Prophetic Software Expansion

Dear Barry:

As you know, we are currently embroiled in the task of teaching Z-80 microcomputers how to talk to our spectrometers and to our minicomputers. One part of this project requires us to convince our Nicolet 1080's that it is socially acceptable to be seen talking to a microcomputer. This necessitates a software mediary as well as some hardware modifications.

One of the first questions that comes to mind when employing such a mediary is "Where do we put it?" Obviously the most expedient place would be somewhere within the confines of the NTCFT program itself. In this regard, the designers of NTCFT were farsighted enough to leave room for expansion in the NTCUSR module, but they were also industrious enough to use most of it themselves.

Since it was feared that the remaining 600_8 ($\sim 400_{10}$) locations would not provide enough room to do everything we wanted to do, another approach was decided upon. Those locations were used to provide a home for AMOS, our Auxiliary Module Operating System.

AMOS has been trained to act as an intercessor between the NTCFT program and up to eight user definable modules through the commands M1-M8. Upon execution of one of these commands, the NTCEXC loads the NTCUSR module and calls upon AMOS. AMOS then checks to see if that module actually exists and if it does, calls it into core. AMOS has its own disk access routines as well as an internal one- and two-letter command decoder and a large number of NTC and Floating Point Package pointers to simplify module programming. The modules themselves are 3000_8 words long (exactly one disk track) for efficient disk storage and reside on most of pages 3 and 4 in Nicolet core.

AMOS alone is still powerless to convince our Nicolet 1080's to talk to our file-handling Z-80, and to achieve this end AMOS will soon be joined by NAHUM, the Nicolet And file-Handler Unification Module. But it goes without saying that before NAHUM,

Cont'd. bottom of p. 238-10.

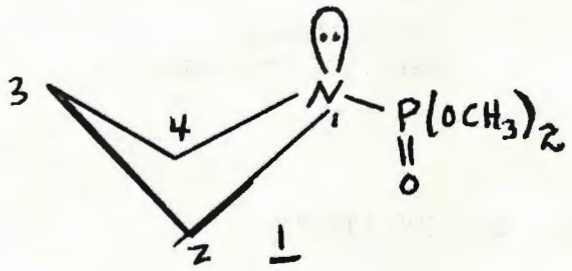
Carleton University
Ottawa, Canada K1S 5B6

June 15, 1978.

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

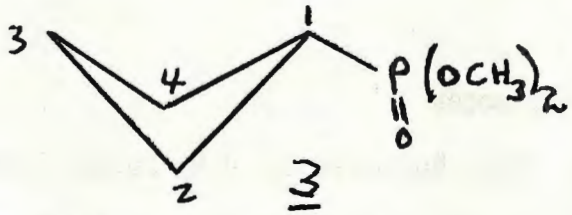
Title: Vicinal ^{13}C-^{31}P Coupling in Amine Phosphonates. A Probe for N lone pair delocalization.

We have recently examined ^{13}C spectra of cyclic amine phosphonates of ring sizes three to nine. Vicinal C-P coupling for N-dimethylphosphonoazetidine 1 and N-dimethylphosphonopiperidine 2 are shown below and are compared to their carbocyclic analogs 3 and 4 respectively.



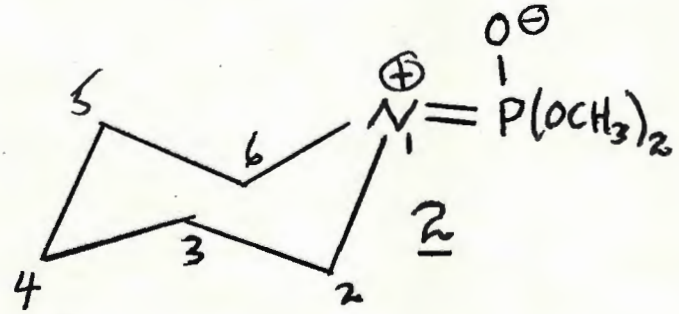
1

$^3J_{P\text{-}N\text{-}C\text{-}C_3} = 18.0$



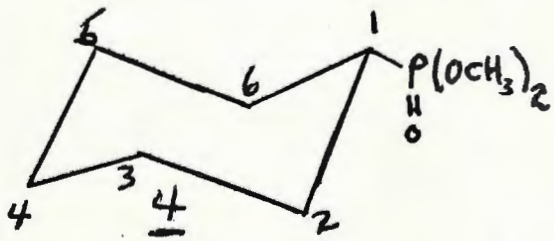
3

$^3J_{P\text{-}C\text{-}C\text{-}C_3} = 18.7$



2

$^3J_{P\text{-}N\text{-}C\text{-}C_{3,5}} = 4.6$



$^3J_{P\text{-}C\text{-}C\text{-}C_{3,5}} = 16.2$

The similar ^3J's for 1 and 3 can be interpreted in terms of highly puckered conformations of the 4-membered rings, with the large dimethylphosphono group (1) equatorial. The nitrogen atom of 1 is viewed as having essentially a localized lone pair, and a pyramidal geometry.

For the 6-membered rings, ^3J is markedly attentuated in 2 vs. 4. Low temperature experiments on 2 give no evidence of a chair conformer with an axial $P(O)(OCH_3)_2$ function. Our view is that the N atom of 2 is trigonal planar, and the N lone pair delocalized into the N-P bond as indicated. This would result in a dihedral angle $P\text{-}N\text{-}C_{2,6}\text{-}C_{3,5}$ of ca 120°. Recent work of Thiem and Meyer (2) indicates that for a dihedral angle of 120° in phosphonates, $^3J_{P\text{-}C}$ would be ca 4Hz, in good agreement with that found in 2.

Amine phosphonate rings larger than six-membered also show small ^3J values, presumably for the same reason. In the azetidines, apparently bond angle strain is too great in the case of a trigonal planar nitrogen, so that the pyramidal N is favored.

We are presently exploring the utility of $^{15}N\text{-}^{31}P$ couplings for monitoring these effects, in collaboration with George Gray of Varian. Best regards and please credit this as usual to John ApSimon's account.

Sincerely,

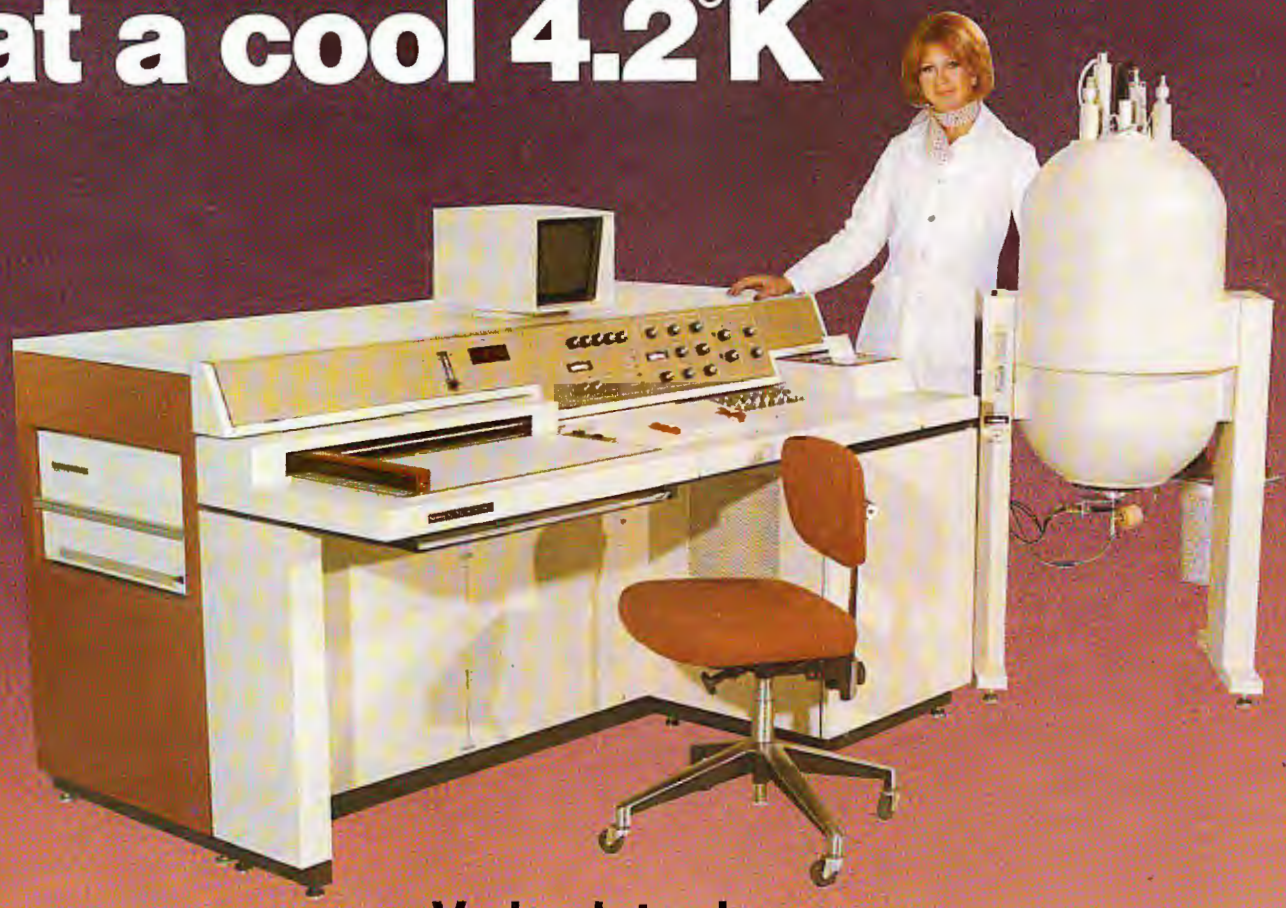
G.W. Buchanan,
Associate Professor.

References

1. G.W. Buchanan and J.H. Bowen. Can. J. Chem. 55, 604 (1977).

2. J. Thiem and B. Meyer. Org. Mag. Res. 11 50 (1978).

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!

The basic instrument is designed for ^{1}H (200 MHz) and ^{13}C (50.3 MHz) observation, but it will accommodate a host of other nuclei with the optional 20-80 MHz broadband accessory.

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 ^{1}H, ^{13}C, ^{19}F, and ^{31}P
- Compatible with RF synthesizer for broadband multi-nuclear operation
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- 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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GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

June 5, 1978

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

Meeting of the German NMR Discussion Group

Dear Barry:

Readers of the Newsletter may be interested to learn that there exists such a thing as a German NMR Discussion Group. This Group was founded in 1974 and has since been gathering informally once a year, but plans to constitute itself as a subsection of the German Chemical Society at this year's meeting, which will take place on September 11-13 at the Monastery of Ettal, beautifully situated in the Bavarian Alps close to Garmisch. The principal topics of the program are to be (1) Dynamic Aspects, (2) Spectral Analysis and Computer Methods and (3) Nuclei of Low Sensitivity and/or with Quadrupole Moments. Torbjörn Drakenberg (Lund), Hanns Fischer (Zürich), Pierre Laszlo (Liège), Felix W. Wehrli (Zug) and Michal Witanowski (Warszawa) have kindly consented to serve as plenary lecturers.

Visitors from abroad who happen to pass through central Europe at around this time and who are anxious to establish contact with this Group should write to me at the above address.

Sincerely yours,

Gerhard

Gerhard Binsch

238-17 UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof.Dr. O. Lutz
Dr. A. Nolle

D-7400 TÜBINGEN 1, den 15.06.1978
Morgenstelle
Telefon (0 70 71) 29 67 14

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

^{55}Mn, ^{95}Mo and ^{31}P in Anions

Dear Professor Shapiro,

In letter No. 228 we reported an oxygen induced isotope effect on the Larmor frequency of ^{55}Mn in a solution of $KMnO_4$ in H_2O, which was enriched in ^{18}O to 99 % (1). Meanwhile we could observe the exchange rate of ^{18}O between the water and MnO_4^- ion for about two years at room temperature. The sample is now reaching the final stat with statistical distribution of the oxygen atoms (see Fig. 1). The ratio of the intensities for the two remaining signals is expected to be about 12:1 because of the ^{18}O and ^{16}O contents of the sample. Continuing our investigations of isotope effects in anions oxygen and sulfur induced isotope effects in the ^{95}Mo NMR spectra of MoO_4^{2-} and MoS_4^{2-} could be observed (1,2). A few months ago we succeeded in detecting a very small oxygen isotope effect of ^{31}P in the phosphate ion (3). We used a sample, of K_3PO_4 in D_2O. The PO_4^{3-} ion was enriched in ^{18}O to about 50 % by D. Staschewski, Kernforschungszentrum Karlsruhe. An example of the observed spectra is given in Figure 2.

Sincerely yours

O. Lutz A. Nolle

(1) K.U. Buckler, A.R. Haase, O. Lutz, M. Müller, and A. Nolle, Z. Naturforsch. 32a, 126 (1977)
(2) O. Lutz, A. Nolle, and P. Kroneck, Z. Physik 282A, 157 (1977
(3) O. Lutz, A. Nolle, and D. Staschewski, Z. Naturforsch. 33a,380(1978

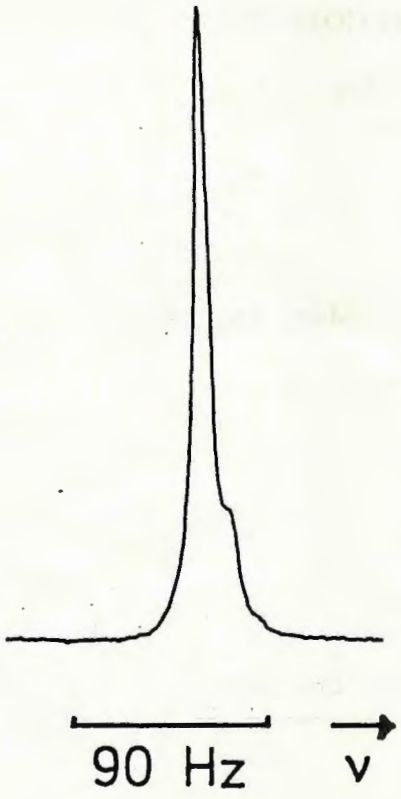

Fig. 1: ^{55}Mn FT NMR signal at 22.311 MHz in a 0.27 molal solution of $KMnO_4$ in H_2O (the water was enriched in ^{18}O to 99 %) about two years after the preparation of the sample. The two remaining signals are due to the $Mn^{18}O_4^-$ and $Mn^{18}O_3{}^{16}O^-$ ions (intensity ratio ≈ 12:1).

Measuring time: 100 s (100 scans)
spherical sample volume: 0,3 ml

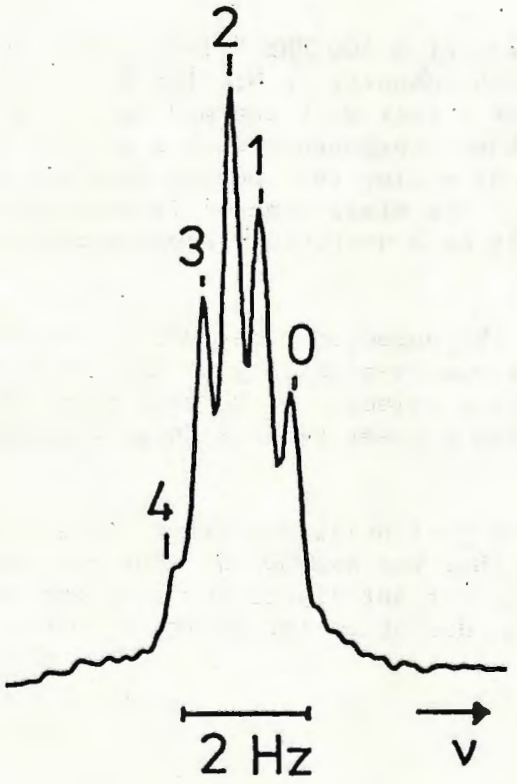

Fig. 2: ^{31}P FT NMR signal at 36.430 MHz in a solution of K_3PO_4 in D_2O, measured with a high-solution probe and with an internal ^2H-lock. The phosphate was enriched in ^{18}O to about 50 %. The signals are due to the phosphate species $P^{16}O_{4-n}{}^{18}O_n{}^{3-}$ (n=0,1,2,3,4)

Measuring time: 200 s (67 scans)
cylindrical sample tube

THE UNIVERSITY OF BRITISH COLUMBIA
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V6T 1W5

DEPARTMENT OF CHEMISTRY

June 16, 1978.

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

A Homebuilt 270 MHz Spectrometer: Chapter I

Dear Barry:

This is the first part of a story which will, I hope, have a happy ending. For reasons which I will not detail here, I decided several years ago to collect components which could eventually be assembled into a multinuclear 270 MHz pulse F.t. spectrometer, at a considerably lower price than the commercially available equivalent.

Stage one involved the purchase from Nicolet of a 100 MHz "TT-23" console (ex Bruker WH-90) fitted with a Nicolet 1080 computer, a Nicolet 293 controller and a Diablo Disk; these were used for over a year with our old Varian HA-100 magnet. Then, last August we interfaced these components with a 270 MHz solenoid and "test" probe from Oxford Instruments, by mixing the 100 MHz from the console with 170 MHz from a frequency-synthesiser. The mixer-adaptor is multinuclear and forms the basis of what will eventually be a completely broadbanded spectrometer.

So far we have been running ^{1}H spectra in the unlocked mode, which is very simple and convenient and, in view of the high frequency-stability of the console/synthesiser, gives adequate quality spectra (see below). Up to this point the total development time, including construction and a great deal of forward planning was less than six-man-months.

Clearly, we still have much to do. We have just built our first ^{1}H, 270 MHz probe, and are encouraged by the ease with which this was assembled. The components for the deuterium lock are now on hand and I do not anticipate any problems either there or in the assembly of a heteronuclear decoupler [at first we intend to use

my old (1966 vintage) decoupler]. We shall shortly be exchanging our 1080 computer for an 1180 which, along with a new disk and pulse programmer will complete the update of the data system.

Clearly the successful construction of other probes is a pivotal element in our programme and I intend to write to you again on this topic as soon as I have positive results to report.

One of my reasons for sending you this particular letter is to encourage others who may have a viable pulse F.t. console with a dead or dying electromagnet, to consider replacing their electromagnet with a supercon. Our experiences here are that the upgrading of a console is relatively straightforward and inexpensive, and that the construction of reasonable quality probes presents no insurmountable barrier.

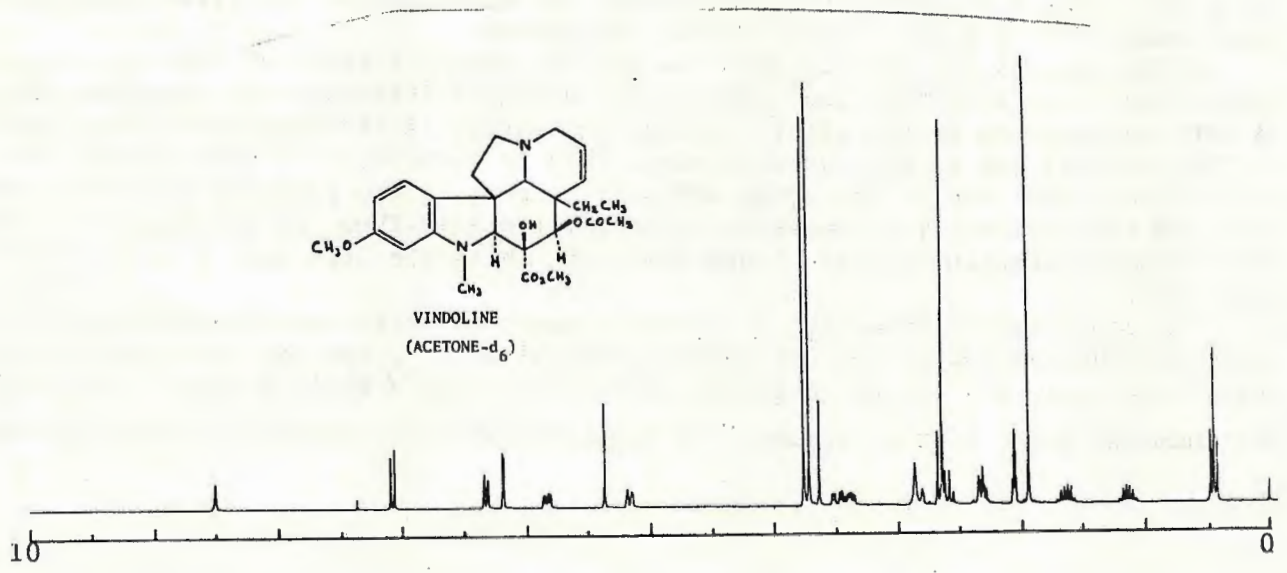
I should end by pointing out that all the electronics design and construction has been carried out by Joe Sallos and Tom Markus of our Departmental Electronics shop. The attached spectrum was run by Laurie Colebrook who is spending his sabbatical from Concordia University in Montreal developing new methods for measuring proton T_1's of complex organic molecules.

With all best regards.

Laurie Colebrook - J. Sallos Tom Markus

Laurie Hall

Laurie Colebrook; Laurie Hall; Tom Markus; Joe Sallos



C. N. R.
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June 20, 1978

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

^{13}C NMR Spectra of Some Phosphonium,Arsonium, Sulfonium and Pyridinium Keto-stabilized Salts and Ylides.[1]

Dear Professor Shapiro:

Over the last years many groups have studied ylides and related salts by ^{13}C NMR Spectroscopy(2,3,4). Most of these investigations involved phosphonium ylides;we have extended these studies to the arsonium, sulfonium and pyridinium keto-stabilized ylides.

The three resonance structures contributing to the noteworthy stability of the carbonyl-substituted ylides are shown:

$$X{=}CH{-}\underset{\displaystyle Ph}{\overset{\displaystyle |}{C}}{=}O \quad (A) \qquad X^{+}{-}\overset{\displaystyle |}{C}H^{-}{-}\underset{\displaystyle Ph}{\overset{\displaystyle |}{C}}{=}O \quad (B) \qquad X^{+}{-}CH{=}\underset{\displaystyle Ph}{\overset{\displaystyle |}{C}}{-}O^{-} \quad (C)$$

X = PH_3P, Ph_3As, Me_2S and $Me_2C_5H_3N$

As the data in the Table show, there is i) a very large increase in the direct C—H and C—P coupling constants in passing from the salt to the ylide, which is consistent with a large increase in the s character of the carbon to hydrogen and carbon to phosphorus bonds ii) the range of the C-1 chemical shifts (50-57 ppm) for P, As and S ylides indicates that this carbon is very strongly shielded in the ylides with respect to conjugated carbanions (120-170 ppm). These results show that a significant negative charge must be localized on the ylide carbon C-1, which thus can be assumed to be sp^2 hybridized with a lone pair of electrons in a p orbital. Resonance structure B therefore best represents the situation of the ylide carbon,although contributions from A and C must also be considered.

In the case of the pyridinium ylide the C-1 chemical shift at 99.0 ppm is more than 40 ppm downfield from the other ylides studied. Therefore the negative charge is not concentrated on the ylidic carbon, but rather is strongly delocalized both to the carbonyl and to the pyridine ring. This is also shown by the upfield shift of C-2 (20.1 ppm) and of the ortho and para carbons of the pyridine ring (12.4 and 14.0 ppm respectively),as compared to the related salt.Thus for the pyridinium ylide the resonance structures A and C are dominant, while the structure B is of lower importance.

The comparison between the different classes of salts and ylides shows: i) in the series of the salts from the C-1 carbon chemical shifts, one may construct an electronegativity scale for the onium groups as follows: $Ph_3P^+ < Ph_3As^+ \ll Me_2S^+ \ll Me_2C_5H_3N^+$.

The chemical shift of the carbonyl C-2 remains basically unchanged through the series of

^{13}C NMR data of some phosphonium, arsonium, sulfonium and pyridinium salts and ylides.

$X - \overset{1}{C} - \overset{2}{CO} - Ph$ (ppm from TMS)

	C-1	C-2	$^1J(C_1-H)$ (Hz)
$Ph_3PCH_2COPh^+Br^-$ [a]	38.8(62.5)	191.4(7.0)	130.0[b]
$Ph_3AsCH_2COPh^+Br^-$	42.6	192.8	135.0[b]
$Me_2SCH_2COPh^+Br^-$	52.7	191.5	144.0
$Me_2C_5H_3NCH_2COPh^+Br^-$	65.0	190.2	-
$Ph_3PCHCOPh$ [a]	50.4(111.7)	184.9(3.0)	164.5[b]
$Ph_3AsCHCOPh$	57.1	181.8	173.5[b]
$Me_2SCHCOPh$	56.0	179.0	178.0
$Me_2C_5H_3NCHCOPh$	99.0	170.0	-

[a] J_{C-P} are in parentheses. [b] Determined for the more soluble compounds: $Ph_2MePCH_2COMe^+Br^-$, $Ph_2MePCHCOMe$, $Ph_3AsCH_2COMe^+Br^-$ and $Ph_3AsCHCOMe$.

the same salts; ii) in the corresponding ylides the mesomeric effects of structures A, B and C add to the inductive effects of the onium groups. Ylide carbon C-1 is deshielded with respect to the salt while carbonyl carbon C-2 is shielded in all the series by a different extent in each series considered.

The different deshielding of the ylide carbon C-1 with respect to the corresponding salt of two series of ylides may be considered as a measure of the different delocalisation of the negative charge from C-1 to the rest of the molecule in the two series. The values reported in the Table show that this delocalization increases in the order: $Me_2S^+ \ll Ph_3P^+ < Ph_3As^+ \ll Me_2C_5H_3N^+$.

The carbonyl C-2 shift difference between ylide and salt can be taken as a measure of the stabilization of the ylide negative charge due to resonance structure C; the Table shows that this stabilization is dependent on the different onium groups, increasing in the order: $Ph_3P^+ < Ph_3As^+ \approx Me_2S^+ < Me_2C_5H_3N^+$.

Sincerely yours

Giovanni Fronza

1) The full paper will be published in J. Organometal. Chem.
2) T.A.Albright, M.D.Gordon, W.J.Freeman and E.E. Schweizer, J.Amer.Chem.Soc., 98 (1976) 6249
3) K.A.O. Starzewski and H.tom Dieck, Phosphorus, 6 (1976) 177
4) P.Froyen and D.G. Morris, Acta Chem. Scandin., B 31 (1977) 256

FACHBEREICH 14 DER UNIVERSITÄT DES SAARLANDES
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Professor Dr. H. Dürr
Universität des Saarlandes 66 Saarbrücken Fachr. 14.1

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

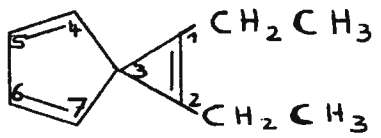
Ihr Zeichen
Ihre Nachricht vom
Unser Zeichen Dü/bi

Saarbrücken, den 23.6.1978

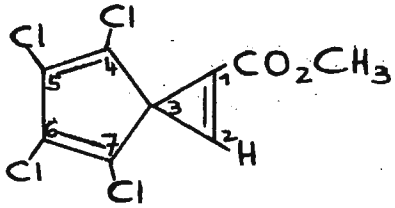
Dear Professor Shapiro!

^{13}C NMR Spectra of [1.2]-Spirenes

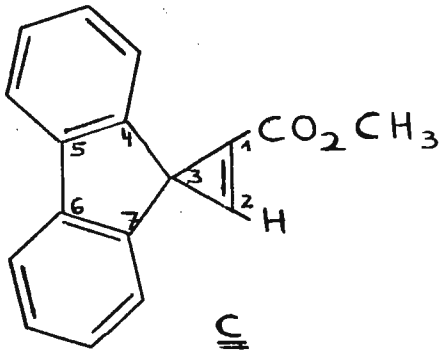
[1.2]-Spirenes 1 are interesting systems which may show spiroconjugation resulting in a change of charge densities [1]. ^{13}C shifts are largely dependent on charge density. Therefore they might serve as a probe for changes of electron density in 1. The ^{13}C shifts of the [1.2]-spirenes 1a-c are compiled in table 1.



1a



b



c

Table 1: ^{13}C shifts of [1.2]-spirenes 1a-c

	δ (C-1)	δ (C-2)	δ (C-3)	δ (C-4/C-7)	δ (C-5/C-6)
1a	118.7 (s)*	118.7 (s)	47.6 (s)	129.1 (d)	139.3 (d)
b	114.7 (s)	118.9 (d)	45.9 (s)	126.6 (s)	131.0 (s)
c	115.1 (s)	121.0 (d)	38.8 (s)	140.2 (s)	146.8 (s)

The C-atoms of the cyclopropene system of 1 show high field shifts. Two resonances in the cyclopentadiene part of 1 are observed: the signal of C-5/C-6 being deshielded whereas the signal of C-4/C-7 is shielded. The electron withdrawing effect of the ester group in 1b and c cannot be seen at the directly substituted C-atom 1, but rather at the neighbouring C-atom 2 showing a downfield shift. The $^{13}C^{1}H$ coupling constants (see table 2) reveal the special bonding situation in the cyclopropene system, too.

Table 2: $^{1}J(^{13}C^{1}H)$ coupling constants [Hz] in [1.2]-spirenes 1a-c

	C-2 - H	C-4/C-7 -H	C-5/C-6 - H
1a	-	166.0	167.0
b	248 [2]	-	-
c	236.8		

The $^{1}J(^{13}C^{1}H)$ values in the cyclopentadiene system vary only slightly by comparison with cyclopentadiene ($^{1}J(^{13}C^{1}H)$ = 170 Hz [3]), the $^{1}J(^{13}C^{1}H)$ coupling constant in the cyclopropene system however is remarkably large. Therefore we conclude from this value a high s-character of the C-H bonds in the three membered ring.

References:

1) a) H.E. Simmons and T. Fukunaga, J.Am.Chem.Soc. 89, 5208 (1967).
b) A. Tajiri and T. Nakajima, Tetrahedron, 27, 6089 (1971).
2) H. Dürr and B. Ruge, Angew. Chem. 84, 215 (1972); Angew. Chem. Intern. Edit. 11, 225 (1972).
3) H. Spiesecke and W.G. Schneider, Tetrahedron Lett. 1961, 468.

Yours sincerely

H. Dürr K.-H. Albert

Professor Dr. H. Dürr Dipl.-Chem. K.-H. Albert

BANGALORE NMR FACILITY

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National Aeronautical Laboratory
Bangalore-560 017

Raman Research Institute
Bangalore-560 006

Tata Institute of Fundamental Research
Bombay-400 005

Ref: NMR/COR/78

Date: June 21, 1978

Prof. C.L.Khetrapal
Mr. P.C. Mathias
Dr. K.V. Ramanathan

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

Operation of Bruker WH-270 in Bangalore:
Preservation of the FT-program against sudden power failures.

-o-

Dear Prof. Shapiro,

After our earlier report in the TAMU-NMR Newsletter, a Bruker WH-270 NMR spectrometer was installed as an inter-institutional facility here in Bangalore. Ever since the installation last year, the instrument is being used extensively not only by scientists of the participating institutions, but also by research workers from all over the country and is operating smoothly round the clock. Our experiences about the performance of this machine have been very encouraging.

However, a problem faced by us here in Bangalore arose from frequent "power-failures" resulting in the loss of the FT-program from the core memory of the computer. In absence of a disc, a "fast-paper-tape-reader" etc., loading the program after each 'power-failure' has been a tedious process, particularly because the mechanical teletype reader has been making errors while reading the program. To overcome this difficulty, we have introduced the following circuit which switches the computer to the STOP mode before the computer power supply decays considerably, as soon as the power failure/fluctuation is sensed. Since no "reading" and "writing" operation is done in the STOP mode, the program in the core does not "fall out".

Since such a problem might be faced by many readers of the TAMU-NMR Newsletter, the circuit (figure 1) may be useful. The circuit senses the absolute line voltage as well as the transient fluctuations. The secondary voltage (proportional to the line voltage) is rectified and compared

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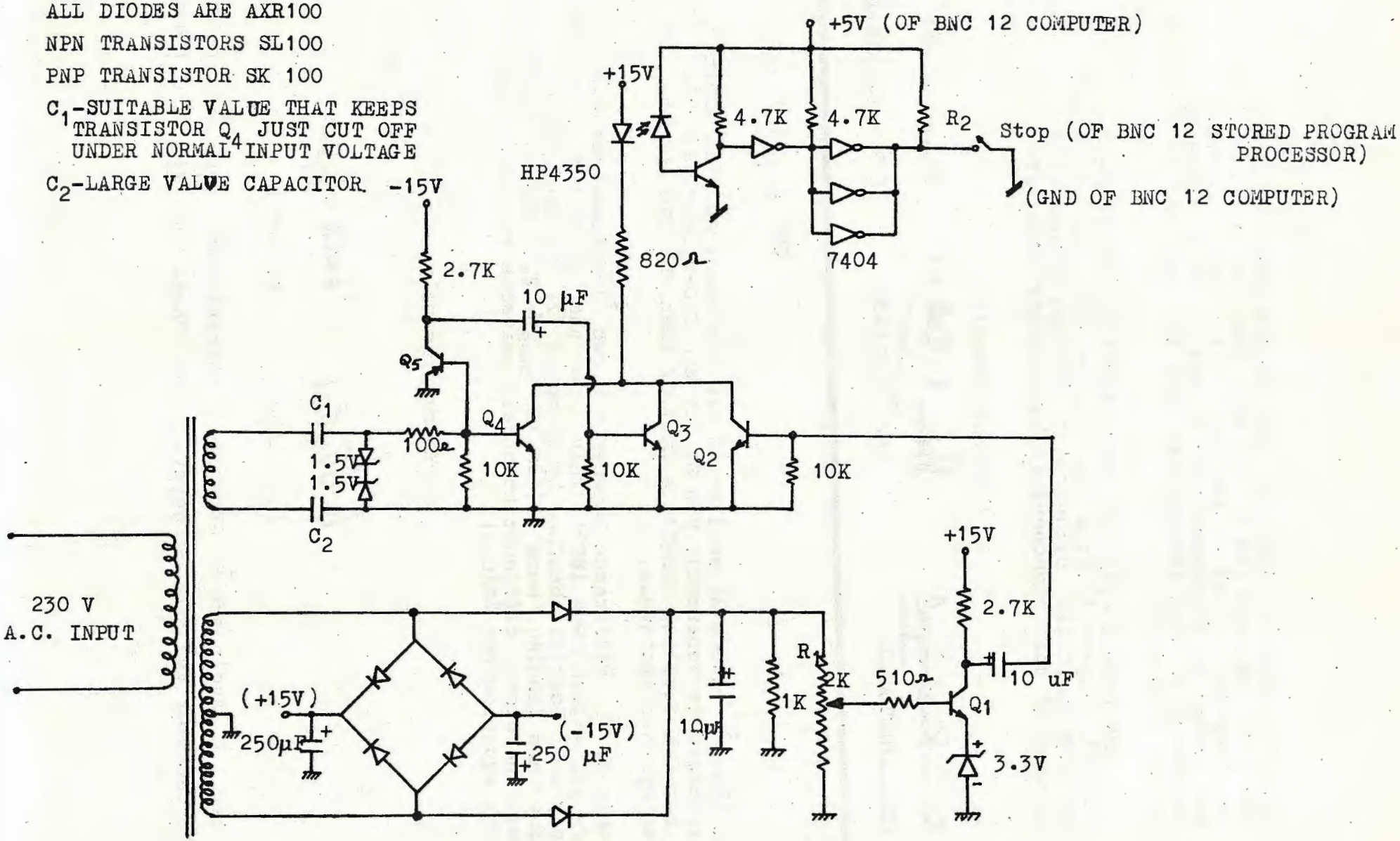
C_1-SUITABLE VALUE THAT KEEPS TRANSISTOR Q_4 JUST CUT OFF UNDER NORMAL INPUT VOLTAGE

C_2-LARGE VALUE CAPACITOR



(Fig.1)

with the Zener voltage Z_1; when this becomes less than the zener voltage (as is the case when the power fails) the computer is put in the STOP mode. The transients are sensed by the capacitors C_1 and C_2 which offer low impedance to high frequencies and the computer is switched to the STOP mode.

The opto couple (HP 4350) isolates the detector circuit (figure 1) from the computer side just to avoid the responsibility being put on the introduced circuit in case of some component failure in the computer.

Yours sincerely,

C.L. Khetrapal (C.L. KHETRAPAL)

P.C. Mathias (P.C. MATHIAS)

K.V. Ramanathan (K.V. RAMANATHAN)

CONT'D. FROM P. 238-28

We note that ^3J gauche as well as ^4J are not resolved. The limit for resolution is apparently 0.5 Hz for the C,D-splitting. This means that C,H coupling constants smaller than 3Hz can not be measured by this technique.

Remarkable is the difference between the two ^3J-values that are both $^3J_{trans}$-values ($\Theta = 180^o$). This shows that substitution effects are important. Results obtained by Sergeyev [2] for cyclohexane underline this finding. Here $^3J(^{13}C,^1H)_{tans} = 8{,}12$ Hz was reported. It seems, therefore, difficult to obtain suitable values to derive a Karplus equation for $^3J(C,H)$.

Yours sincerely,

H. Günther

R. Aydin

[1] H. Seel, R. Aydin and H. Günther, Z. Naturforsch. 33b, 353 (1978).

[2] V.A. Chertkov and N.M. Sergeyev, J. Am. Chem. Soc. 99, 6750 (1977).

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Fachbereich 8, Organische Chemie II
Prof. Dr. H. Günther

5900 Siegen 21, den 23 June 1978
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Gesamthochschule Siegen, Postfach 21 02 09, 5900 Siegen 21

Prof. Bernard L. Shapiro
Texas A&M University
College of Science
Department of Chemistry
College Station
Texas 77843 - USA

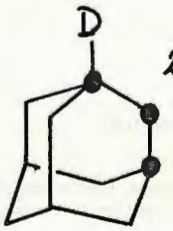
New Address - Position available - C,D coupling in Adamantane

Dear Barry,

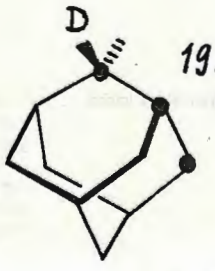
as you note from above, our group has moved to a new university and we are just starting to get our different projects on the road again.

At the moment I would like to announce the open position for a postdoctoral fellow, organic or physical chemist having basis experience in nmr. The contract runs for 1 year and may be extended. Salary approximately DM 3300.- monthly. Work includes participation in several nmr projects dealing with $^{13}C,^{1}H$ coupling constants, valence isomerization, and nmr of "other" nuclei. Applications should include two references.

As for our research, in connection with the program of measuring C,H-couplings from highly deuterated systems (for latest results see our work on naphthalene[1]) we were interested to derive $^{3}J(^{13}C,^{1}H)$ values in saturated systems for specific dihedral angles. Adamantane seemed a suitable candidate and, from synthetic considerations, it was worth-while to investigate the possibility of measuring C,D-couplings for the mono-substituted systems. The following results were obtained (^{13}C, ^{1}H-coupling obtained by multiplication with γ_H/γ_D = 6,5144 in brackets):



20.14 (131.21)
(-) 0.57 (-3.71)
0.85 (5.57)



19.32 (125.86)
(-) 0.50 (-3.26)
1.10 (7.17)

Cont'd. bottom of p. 238-27.

238-29

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BRUKER SPECTROSPIN (CANADA) LTD.

June 29, 1978

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

TITLE: POSTDOCTORAL POSITION AVAILABLE

Dear Professor Shapiro,

As a result of expansion within this branch of the Bruker group of companies, we wish to make a postdoctoral position available beginning in September or October this year.

We are equipped with a 'fully-loaded' WP-80 Spectrometer and will add a similarly equipped WP-200 in October. There will be a certain amount of routine work involved in terms of running customer samples. However, since the spectrometers are not always occupied, the position should appeal to those who wish to persue an independent line of research in a commercial environment and remain free from the fetters of a teaching load.

The position is open to NMR spectroscopists of any persuasion and will be initially for one year. There is a very real possibility that the position would be made permanent after that time.

Interested candidates should contact me in writing at the above address.

Sincerely yours,

BRUKER SPECTROSPIN (CANADA) LTD.

Martin Smith

Dr. Martin A. R. Smith
Product Manager

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DEPARTMENT OF CHEMISTRY, B-014
LA JOLLA, CALIFORNIA 92093

June 21, 1978

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

Re: Protected Homo-oligopeptide ^{1}H NMR Assignments by a "Guest-Host" Procedure

Dear Professor Shapiro:

The conformations of linear homo-oligopeptides are of interest for understanding the processes of helix and β sheet formation.[1] In solution, infrared, laser Raman and circular dichroism studies can indicate the presence of helical or β-like structures, but high resolution ^{1}H NMR studies are needed to investigate specific interactions along the homo-oligopeptide chain. Critical to the NMR studies are the resolution and unequivocal assignments of the individual NH and α-CH resonances of each homo-oligopeptide residue.

Professor Murray Goodman and I in collaboration with Professor Fred Naider (City University of New York) have recently observed the 220 MHz ^{1}H NMR spectrum of a protected linear hexamethionine, Boc-Met$_6$-OMe, at 1.9 x 10^{-3} M in $CDCl_3$ (Fig. 1). Six individual NH doublets and a 2:1:2:1 α-CH resonance pattern in the upfield direction are resolved. The upfield NH and α-CH couple to each other and can be assigned to the N-terminal residue, as the urethane linkage (ROCOHNR) causes upfield shifts from normal peptide linkages (ROCHNR). Homonuclear decoupling reveals that in general a more shielded α-CH couples to a more deshielded NH as shown in the table. However the decoupling experiments do not yield assignments and further information is necessary.

Assignments for the α-CH peaks of water-soluble homo-oligopeptides can be obtained by pH titrations,[2] use of lanthanide reagents[3] and substitution with isotopes such as deuterium.[4] The first two methods do not seem viable for protected homo-oligopeptides in organic solvents, and the third requires extensive synthetic efforts with expensive isotopically enriched amino acids to obtain assignments for a single homo-oligopeptide. As an alternative, we propose that the label included in the "host" homo-oligopeptide chain need not be an isotopically enriched amino acid in every case but merely a "guest" amino acid with a different side chain. To obtain assignments for Boc-Met$_6$-OMe, we chose glycine as a "guest" and synthesized the six co-oligopeptides with one glycine and five methionine residues. The NMR spectra for 1 x 10^{-3} M solutions of Boc-Met$_6$-OMe and the six co-oligopeptides are compared in Fig. 2A-G. The glycine NH as a triplet and the glycine α-CH_2 at ~3.9 ppm are clearly distinguished from methionine residues in most cases. The methionine resonances of the co-oligopeptides (Fig. 2A-F) are less than 0.1 ppm different in shift from the methionine resonances of the homo-oligopeptide (Fig. 2G). Arrows are placed in Fig. 2 to indicate the methionine NH and α-CH resonance missing in each co-oligopeptide. Each pair of missing resonances are precisely those coupled to each other in the homo-oligopeptide. Thus the six co-oligopeptides together give unequivocal assignments for Boc-Met$_6$-OMe in 99% $CDCl_3$/1% DMSO-d_6. Extrapolation of chemical shift data at various amounts of DMSO-d_6 to $CDCl_3$ yields the assignments in $CDCl_3$ given in the table.

The assignments for the di- to hepta-peptide are available in a recent publication.[5] We close with the remark that protected homo-oligopeptides are often only soluble in weakly interacting media like $CDCl_3$ in the 10^{-3} - 10^{-5} M range. Thus ^1H NMR data on these compounds require extensive efforts on NMR time averaging.

Sincerely,

Anthony Ribeiro

Anthony Ribeiro

1. F. Naider and M. Goodman in "Bioorganic Chemistry Volume III: Macro- and Multimolecular Systems" Academic Press, New York, 1977, pp 177-199.

2. M. Sheinblatt, J. Amer. Chem. Soc., 88, 2845 (1966).

3. M. Anteunis and J. Gelan, J. Amer. Chem. Soc., 95, 6502 (1973).

4. A. Nakamura and O. Jardetzky, Biochemistry, 1, 1226 (1968).

5. A.A. Ribeiro, M. Goodman and F. Naider, J. Amer. Chem. Soc, 100, 3903 (1978).

TABLE I

^1H NMR Assignments for Boc-Met_6-OMe in $CDCl_3$ (A)

α-CH	4.08	4.26	4.29	4.44	4.61	4.66
Coupled NH	5.52	7.90	7.70	7.40	7.16	7.09
Residue Assignment	Met^1	Met^2	Met^3	Met^4	Met^5	Met^6

(A) Chemical Shifts (δ) in PPM Downfield from TMS

FIGURE 1.

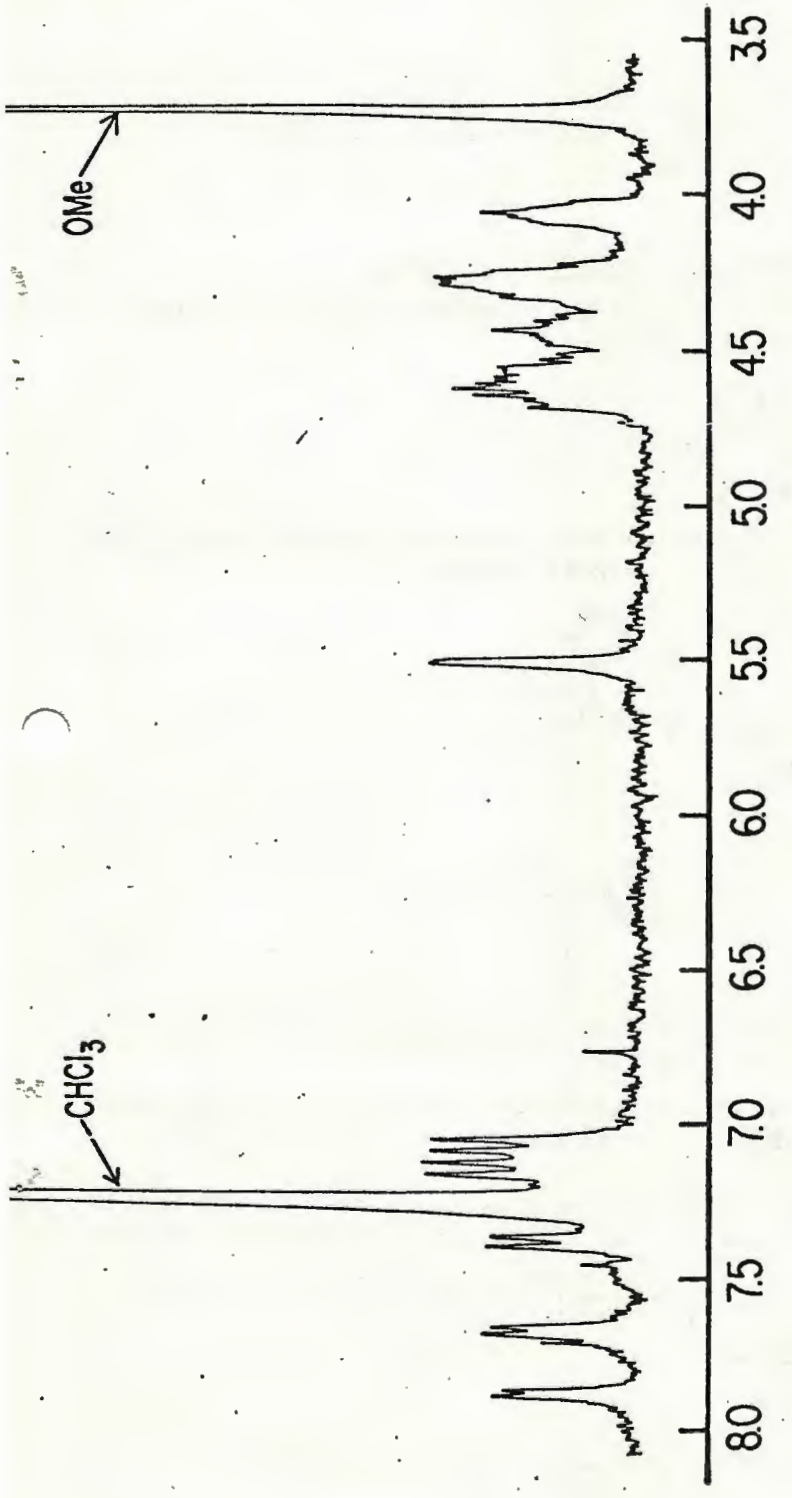
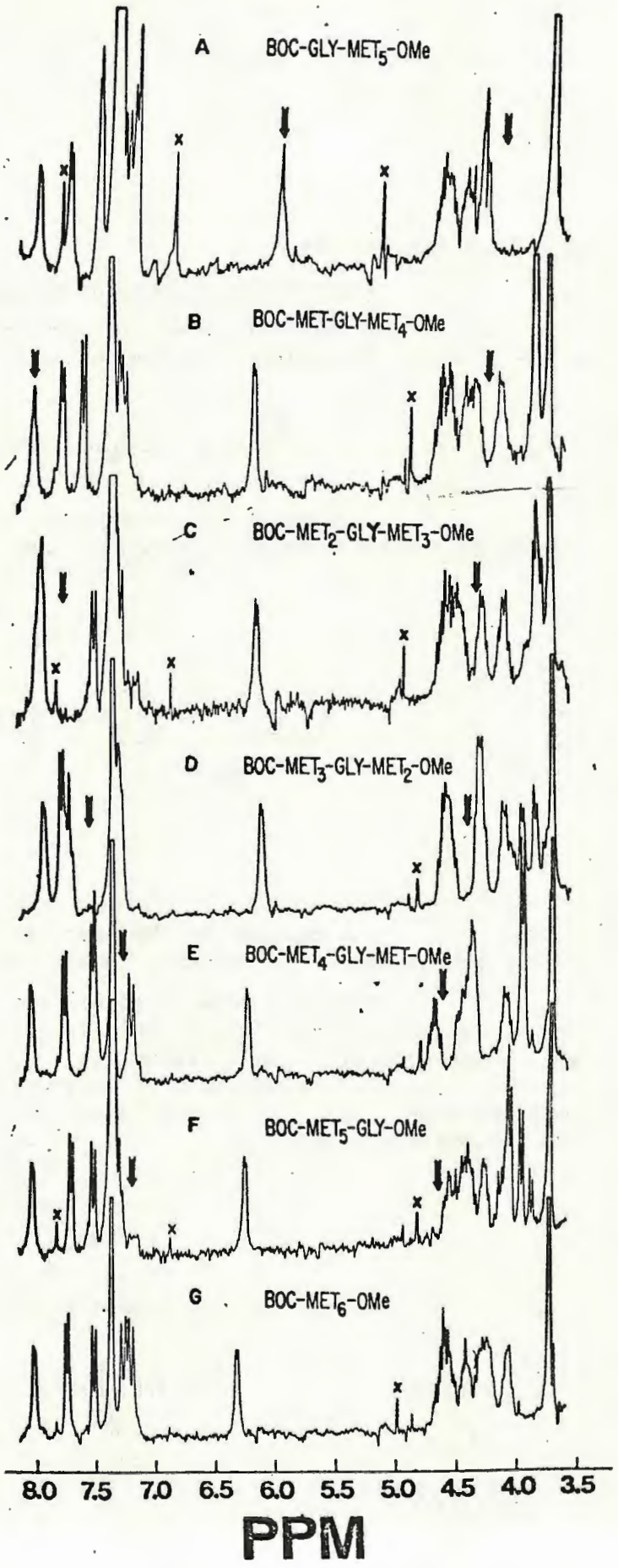


FIGURE 2.



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FACULTÉ DES SCIENCES ET TECHNIQUES DE SAINT-JÉROME

Laboratoire des Organométalliques
J. C. MAIRE, Professeur.

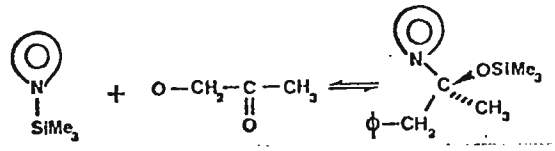
26th june, 1978

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

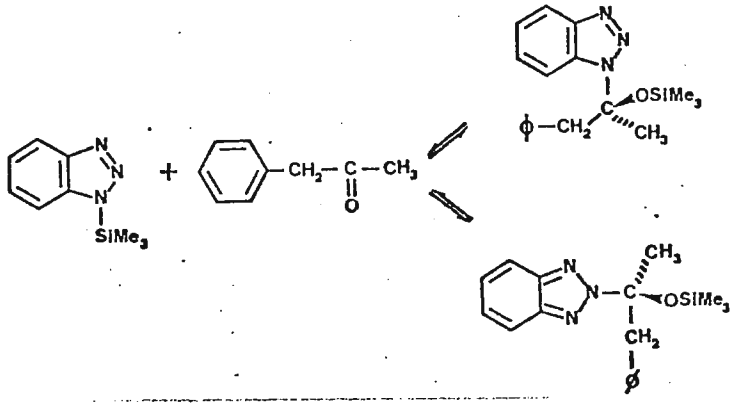
Dear Professor Shapiro,

Addition of 1-trimethylsilylazole on methylbenzylketone

We have shown earlier that N-trimethylsilylazoles were giving, at room temperature, a reversible addition with methylbenzylketone.



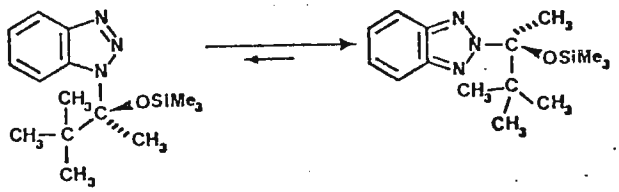
Starting with 1-trimethylsilylazole, we obtained two different addition compounds corresponding to nitrogens 1 and 2 of the benzotriazole.



One can see on the spectra 1 and 2 the benzylic CH_2 of the addition compounds are giving on AB system - (Assignements are given on spectrum 2).

Usually, isomers of benzotriazole substitued on nitrogen 2 are not observed on equilibrium conditions. This is probably coming from a strong steric hindrance of the isomer substitued on position 1.

In the way to give a proof, we tried the same experience with the pinacolone. We hoped, in that case, a larger steric hindrance leading to a predominant nitrogen 2 substitued isomer.

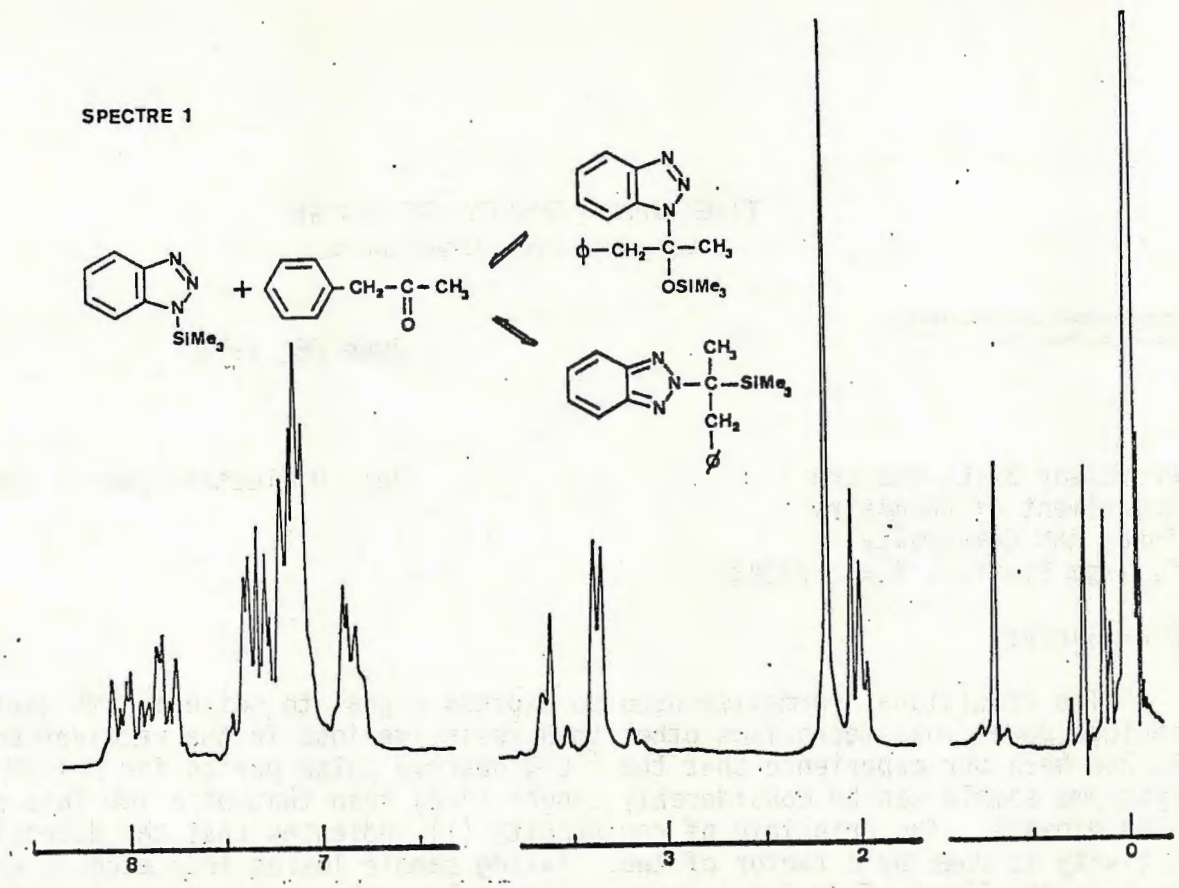


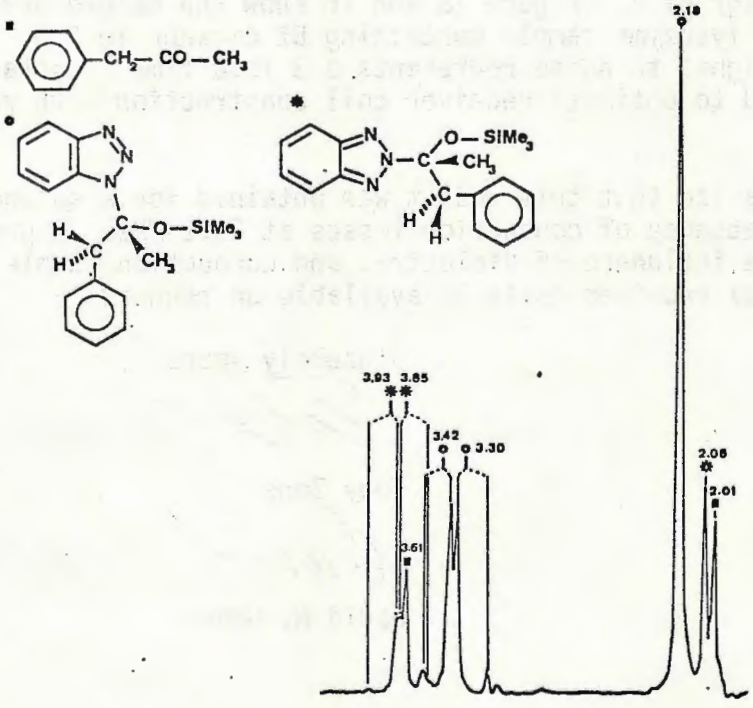
Unfortunately, with that ketone, we did not observe any addition.

Yours sincerely,

J.C. MAIRE J.P. GASPARINI R. GASSEND

SPECTRE 1





SPECTRE 2

THE UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH 84112

DEPARTMENT OF CHEMISTRY
CHEMISTRY BUILDING

June 26, 1978

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

Re: Dielectric sample loss

Dear Barry:

The traditional formalism used to express signal to noise in NMR does not include power loss mechanisms other than resistive loss in the receiver coil. It has been our experience that the ^{13}C $\frac{\pi}{2}$ observe pulse period for a 4 mM HEW lysozyme sample can be considerably longer ($\approx$ 2) than that of a low loss sample like dioxane. The principle of reciprocity (1) indicates that the detection sensitivity is down by a factor of two. Taking sample losses into account we find that in the limit of dominance by dielectric loss the signal to noise ratio is dependent on the inductance of the receiver coil ($S/N \propto L^{-\frac{1}{2}}$).

In order to increase the detection sensitivity of our house built 22 mm probe system (236-6) on high dielectric loss samples we have reduced the inductance of the receiver coil by a factor of 4. Figure 1a and 1b show the before and after results obtained on a 4 mM lysozyme sample containing 8% dioxane in D_2O. The dramatic increase in ^{13}C signal to noise represents a 3 fold time advantage and clearly emphasizes the need to optimize receiver coil construction with respect to samples.

We would like to emphasize that this result was obtained for a solenoidal receiver coil system in the absence of conduction losses at 25.2 MHz. A preprint of this work describing the influence of dielectric and conduction sample loss for solenoidal and Helmholtz receiver coils is available on request.

Sincerely yours,

Toby Zens

Toby Zens

David M. Grant

David M. Grant

1. D. I. Hoult and R. E. Richards, J. Magn. Resonance, 24, 71 (1976).

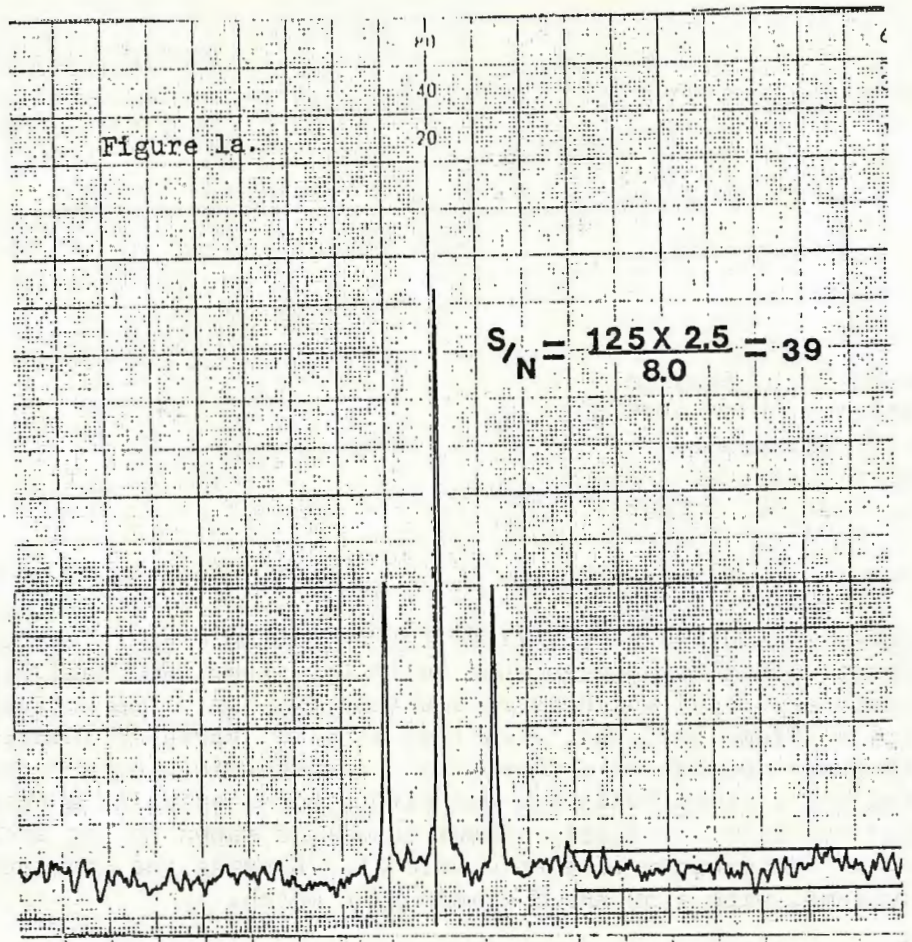


Figure 1a.

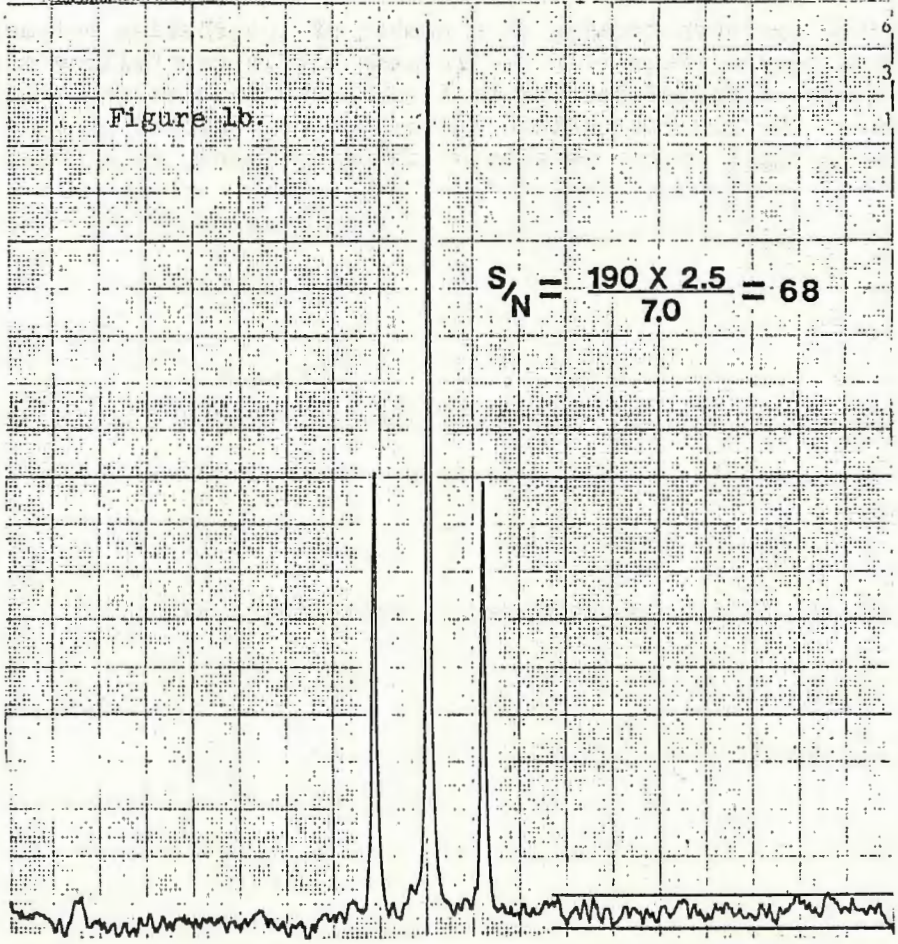


Figure 1b.

IBM

RESEARCH LABORATORY

International Business Machines Corporation

5600 Cottle Road
San Jose, California 95193

June 27, 1978

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

Dear Barry:

We started developing a capability for doing magic angle spinning experiments about a year ago when Colin Fyfe from the Chemistry Department at Guelph was here on sabbatical. The prime motivation was chemical applications, and, with that in mind, variable temperature operation was considered a necessity. A commercial instrument was modified and a probe built for use with a novel spinning apparatus designed by Colin. A fairly recent result is shown in the enclosed figure, a ^{13}C spectrum of acetic acid at 77K using the standard PENIS scheme, with a 50 kHz Hartmann-Hahn match.

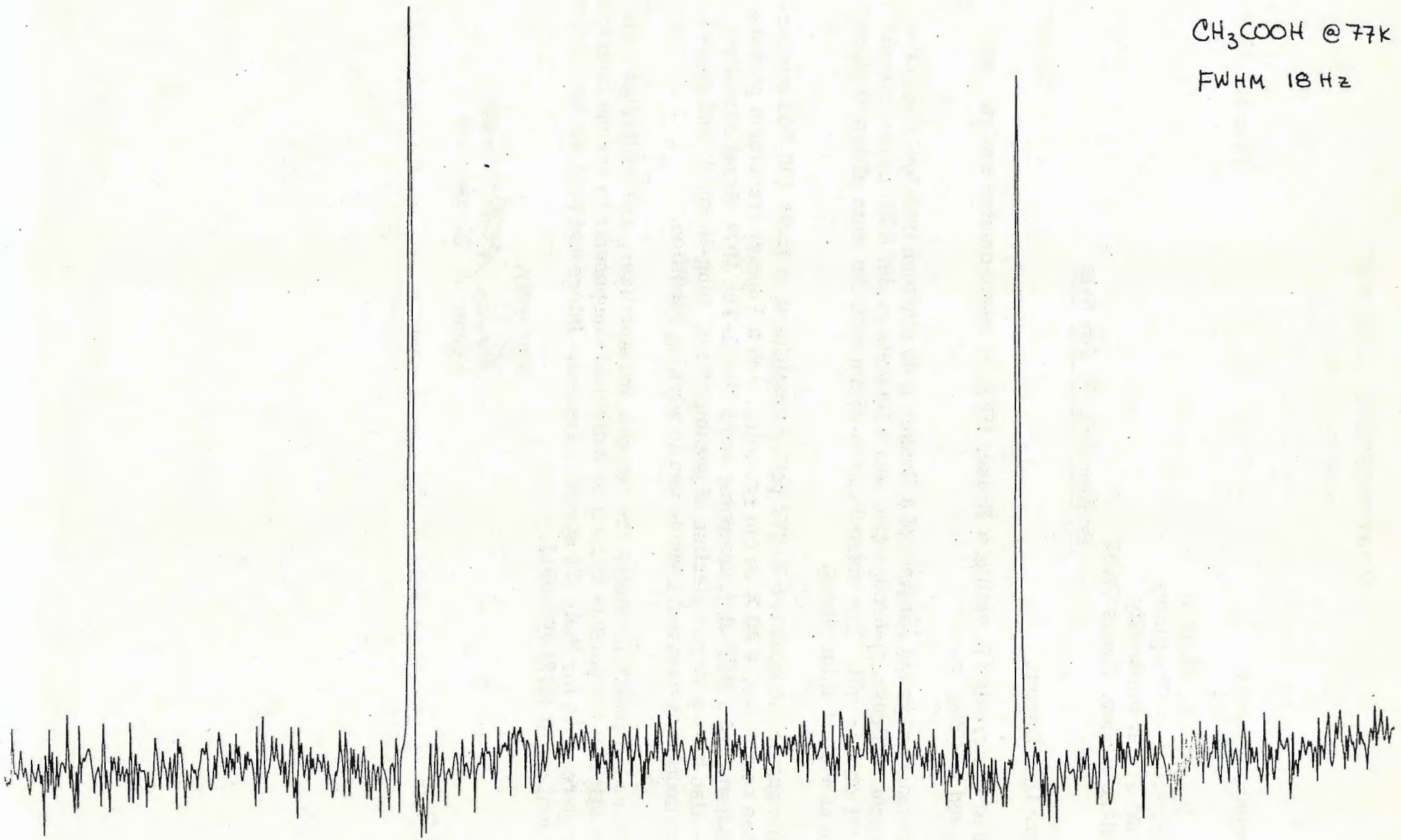
Jim Lyerla has been looking at a number of interesting polymer problems, achieving narrow lines (<10 Hz) in some highly crystalline materials. We have also obtained results in fluxional molecules and charge transfer complexes. We plan to publish the results of initial studies on these systems, as well as the details of the experiment, in a month or so.

Best regards,

C. S. Yannoni

/aj
Enclousre

Short Title: Low Temperature Magic Angle Spinning



238-40

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY

June 15, 1978

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

Bruker HFX-90 For Sale

Dear Dr. Shapiro,

We are interested in selling a Bruker HFX-90 spectrometer system, purchased in 1968.

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We are interested in selling the magnet, prestabilizer, and chiller as a unit. We will sell the console system or individual components to anyone interested in spare parts for their HX system consoles. Interested persons should write or call me at (312) 492-5514.

Sincerely,

Kenner A. Christensen

Kenner A. Christensen

KAC:cs

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DEPARTMENT OF CHEMISTRY DAVIS, CALIFORNIA 95616

June 8, 1978

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

NMR Spectroscopist Position Open

Dear Barry;

The University of California, Davis, will have an opening for an NMR spectroscopist for our new biological Magnetic Resonance Facility, as described below.

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In compliance with federal and state laws and University policy, the University of California does not discriminate on the basis of race, color, national origin, religion, sex, handicap, age, or against disabled veterans or veterans of the Vietnam era. The University of California is an affirmative action/equal opportunity employer.

Sincerely yours,

Gerd

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

GNL:jkg

University of Houston
Central Campus
Houston, Texas 77004

Department of Chemistry
713/749-2612

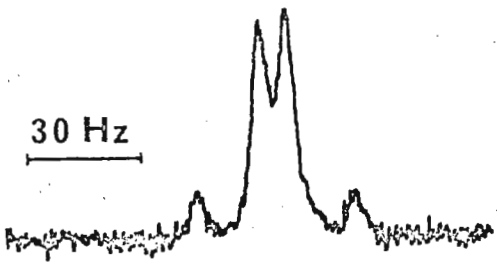
June 19, 1978

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

Dear Barry:

This letter is intended to introduce and illustrate the idea of chiral aqueous lanthanide shift reagents.

As is well known the lanthanide ions in aqueous solution form complexes of higher than 1:1 stoichiometry. With bidentate chiral ligands the 1:1 complex will be chiral and, provided the second ligand binds with a given stereochemical preference, will provide not only a chiral environment for the second ligand but, by virtue of the anisotropic magnetic susceptibility of the central ion, also the means of observing the chiral interaction in the shifted NMR spectrum. In this way it is possible to resolve the spectra of enantiomeric mixtures as well as of enantiotopic protons of α-hydroxycarboxylates. The latter possibility, which seems to be more spectacular, is illustrated by the 100 MHz spectrum of 20 mM glycolate ($HOCH_2COO^-$) taken in the presence of 130 mM L-lactate ($CH_3CHOHCOO^-$) and 50 mM Pr Cl_3. Originally a singlet, the spectrum is now an AB quartet, i.e. the enantiotopic protons have become diastereotopic. I should emphasize that these phenomena were observed under conditions of rapid ligand exchange relative to the chemical shift difference between complexed and uncomplexed ligands.



Sincerely,

Jacques

Jacques Reuben,
Associate Professor
of Chemistry

JR/ecj

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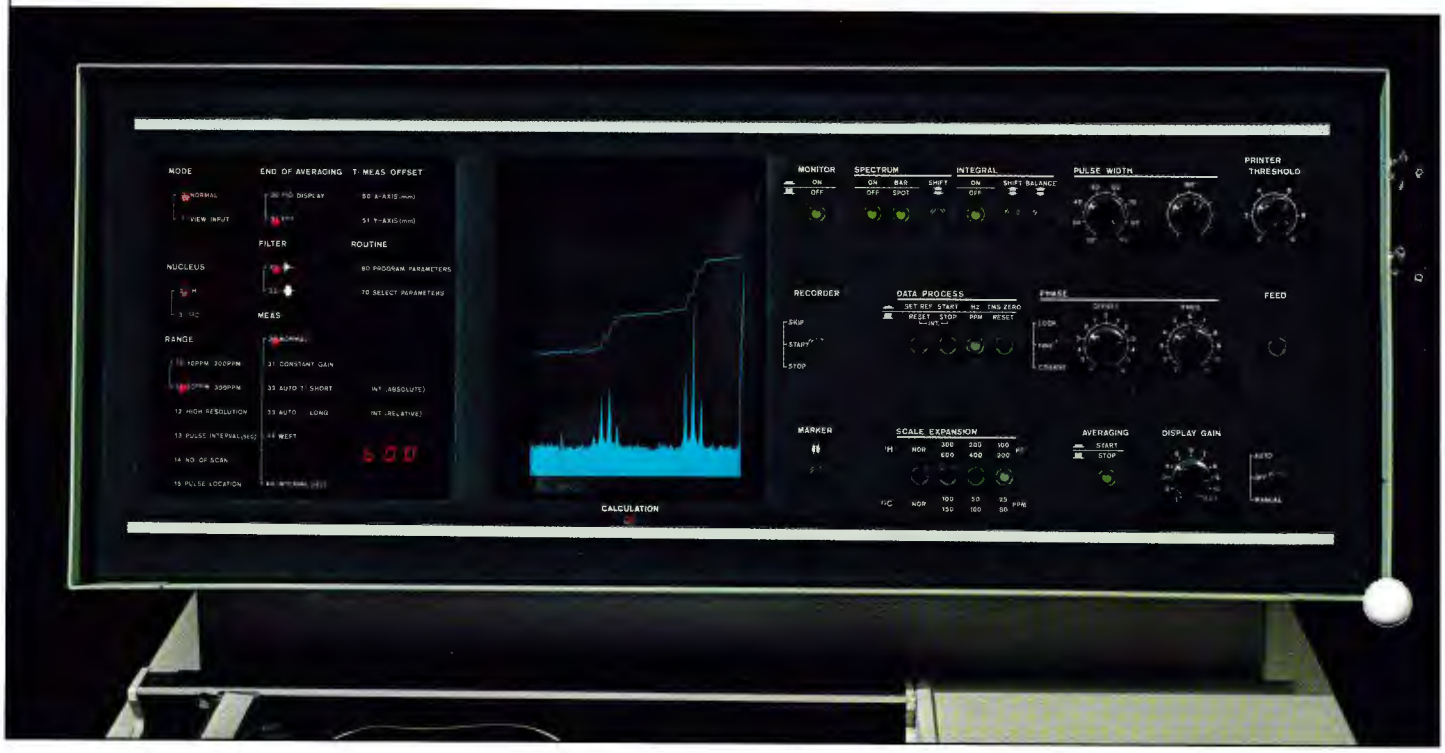

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University of Illinois at Urbana-Champaign

School of Chemical Sciences

Urbana, Illinois 61801

June 20, 1978

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

Title: Automated T_2 Runs

Dear Barry:

In connection with our T_2 experiments on chloroplast membranes, we have made simple additions to automate our home built pulsed NMR spectrometer. When the CPMG echoes are milliseconds apart but the complete train of echoes last few seconds, the averager is synchronized to sample a data point at the top of each echo and the data reduction procedure has been pretty well optimized.

The train of 180° pulses from the CPMG sequence itself is used as an external time base with an appropriate delay to acquire a data point at the top of each echo in the signal averager. A PDP-8f computer is interfaced to the signal averager and using the "FNEW" user function feature of "FOCAL" conversational language, a simple assembly language program is written to read the data from the signal averager. Since we use only a Low Speed Reader to read the "FOCAL" paper tape, the machine routine to transfer the data from the signal averager is put in the place of High Speed Reader. A program in "Focal" conversational language is written for the least-squares analysis of the data to extract T_2.

The "FNEW" user function routine of "FOCAL" with pre-selected arguments is particularly useful to start the averager, and/or, to read the data points, and/or, to stop the averager as and when it is required in the conversational program used for data manipulation. Details are available upon request.

Sincerely yours,

S. Rajan

H. S. Gutowsky

McMASTER UNIVERSITY
Department of Biochemistry

HEALTH SCIENCES CENTRE,
1200 MAIN STREET WEST,
HAMILTON, ONTARIO, CANADA.
L8S 4J9
TEL. (416) 525-9140 EXT. 2457

June 20, 1978

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

Spectral subtraction of the complementary pentaribonucleotides CpApApUpG and CpApUpUpG

Dear Dr. Shapiro:

During the course of our work on the effect of terminal dangling or unpaired bases on the stability of the helical duplex formed by CpApUpG (1) we also examined the complementary sequences CpApApUpG and CpApUpUpG in order to compare any stabilization provided by a dangling base relative to an additional internal A·U base pair. One aspect of this work reported here was the methodology used in determining the chemical shifts of the base protons in the spectrum of the mixture of the two pentaribonucleotides and is illustrated by the sequence CpApApUpG.

The base protons of the individual sequences CAAUG and CAUUG were assigned by comparison to the data on CAUG (2) (Table 1). When these complementary pentanucleotides were mixed and the spectrum recorded at 70°C (Fig. 1a) the purine base protons displayed chemical shifts which were nearly identical to those of the single strands. However, the pyrimidine H-6 signals could not be assigned directly because of the overlap of these resonances. This problem was overcome by computer subtraction of the separate pentanucleotide spectra from that of the mixture as shown in Fig. 1a-c. This technique also allowed the complete assignment of the pyrimidine H-5 and ribose anomeric protons. Spectral subtraction of mixtures of complementary oligonucleotides is limited to only the high temperature spectra since the interstrand base pairing is at a minimum.

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

D. Hughes
D.W. Hughes
Dept. of Chemistry

P Romaniuk
P.J. Romaniuk
Dept. of Biochemistry

R. Grégoire
R.J. Grégoire
Dept. of Biochemistry

Dr. B.L. Shapiro June 20, 1978

1. P.J. Romaniuk, D.W. Hughes, R.J. Grégoire, T. Neilson and R.A. Bell, J. Am. Chem. Soc. 100, 3971 (1978).

2. D.W. Hughes and P.J. Romaniuk, TAMU-NMR Newletters 229, 39 (1977); P.J. Romaniuk, T. Neilson, D.W. Hughes and R.A. Bell, Can. J. Chem. In press.

TABLE 1 Chemical shifts obtained in neutral D_2O containing 1.0 M NaCl at 70°C (Concentration: 1.1×10^{-2}M)

Proton	CAUG	CAAUG	12345 CAAUG GUUAC
C(1)H-6	7.662	7.623	7.630
A(2)H-8	8.346	8.268	8.274
A(2)H-2	8.196	8.134	8.141
A(3)H-8		8.255	8.261
A(3)H-2		8.079	8.089
U(4)H-6	7.692	7.654	7.661
G(5)H-8	7.962	7.942	7.945

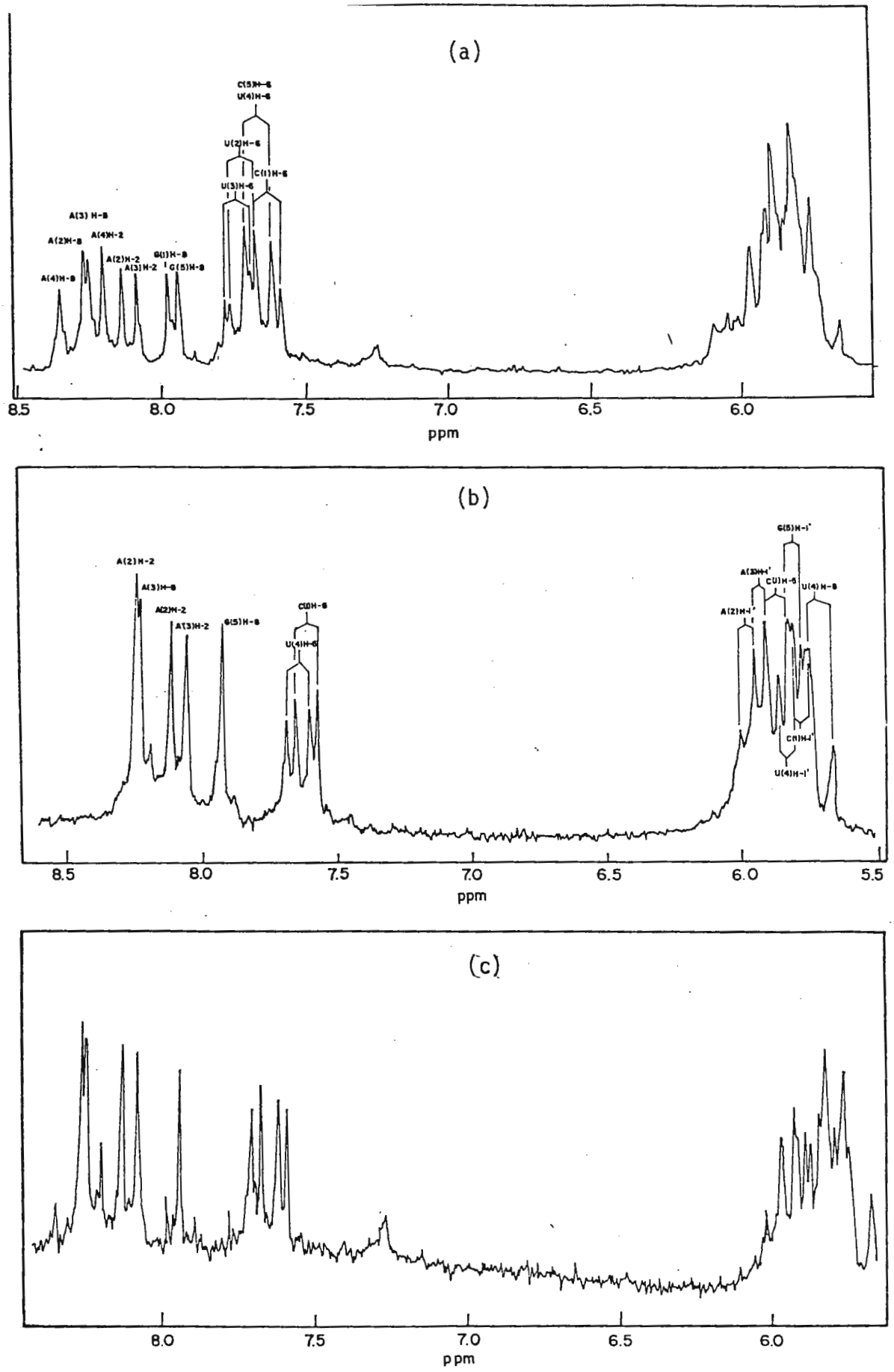


FIGURE 1 (a) 90 MHz spectrum of the mixture of CAAUG and CAUUG at 70°C.
(b) Spectrum of CAAUG at 70°C.
(c) Difference spectrum of CAAUG obtained by subtraction of the spectrum of CAUUG from that of the mixture.

National Research Council Canada
Conseil national de recherches Canada

Division of Chemistry
Division de chimie

File Référence

June 21, 1978

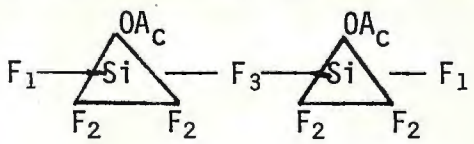
Prof. B.L. Shapiro
Dept. of Chemistry
Texas A and M University
College Station, Texas 77843
U.S.A.

Dear Barry,

More Unusual Fluoride Complexes

From a knowledge of substituent effects upon boron-fluorine coupling constants (1) we propose that the 1:1 complex of BF_3 and CN^- has the structure $CN\text{-}BF_3^-$ and the 2:1 complex is $F_3B\text{-}CN\text{-}BF_3^-$. The chemical shift in the former is -127.5 with $J_{B-F} = 26.8$. The nitrogen coordinated BF_3 of the 2:1 complex has $\delta = -130.1$ and $J_{B-F} = 24.4$; the carbon coordinated BF_3 has $\delta = -136.1$ with no resolvable spin coupling. In the spectrum A is the 1:1 complex, B and C arise from the 2:1 complex and D from BF_4^-.

The following fluorine bridged silicon species is formed in the reaction of a slight excess of SiF_4 with tetramethylammonium acetate.



$J_{1-2} = 18$ $J_{1-3} = 0$ $J_{2-3} = 52$

$\delta_1 = -128.1$ $\delta_2 = -123.9$ $\delta_3 = -84.6$

The broadened lines in the spectrum are from $SiF_6^=$ and $SiF_4OA_c^-$ which are exchanging rapidly with a little excess SiF_4.

Best wishes,

S. Brownstein

(1) J.S. Hartman and J.M. Miller, Inorg. Chem. 13, 1467 (1974).

SB/dh

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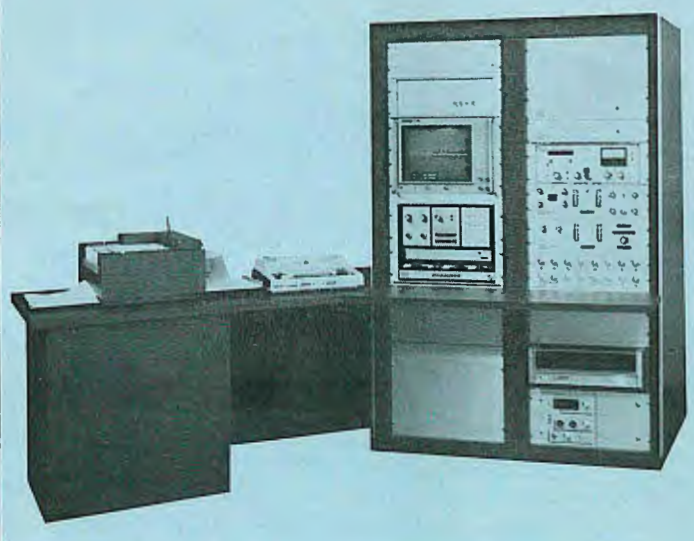
NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET



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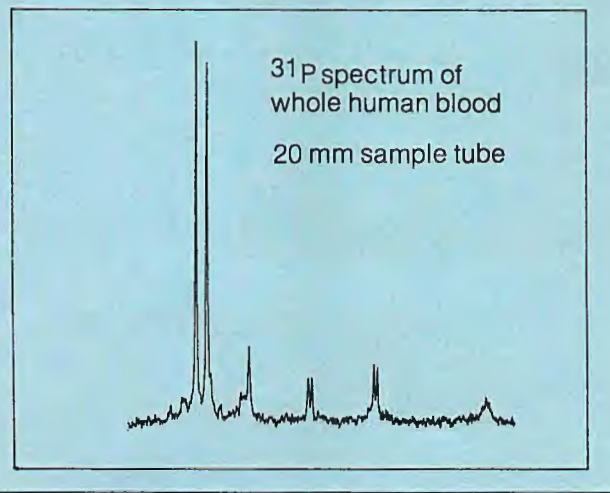

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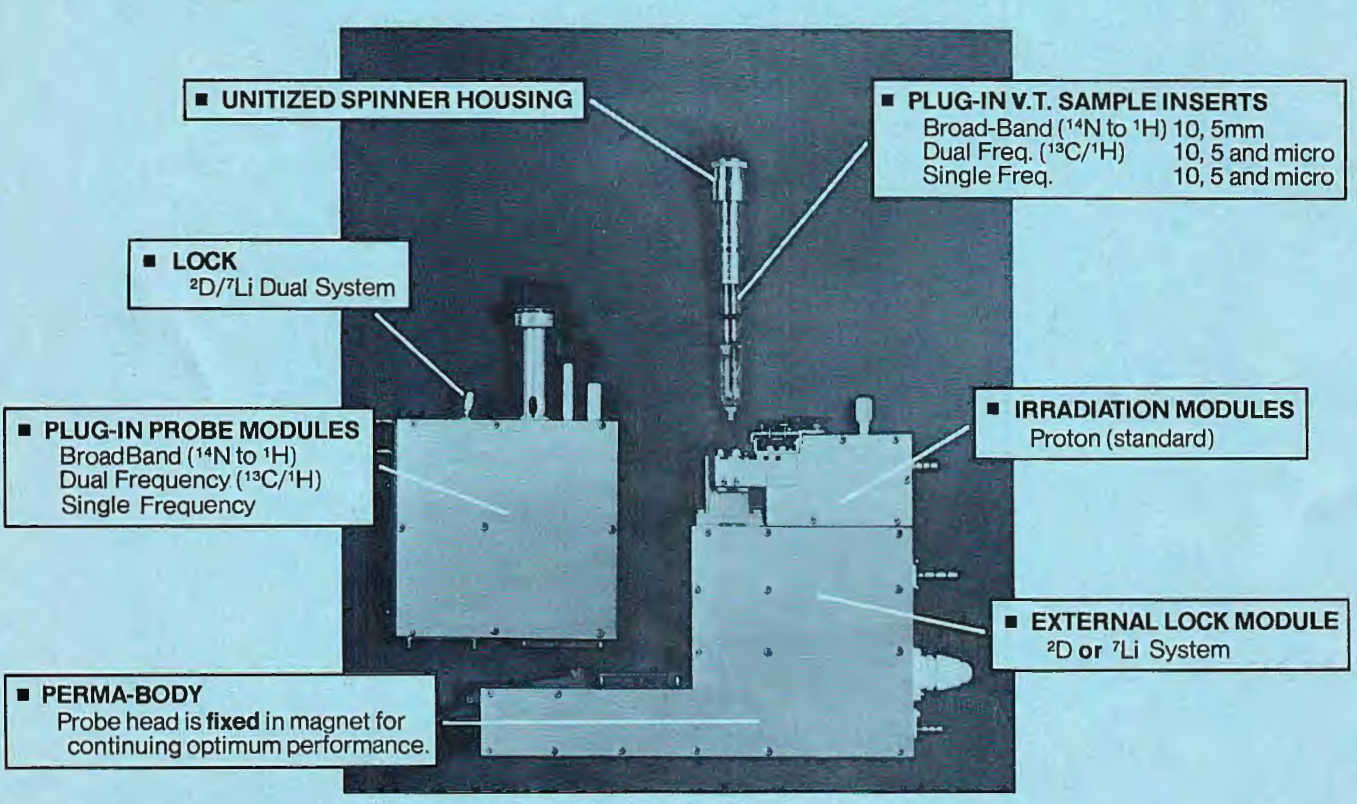

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