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"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 Kaptein

P.S. Please credit this contribution to the account of Dr. W.D. Weringa
**Fig. 1**

RNase A, 1.5 mM in D$_2$O

- light
- dark
- light–dark

**Fig. 2**

RNase, 1.5 mM in D$_2$O, pH = 7.0

- RNase A
- RNase A, CIDNP
- RNase S, CIDNP
- RNase A + 2'-CMP
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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 course further information on all aspects of the conference. Contact: Association of British Spectroscopists, P.O. Box 109, Cambridge CB1 2HY, United Kingdom.

With best regards,

Yours sincerely

Per Ahlberg and Carin Engdahl
Dear Dr. Shapiro,

We wish to communicate results on the subject:
"Transfer of $^{13}\text{C}$ 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 °C as shown by band shape temperature dependence of some of its $^1\text{H}$ n.m.r. bands.\(^2\) However, due to its broad and nonstructured bands, the temperature dependence is not easy to interpret and therefore we turned to $^{13}\text{C}$ n.m.r. which yields a simple spectrum of I when the protons are de­coupled.

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

An extra $^{13}\text{C}$-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 °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 an intensity drop of the 2,8- and 4,6-singletts to about half their size before saturation.
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 methyl groups 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 $^{13}\text{C}$ 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°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 $^{13}\text{C}$ 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


Cont'd. bottom of p. 238-4.
MICROPROCESSOR INTERFACING BETWEEN A TELETYPE AND THE C 1024 TIME AVERAGING COMPUTER

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 teletype printing. Microprocessor use provides an elegant solution to perform such functions.

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 multiplexer 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 preceding section three operating signals C₀, C₁, C₂ must be employed: C₀ to monitor the advance of the CAT and the simultaneous multiplexer channel choice, C₁ to control the NDRO, and C₂ 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

Fig. 4a) Control signals C₁, C₂ for the CAT are shifted from TTL levels to (-3V, 0V) logical levels, through transistors Q₁₇ and Q₁₈ (2N 2907). The logical output levels (-12V, 0V) of bits from pins 10 to 25 of P₁ are shifted to TTL levels through transistors Q₁ to Q₁₆ (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. 4b) 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 C₀ is also used as the address advance control.
June 6, 1978

Dear Barry:

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

![Propyl cation](image)

Although we have not yet obtained really satisfactory spectra, its proton spectrum (-38°C in CD$_3$CN) 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 3,3'-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 \(\pi\)-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 \(\pi\)-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 \(\pi\)-system.

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

Sincerely,

Dennis J. Sardella
Associate Professor

---

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
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 NTCPT program itself. In this regard, the designers of NTCPT 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 6008 (≈40010) 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 NTCPT 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 30008 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,
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.

\[ \begin{align*}
\text{3. } & J_{P-N-C-C_3} = 18.0 \\
\text{4. } & J_{P-N-C-C_3} = 4.6 \\
\text{5. } & J_{P-N-C-C_3} = 16.2
\end{align*} \]
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 attenuated in 2 vs. 4. Low temperature experiments on 2 give no evidence of a chair conformer with an axial P(0) (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-N-C$_2$-C$_3$ of ca 120°. Recent work of Thiem and Meyer (2) indicates that for a dihedral angle of 120° in phosphonates, $^3J_{P-C}$ would be ca 4 Hz, 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 $^{15}N$-$^{31}P$ 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
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 'H (200 MHz) and 13C (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 wish list:

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- 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.

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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 Lasslo (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 Binsch
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 KMnO4 in H2O, which was enriched in 18O to 99 % (1). Meanwhile we could observe the exchange rate of 18O between the water and MnO4− ion for about two years at room temperature. The sample is now reaching the final state 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 18O and 16O contents of the sample. Continuing our investigations of isotope effects in anions oxygen and sulfur induced isotope effects in the 95Mo NMR spectra of MoO42− and MoS42− could be observed (1,2). A few months ago we succeeded in detecting a very small oxygen isotope effect of 31P in the phosphate ion (3). We used a sample, of K3PO4 in D2O. The PO43− ion was enriched in 18O 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

Fig. 1: $^{55}$Mn FT NMR signal at 22.311 MHz in a 0.27 molal solution of KMnO$_4$ in H$_2$O (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$^{13}$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$_3$PO$_4$ in D$_2$O, measured with a high-solution probe and with an internal $^2$H-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
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 T1's of complex organic molecules.

With all best regards.

Laurie Colebrook; Laurie Hall; Tom Markus; Joe Sallos
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:

\[ \text{X} = \text{CH} - \text{C} = \text{O} \quad (A) \]
\[ \text{X}^+ - \text{CH}^- - \text{C} = \text{O} \quad (B) \]
\[ \text{X}^+ - \text{CH} \equiv \text{C} - \text{O}^- \quad (C) \]

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 theonium groups as follows: Ph$_3$P$^+$ < Ph$_3$As$^+$ < Me$_2$S$^+$ < Me$_2$C$_2$H$_5$N$^+$. The chemical shift of the carbonyl C-2 remains basically unchanged through the series of
The full paper will be published in J. Organometal. Chem.
3) K. A. O. Starzewski and H. Tom Dieck, Phosphorus, 6 (1976) 177

Sincerely yours

Giovanni Franza
Dear Professor Shapiro,

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

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

![Chemical structures: 1a, 1b, 1c]

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

<table>
<thead>
<tr>
<th></th>
<th>$\delta$ (C-1)</th>
<th>$\delta$ (C-2)</th>
<th>$\delta$ (C-3)</th>
<th>$\delta$ (C-4/C-7)</th>
<th>$\delta$ (C-5/C-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>118.7 (s)*</td>
<td>118.7 (s)</td>
<td>47.6 (s)</td>
<td>129.1 (d)</td>
<td>139.3 (d)</td>
</tr>
<tr>
<td>1b</td>
<td>114.7 (s)</td>
<td>118.9 (d)</td>
<td>45.9 (s)</td>
<td>126.6 (s)</td>
<td>131.0 (s)</td>
</tr>
<tr>
<td>1c</td>
<td>115.1 (s)</td>
<td>121.0 (d)</td>
<td>38.8 (s)</td>
<td>140.2 (s)</td>
<td>146.8 (s)</td>
</tr>
</tbody>
</table>
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 13C-1H coupling constants (see table 2) reveal the special bonding situation in the cyclopropene system, too.

Table 2: 1J(13C-1H) coupling constants [Hz] in [1,2]-spirenes 1a-c

<table>
<thead>
<tr>
<th></th>
<th>C-2 - H</th>
<th>C-4/C-7 - H</th>
<th>C-5/C-6 - H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-</td>
<td>166.0</td>
<td>167.0</td>
</tr>
<tr>
<td>1b</td>
<td>248.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1c</td>
<td>236.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 1J(13C-1H) values in the cyclopentadiene system vary only slightly by comparison with cyclopentadiene (1J(13C-1H) = 170 Hz 3), the 1J(13C-1H) 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:

Yours sincerely

Professor Dr. H. Dürr  Dipl.-Chem. K.-H. Albert
Operation of Bruker WH-270 in Bangalore: Preservation of the FT-program against sudden power failures.

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
ALL DIODES ARE AXR100
NPN TRANSISTORS SL100
PNP TRANSISTOR SK 100

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

$C_2$ - LARGE VALUE CAPACITOR, $-15V$

$R_2$ - STOP (OF BNC 12 STORED PROGRAM
PROCESSOR)
(GND OF BNC 12 COMPUTER)

230 V
A.C. INPUT

(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. Khetrparal (P.C.MATHIAS) (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 ($\Theta = 180^0$). This shows that substitution effects
are important. Results obtained by Sergeyev [2] for cyclohexane
underline this finding. Here $^3J(13C,1H)$ $\tan \theta = 8,12$ 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

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 basic 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 $^{13}C,^1H$ 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 $3\gamma(13C,^1H)$ 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 ($^{13}C, ^1H$-coupling obtained by multiplication with $\gamma_H/\gamma_D = 6.5144$ in brackets):

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

Dr. Martin A. R. Smith
Product Manager

MARS/df

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Phone (415) 493-3173

2410 Dunwin Drive, Unit 4  
Mississauga, Ontario, Canada, L5L 1J9  
Phone (416) 625-2374
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 \(\beta\) sheet formation. In solution, infrared, laser Raman and circular dichroism studies can indicate the presence of helical or \(\beta\)-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 \(\alpha\)-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\(_5\)-Ome, at \(1.9 \times 10^{-3}\) M in CDCl\(_3\) (Fig. 1). Six individual NH doublets and a 2:1:2:1 \(\alpha\)-CH resonance pattern in the upfield direction are resolved. The upfield NH and \(\alpha\)-CH couple to each other and can be assigned to the N-terminal residue, as the urethane linkage (ROC0HNR) causes upfield shifts from normal peptide linkages (ROCHNR). Homonuclear decoupling reveals that in general a more shielded \(\alpha\)-CH couples to a more deshielded NH as shown in the table.

Assignments for the \(\alpha\)-CH peaks of water-soluble homo-oligopeptides can be obtained by pH titrations, use of lanthanide reagents and substitution with isotopes such as deuterium. 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\(_5\)-Ome, we chose glycine as a "guest" and synthesized the six co-oligopeptides with one glycine and five methionine residues. The NMR spectra for \(1 \times 10^{-3}\) M solutions of Boc-Met\(_5\)-Ome and the six co-oligopeptides are compared in Fig. 2A-G. The glycine NH as a triplet and the glycine \(\alpha\)-CH at \(\approx 3.9\) 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 \(\alpha\)-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\(_5\)-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. We close with the remark that protected homo-oligopeptides are often only soluble in weakly interacting media like CDCl₃ 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


**TABLE I**

<table>
<thead>
<tr>
<th>Chemical Shifts (δ) in ppm downfield from TMS</th>
<th>Met₁</th>
<th>Met₂</th>
<th>Met₃</th>
<th>Met₄</th>
<th>Met₅</th>
<th>Met₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CH</td>
<td>4.08</td>
<td>4.26</td>
<td>4.29</td>
<td>4.44</td>
<td>4.61</td>
<td>4.66</td>
</tr>
<tr>
<td>Coupled NH</td>
<td>5.52</td>
<td>7.90</td>
<td>7.70</td>
<td>7.40</td>
<td>7.16</td>
<td>7.09</td>
</tr>
<tr>
<td>Residue Assignment</td>
<td>Met₁</td>
<td>Met₂</td>
<td>Met₃</td>
<td>Met₄</td>
<td>Met₅</td>
<td>Met₆</td>
</tr>
</tbody>
</table>
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 substituted on nitrogen 2 are not observed on equilibrium conditions. This is probably coming from a strong steric hindrance of the isomer substituted 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 substituted isomer.

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

Yours sincerely,

J.C. MAIRE

J.P. GASPARINI

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

June 26, 1978  

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 NMR 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$_2$O. 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  
David M. Grant  

Figure la.

\[ S'_{N} = \frac{125 \times 2.5}{8.0} = 39 \]

Figure lb.

\[ S'_{N} = \frac{190 \times 2.5}{7.0} = 68 \]
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

Short Title: Low Temperature Magic Angle Spinning
June 15, 1978

Bruker HFX-90 For Sale

Dear Dr. Shapiro,

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

The magnet system consists of a Bruker E 40 eighteen inch low impedance magnet, a Bruker prestabilizer, and a Haskris model R200 closed circuit water chiller unit. The magnet gap is 25mm with the shim plates in place, 30mm without shim plates.

The console includes two B-SV2 power amplifiers, a B-ST 100/700 temperature controller, a 60 X 30 cm recorder, and a Fourier transform package consisting of a PDP-8/L computer and a Fabri-Tek 1074 signal averager. We also have a large selection of preamplifiers, plug-in units, and probes. The magnet system and console are in working condition.

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

KAC:cs
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.

NMR Spectroscopist

Assistant or Associate Research NMR Spectroscopist to supervise new Biological Magnetic Resonance Laboratory consisting of 200 MHz and 360 MHz Multinuclear FTNMR Spectrometers. Candidate must show strong evidence for productive research, as position involves advising and collaborating with biological science faculty as well as pursuing independent research. Responsibilities also include spectrometer maintenance and development, supervising one or more technicians as well as training and scheduling users. Ph.D. in Chemistry or equivalent degree, thorough background in FTNMR and hardware/software experience essential; some experience in biological FTNMR application highly desirable. Salary $17,500-$20,500, depending upon qualifications and experience. Send curriculum vitae, bibliography and three letters of reference to Professor G.N. La Mar, Department of Chemistry, University of Calif­ornia, Davis, CA 95616. The final date of application for the position will be July 17, 1978.

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 N. La Mar
Professor of Chemistry
Co-director, UCD Biological Magnetic Resonance Facility
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 (HOCH₂COO⁻) taken in the presence of 130 mM L-lactate (CH₃CH(OH)COO⁻) and 50 mM PrCl₃. 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 Reuben,
Associate Professor of Chemistry
The R-600 control panel is simple to operate, easy to understand.
Perkin-Elmer's Model R-600 is a high-performance, low-cost instrument for routine proton observation at 60 MHz. It's the first commercially available NMR spectrometer with a dedicated digital microcomputer that doesn't require a computer expert. The R-600 utilizes the proven R-24 Series magnet system. And because it's a permanent magnet NMR, there are no special requirements for water or power. Just plug it in.

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With superb sensitivity, the R-600 lets you run routine experiments on a small scale. Your sample requirements drop from milligram sizes to 500 micrograms or less. But you'll still get the same quality spectra.

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Not only is the microcomputer easy to operate, it also does most of the work. And the R-600 is the first FT NMR with controls arranged for operation like a conventional continuous wave instrument. Programming was designed by an NMR spectroscopist, so operational parameters and commands are user oriented. With just ten keys, the control panel simplifies setting the operating conditions and readout of the measurements.

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---

**PERKIN-ELMER**
Expanding the world of analytical chemistry
June 20, 1978

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

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.W. Hughes
Dept. of Chemistry

P.J. Romanuk
Dept. of Biochemistry

R.J. Gregoire
Dept. of Biochemistry


### TABLE 1

<table>
<thead>
<tr>
<th>Proton</th>
<th>CAUG</th>
<th>CAAUG</th>
<th>GUUC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(l)H-6</td>
<td>7.662</td>
<td>7.623</td>
<td>7.630</td>
</tr>
<tr>
<td>A(2)H-8</td>
<td>8.346</td>
<td>8.268</td>
<td>8.274</td>
</tr>
<tr>
<td>A(2)H-2</td>
<td>8.196</td>
<td>8.134</td>
<td>8.141</td>
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<td>A(3)H-8</td>
<td>8.255</td>
<td>8.255</td>
<td>8.261</td>
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<td>A(3)H-2</td>
<td>8.079</td>
<td>8.079</td>
<td>8.089</td>
</tr>
<tr>
<td>U(4)H-6</td>
<td>7.692</td>
<td>7.654</td>
<td>7.661</td>
</tr>
<tr>
<td>G(5)H-8</td>
<td>7.962</td>
<td>7.942</td>
<td>7.945</td>
</tr>
</tbody>
</table>

Chemical shifts obtained in neutral D₂O containing 1.0 M NaCl at 70°C (Concentration: 1.1 x 10⁻₂M)
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.
More Unusual Fluoride Complexes

From a knowledge of substituent effects upon boron-fluorine coupling constants (1) we propose that the 1:1 complex of BF₃ and CN⁻ has the structure CN-BF₃⁻ and the 2:1 complex is F₃BF-CN-BF₃⁻. The chemical shift in the former is -127.5 with J₈ = 26.8. The nitrogen coordinated BF₃ of the 2:1 complex has δ = -130.1 and J₈ = 24.4; the carbon coordinated BF₃ has δ = -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 BF₄⁻.

The following fluorine bridged silicon species is formed in the reaction of a slight excess of SiF₄ with tetramethylammonium acetate.

\[ \text{J}_{1-2} = 18 \quad \text{J}_{1-3} = 0 \quad \text{J}_{2-3} = 52 \]
\[ \delta_1 = -128.1 \quad \delta_2 = -123.9 \quad \delta_3 = -84.6 \]

The broadened lines in the spectrum are from SiF₆²⁻ and SiF₄OAc⁻ which are exchanging rapidly with a little excess SiF₄⁻.

Best wishes,

S. Brownstein

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