

NMR

NEWSLETTER

NO. 327

DECEMBER 1985

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FORTHCOMING NMR MEETINGS (Additional listings are solicited)

British Radiofrequency Spectroscopy Group - April 9-11, 1986; Oxford University, Oxford OX1 3QR England; see Newsletter No. 323, p. 23.

27th ENC - April 13-17, 1986; Hilton Hotel, Baltimore, Maryland; see Newsletter No. 323, p. 31.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

XII International Conference on Magnetic Resonance in Biological Systems - September 8-12, 1986; Todtmoos, West Germany; see page 34.

1986 Eastern Analytical Symposium - October 6-10, 1986; Hilton Hotel, New York; see Newsletter No. 325, p. 27.

Suggestions for other types of articles, news items, etc., to appear in the Newsletter would be welcomed. Please make your wishes known.

All Newsletter Correspondence
 Should be Addressed to:

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

DEADLINE DATES

No. 329 (February) ---- 24 January 1986

No. 330 (March) ----- 28 February 1986

**ABBOTT**

Abbott Laboratories
Abbott Park, Illinois 60064

October 9, 1985

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

NMR Lab Automation

Dear Professor Shapiro:

NMR laboratory automation is used at Abbott to increase the throughput and response time of the lab. The NMR lab has four superconducting NMR spectrometers, a Nicolet NT-360, a General Electric QE-300 with an auto-sampler, a GN-300 and a GN-500, and a VAX 11/780 computer.

The VAX 11/780 is used for data processing and data archiving. The data are transferred from each of the spectrometers via a VAX program written at Abbott which emulates the transfer protocol of the spectrometers. Each spectrometer supports background transfer of data through a serial RS-232 port at a transfer rate of 9.6 kbaud. Two programs are used on the VAX to process the data: 1D spectra are processed with NMR1 (New Methods Research, Syracuse NY) and 2D spectra are processed with FTNMR (Dennis Hare, Seattle WA). The data are saved with a data management system called "ARCHIVER" (Strategic Information, Burlington MA).

The VAX programs written at Abbott are in FORTRAN. The programs are controlled through VMS command procedures and queue managers. The system of programs and command procedures perform the following functions: 1) schedule the transfer of data from each spectrometer, 2) transfer the data to the VAX, 3) convert the data from spectrometer format to application program format (NMR1 or FTNMR), 4) enter the sample label and spectral parameters in the data base and 5) archive the raw data to magnetic tape.

DATA TRANSFER. Each spectrometer is connected with a direct line to the VAX. The direct lines are managed as separate queues, each with a job limit of one. This allows multiple file transfer from a given spectrometer initiated by several users with no conflict for access. The data are transferred from the spectrometer to the VAX one file at a time, and stored on the VAX as a direct image of the data transferred.

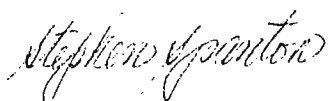
a

DATA CONVERSION. Conversion of the data on the VAX to application program format is performed by a separate program. The data are stored as an image of the spectrometer data since any new programs will have to support raw spectrometer data conversion and therefore will also be able to reprocess any of the archived data. A separate file of parameters is also generated by the conversion program because FTNMR does not support any parameter reporting.

DATA ARCHIVING. A data base is maintained that allows for the generation of an unique sample identification and file name for each spectrum. Each spectrum is entered into the data base automatically. The parameters stored with the spectrum (comment, date run, experiment, observed nucleus, spectrometer name, etc) are decoded and entered into the data base. The raw data are then archived, including the unique sample identification generated above and the comment that was entered at the spectrometer console at the time the spectrum was acquired.

The use of the VAX computer as a data processing computer has greatly increased the productivity of the NMR lab. The automatic tracking and archiving of the sample data has substantially reduced the clerical overhead of routine NMR.

Sincerely yours,



Stephen Spanton, Ph.D.
Abbott Laboratories
Department 417, AP9
Abbott Park, IL 60064

SS:dmh



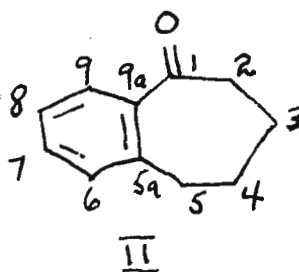
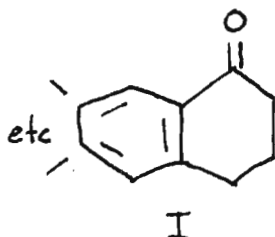
Carleton University
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October 22, 1985.

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

Title: "¹³C Signal Assignments in Polycyclic Aromatic Ketones
Via CCC2D Experiments"

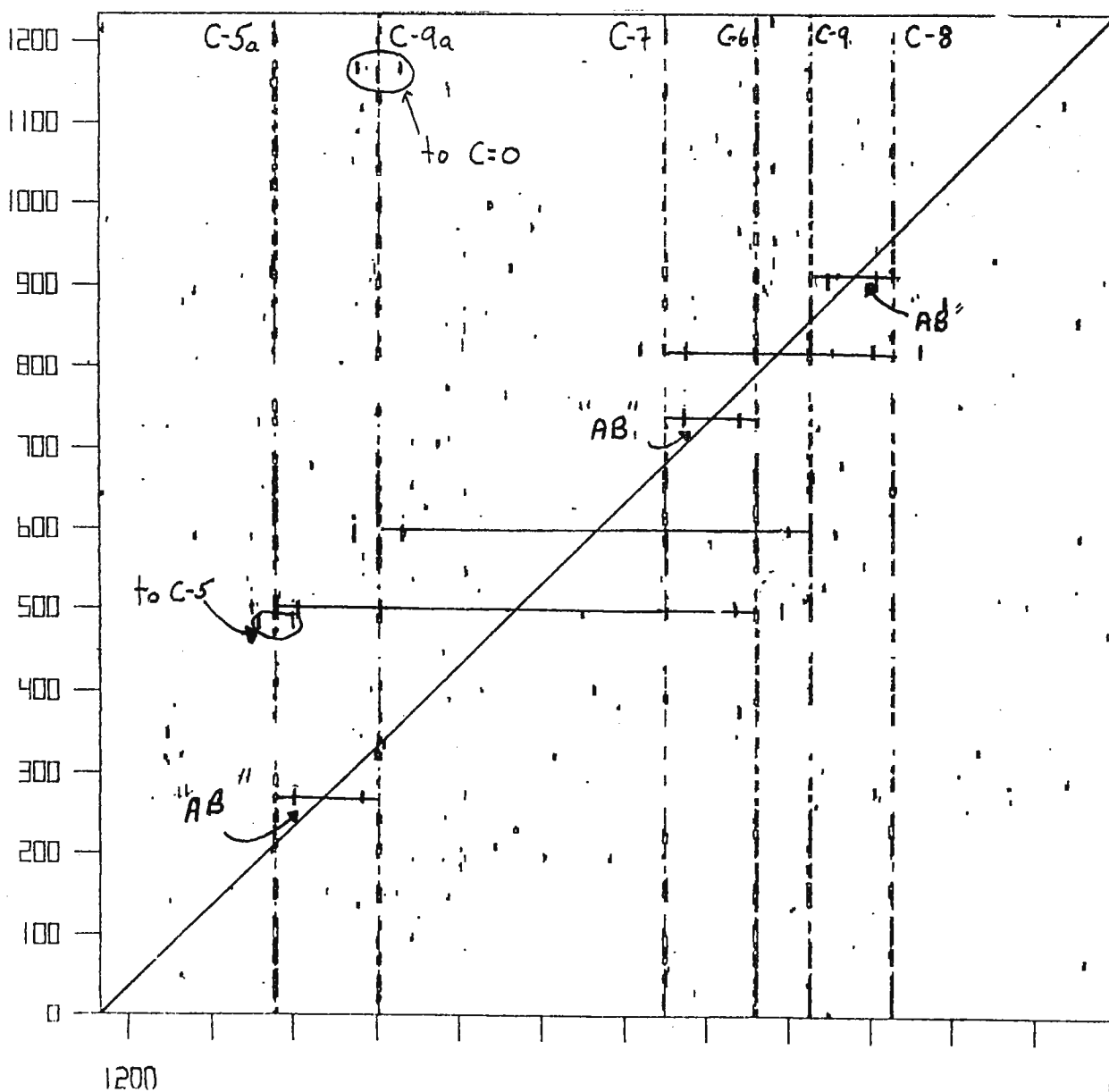
For the past several years, we have been collaborating with Prof. R.H. Wightman of this department with a view to the complete analysis of the ¹³C spectra of his synthetic polycyclic aromatic systems.^(1,2) Recently we have begun to examine tricyclic α -tetralone (I) and benzosuberone II derivatives which are either linearly or angularly benz-annulated.



Survey of the existing literature for the parent compounds I and II indicated no general agreement regarding the ¹³C resonance assignments despite the use of such exotic techniques such as CIDNP.⁽³⁾ It turns out that the CCC2D experiment works very well for these materials and the results for the aromatic region of benzosuberone are included here.

References

1. G.W. Buchanan and R.H. Wightman. Can. J. Chem. 51 2357 (1973).
2. G.W. Buchanan, R.H. Wightman and M.E. Isabelle. Org. Mag. Res. 16 156 (1981).
3. H.M. Maurer and J. Bargon. Org. Mag. Res. 13 430 (1980).



These spectra were obtained on our Varian XL-200. In cases where the shift difference between connected carbons is less than ca. 200 Hz then the outer components of the connected doublets are not visible, since one is seeing effectively "AB" spectra. For the lowest field aromatic carbon, that arising from C-5a, there is an additional doublet, with $J_{CC} \approx 40$ Hz, which arises from $^1J_{CC}$ to the aliphatic C-5 site. In the case of C-9a there is an extra doublet, due to coupling to the C=O, with $^1J_{CC} \approx 50$ Hz.

G.W. Buchanan

G.W. Buchanan,
Professor of Chemistry.



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Prof. B. L. Shapiro
Dept. of Chemistry
Texas A & M University
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TX 77843-3255

October 9, 1985

MICRO-PROGRAM FOR J-MODULATED SPIN-ECHO - MODIFICATION WITH DATA-SAVING
FEATURE FOR LONG TERM RUNS

...

Dear Prof. Shapiro:

The J-modulated spin-echo experiment has become a very routine one in C-13 nmr spectroscopy; in the resulting spectrum, resonances due to quaternary and methylene carbons are phased in one direction and those due to methine and methyl carbons are phased in the opposite direction and often one such experiment is sufficient to assign all resonances in an organic compound. The main drawback in the above-mentioned micro-program provided by IBM or Bruker for their ASPECT owners was the absence of any data-saving feature; in the (often common) event of power failures and other kinds of interruptions of such runs set for overnight or the week-end, all the data gathered are irretrievably lost. Since we routinely run such experiments for overnight and week-end, we modified the micro-program by adding the data-saving feature as follows:

The number of scans for each loop could be set suitably for being written on to the disk at desired intervals. In addition to the requirements of PW=RD=0.0, DS should also be set to zero. Also, it is advisable to delete any old TEMP file before starting the AU sequence so that one can be sure that any TEMP file found on the disk subsequently is due to the experiment run last.

We hope the owners of the ASPECT systems will find the above modification very useful.

ED JMSE.LSTH

```

1 ZE
2 D1 BB
3 P1 PH1
4 D2 DD
5 P2 PH2
6 D2 BB
7 GQ=2 BB
8 WR TEMP
9 LD TO 2: TIMES 50
10 DD
11 EXIT
PH1=A0 A0 A2 A2 A1 A1 A3 A3
PH2=A0 A2 A0 A2 A1 A3 A1 A3

```

Thanking you,

Sincerely yours,

Francis R. Keane

Puliur R. Srinivasan

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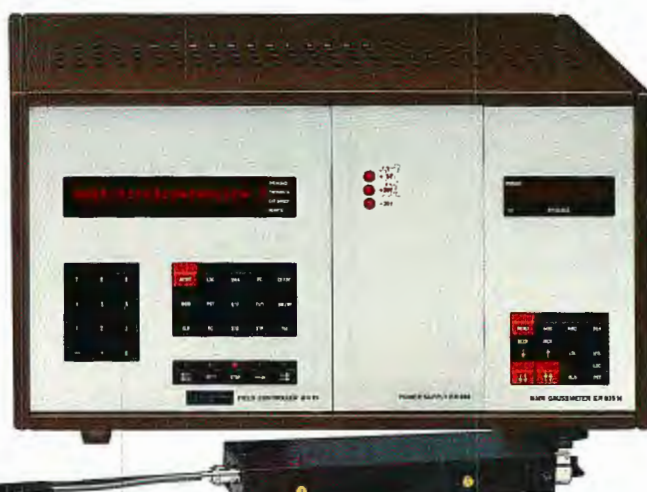
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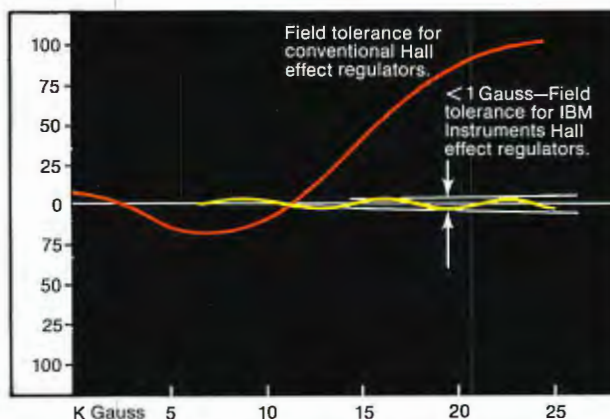
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Prof. Dr. H. Günther

Universität – Gesamthochschule – Siegen · Postfach 101240 · D-5900 Siegen

Siegen, November 19, 1985

Prof. Dr. B. L. Shapiro
Texas A&M University
Department of Chemistry
College Station, Texas 77843-3255

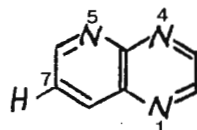
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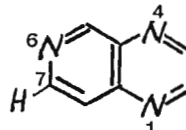
*Beat the Deadline: Refocussed INEPT with Selective
¹H-Decoupling*

Dear Barry,

during our ¹⁵N work on protonation and metal interactions of nitrogen heterocycles, selective ¹H-decoupling in combination with refocussed INEPT has proved to be a valuable tool for solving assignment problems. To our knowledge, v. Philipsborn and coworkers were the first who used this approach⁽¹⁾, which was recently also applied to ²⁹Si-NMR⁽²⁾. As an example we cite results for the two azu-naphthalenes **1** and **2** where a differentiation of the pyrazine nitrogen resonances was achieved.



1



2

While ¹³C, ¹H- as well as ¹⁵N, ¹H-shift correlations established the connectivities, selective ¹H-decoupling provided the necessary independent information for the absolute assignment. Irradiation of 7-H in **1**, which is clearly recognized as the M-part of the ¹H-AMX-system, yields a triplet splitting (1.3 Hz) for the signal at 44.1 ppm (highfield from ext. CD₃¹⁵NO₃). Only N-1 can have two ³J interactions of this magnitude. An analogous experiment was done for **2** with 7-H which is here identified through its large ²J coupling to N-6. The final assignments are as follows: **1** (N-1, N-4, N-5) 44.1, 50.1, 63.2 ppm; **2** (N-1, N-4, N-6) 53.8, 52.8, 58.4 ppm. For **1** the data agree with results of Stefaniak et al.⁽³⁾, which were based on shift calculations.

Best regards,

K. Finneiser

H. Günther

(1) W. Städeli, P. Bigler and W. v. Philipsborn, Org. Magn. Reson. 16, 170 (1981).

(2) J. Schraml, J. Magn. Reson. 59, 515 (1984).

(3) L. Stefaniak, J. D. Roberts, M. Witanowski, and G. A. Webb, Org. Magn. Reson. 22, 201 (1984).

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23rd October 1985

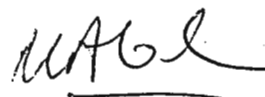
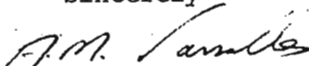
Professor B.L. Shapiro
Texas A & M University
Department of Chemistry
College Station, TX 77843
USA.

Mobile components in flash pyrolysis coal tar

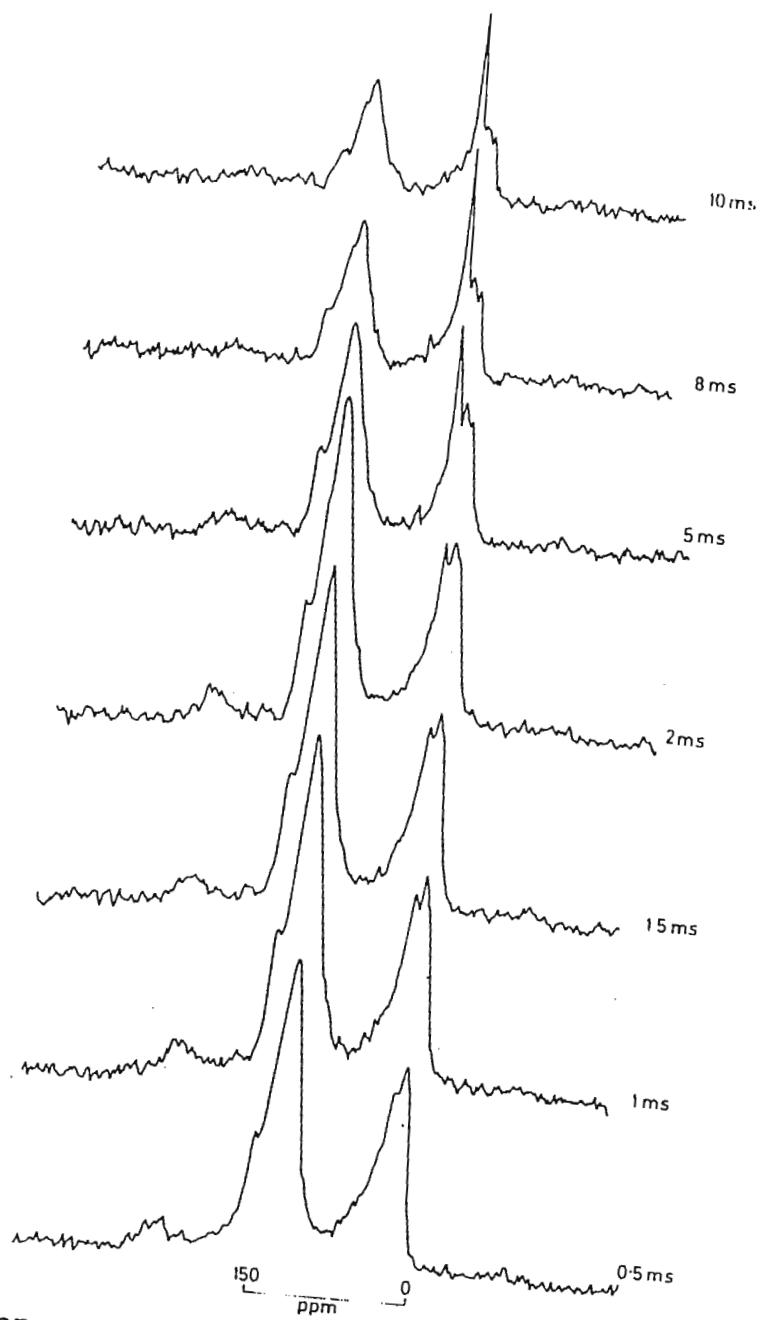
Dear Barry,

We routinely measure the aromaticity (fraction of aromatic carbon) of coals and their liquefaction products (chars, residues, tars) by carbon-13 NMR. Normally the tars are examined by solution NMR, but occasionally because some are only sparingly soluble in deuteriochloroform, the aromaticity is measured by solid state carbon-13 NMR. For many tars, this does not raise any additional problems and we have shown that aromaticities measured in solution and in the solid state are in agreement. However recently while examining a suite of flash pyrolysis tars, one of them had a component which had an extremely long T_{CH} . The chemical shift of this component (30ppm) indicates that it comprises CH_2 groups in long alkyl chains (Figure 1). Since the T_{CH} of this component is clearly longer than the $T_{1\rho}$ for the rest of the tar, a quantitative measurement of the aromaticity can not be obtained using cross polarisation NMR. Accordingly we have measured the aromaticity of this material using a simple Bloch decay method coupled with high power proton decoupling and found a much lower aromaticity than that obtained by CP NMR (Figure 2). The higher aromaticity found in the CP experiments results from the inability to detect the highly mobile aliphatic material incorporated within the tar matrix.

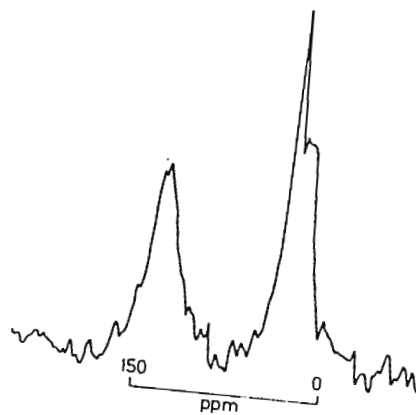
Sincerely



A.M. Vassallo and M.A. Wilson



1. EFFECT OF CONTACT TIME ON SPECTRUM OF ACLAND TAR



2. BLOCH DECAY SPECTRUM OF ACLAND TAR

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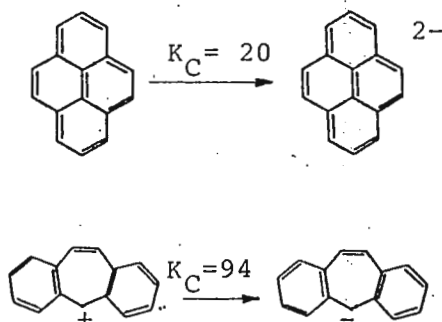
Professor Bernard L. Shapiro
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Oct 29, 1985

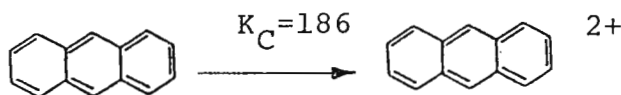
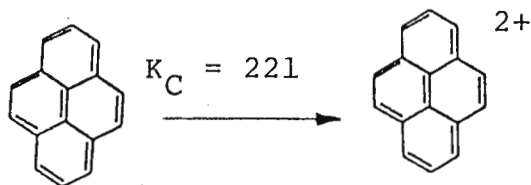
Lower than expected C-13 chemical shift/charge factors

Dear Barry,

The relation between NMR chemical shifts and electron densities is still attracting a lot of attention. In delocalized anions, where ion-pairing and aggregation could have profound influence on the charge distribution, organic chemists seem to prefer experimental estimates of the charge density pattern. Our recent C-13 NMR studies of a variety of conjugated polycyclic carbanions showed in many cases sensitivity factors to charge that were significantly lower than the commonly quoted 160 ppm/e. Especially low values were obtained for strongly paratropic dianions. In general, a very nice correlation was obtained by plotting the ring current contribution to the H-1 chemical shifts (X_H) vs. K_C . The data could be explained by a model which describes the C-13 shifts from a charge term and an anisotropy term. The relation between X_H and K_C is explained from E which influences both C-13 chemical shifts and X_H .



If this proposal is true then oxidation to paratropic dications should give $K_C > 160$ ppm/e. As shown below this prediction seems to be correct. This observation also excludes the possibility that anion-alkali metal charge transfer is responsible to the low K_C values obtained for paratropic dianions.



Best regards

Ulf Edlund

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| | | | 203 | 2.60 | 2.50 | 2.40 |
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| | | | 203 | 4.35 | 4.25 | 4.15 |
| NE-H5 Blue | 528-PP | 220-360 MHz: Research, FT applications. A superior sample tube for ultimate resolution and sensitivity. Compatible with vortex plugs and coaxial inner cells. | 178 | 6.65 | 6.55 | 6.45 |
| | | | 203 | 7.15 | 7.05 | 6.95 |

10MM O.D. NMR SAMPLE TUBES

| Catalog Number | Comparable Wilmad Catalog Numbers | Recommended Use | Length MM | Price each | | |
|----------------|--|--|--------------|---------------|--------|--------|
| | | | | 1-24 | 25-49 | 50-up |
| NE-L10 | 513-1PP | 60MHz: Routine analysis, quality control. Compatible with vortex plugs. Not recommended for use with coaxial inner cells. | 178 | \$7.50 | \$7.25 | \$6.75 |
| | | | 203 | 8.25 | 8.00 | 7.50 |
| NE-M10 | 513-5PP | 90-100 MHz: General research, FT applications. Compatible with vortex plugs and coaxial inner cells. | 178 | 12.25 | 11.75 | 11.00 |
| | | | 203 | 13.00 | 12.50 | 11.75 |
| NE-H10 | 513-7PP | 100 MHz and up: Research, FT applications. Compatible with vortex plugs and coaxial inner cells. | 178 | 14.25 | 13.75 | 13.00 |
| | | | 203 | 15.00 | 14.50 | 13.75 |

Note: Flat bottoms are available at no additional charge. Specify when ordering.



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DEPARTMENT OF CHEMISTRY

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

30 October 1985

Dear Professor Shapiro

ACOUSTIC RINGING REDUCTION

Acoustic ringing often sets limits on the sensitivity of wide-line spectroscopy which are more severe than those imposed by the available signal-to-noise ratio. As Morris and Toohey¹ have pointed out, the main cause of such ringing lies in the acoustic vibrations induced by the radiofrequency pulse in any metal in the vicinity of the r.f. coil. They propose a useful pulse hardware modification to reduce ringing, with some concomitant loss of spectral range.

It seems sensible to supplement such methods with a direct modification of the most substantial source of the ringing. In many spectrometers such as our own Bruker WH400, this is the Al of which the can is made. Al is particularly prone to acoustic ringing.

So far we have only investigated the simple expedient of replacing the Al can with a plastic (polypropylene) copy. Because there is no conductive coating on the inside of the can, we experience a few problems with r.f. tuning, particularly on the decoupler ¹H channel. These are, however, not important in most wide-line work, and we have found no loss of signal or increase in r.f. artefacts.

Using the plastic can, we find that the acoustic ringing is reduced by a factor of up to 60, with the biggest advantage being found at higher frequencies. Thus Fig. 1 shows a ¹⁷O n.m.r. spectrum at 54.2 MHz of an aqueous metal complex (in which the solute resonances are barely discernible at the baseline). The upper spectrum is with the plastic can, the lower with the standard metal one, and 60x more ringing.

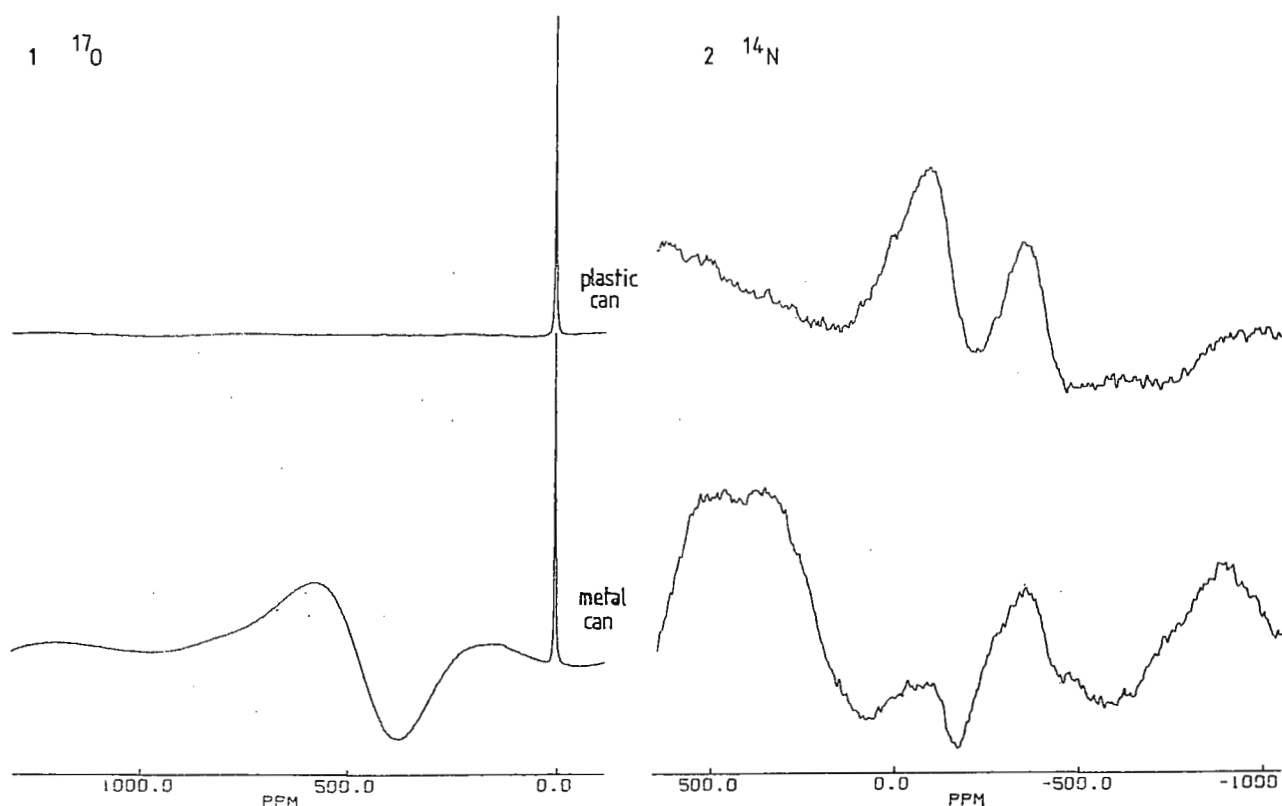


Fig. 2 shows a smaller (x3) but useful gain with a ^{14}N spectrum (28.9 MHz) of a nitrogenous coal tar. The broad peaks at ca. 50 and 350 δ (ref. CH_3NO_2) arise from aromatic and aliphatic N respectively. The aromatic peak is virtually lost in the lower spectrum (metal can). The information gain is actually greater than x3, because the ringing also lasts less time in the upper (plastic can) spectrum. This increases the apparent mean linewidth of the ringing response, making it easier to tell apart from the true spectrum. A similar gain is apparent in ^{95}Mo (26.1 MHz) spectra. Although the intensity of the ringing is not reduced in this case, its mean linewidth increases from 8 to 23 kHz.

Further improvements could no doubt be gained by a thorough attention to probe materials and screening. However, even the present results demonstrate an inexpensive way of improving spectrometer performance.

Yours sincerely

Oliver Howarth

Eirian H Curzon

Oliver W Howarth

Eirian H Curzon

¹ G A Morris and M J Toohey, *J. Magn. Res.*, **63**, 629, (1985)



(303)491-6480

Colorado State University
Fort Collins, Colorado
80523

November 18, 1985

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

Subject: Progress in Magic-Angle Spinning

Dear Barry:

As many of your readers may know, our lab and the adjacent NSF-funded Regional IMR Center have employed a variety of magic-angle spinning systems over the past eight years. During the past several months we have had considerable success by modifying MAS systems developed elsewhere for use in specific applications here.

Steve Dec, a post-doc in our group, has found a scaled-down version of what we call the "Wind-mill" spinner (R.A. Wind, F.E. Anthonio, M.J. Duijvestijn, J. Smidt, J. Trommel and C.M.C. Devette, J. Magn. Reson., 52, 424 (1983)) to be especially useful in ²⁷Al work. These spinners are made of Torlon, have outer diameters of 6 mm, sample volumes of about 0.070 mL and spin routinely at about 11.0-11.5 kHz.

We have also become intrigued with Ian Gay's spinner design (I.D. Gay, J. Magn. Reson., 58, 413 (1984)) for sealed glass samples, which are especially attractive for studies of surface systems. Graduate student Bob Zeigler has duplicated Ian Gay's published design, which employs 5-mm (o.d.) glass tubes, and has found it to be useful for natural abundance ¹³C samples in which S/N is not a major problem. For surface systems in which there are serious S/N difficulties he has found that scaling up the design to 8 mm (o.d.) is highly useful; these scaled-up spinners readily spin up to about 3 kHz. Bob and Chuck Bronnimann (Research Associate in the NMR Center) have found that the 5-mm design is well-suited to ¹H experiments by the CRAMPS (combined rotation and multiple pulse spectroscopy) approach; the 5-mm Ian Gay spinner, with its "external" position of the rf coil, is quite adaptable to the H₁ requirements of this technique.

We have also had success with the remarkably stable triple-bearing Chemagnetics spinner in our angle-flipping 2D experiment (A. Bax, N.M. Szeverenyi and G.E. Maciel, J. Mag. Reson., 55, 494 (1983)). This spinner, which we typically operate at about 3 kHz, has been used without trouble by graduate student Maziar Sardashti for most of the time during more than a year in a mode that requires jerking the spinning axis from 90° or 0° to the magic angle in about 300 ms, and repeating this brutal procedure every second or so.

Experiments with these and other spinner designs continue.

Sincerely,

Gary E. Maciel
Professor

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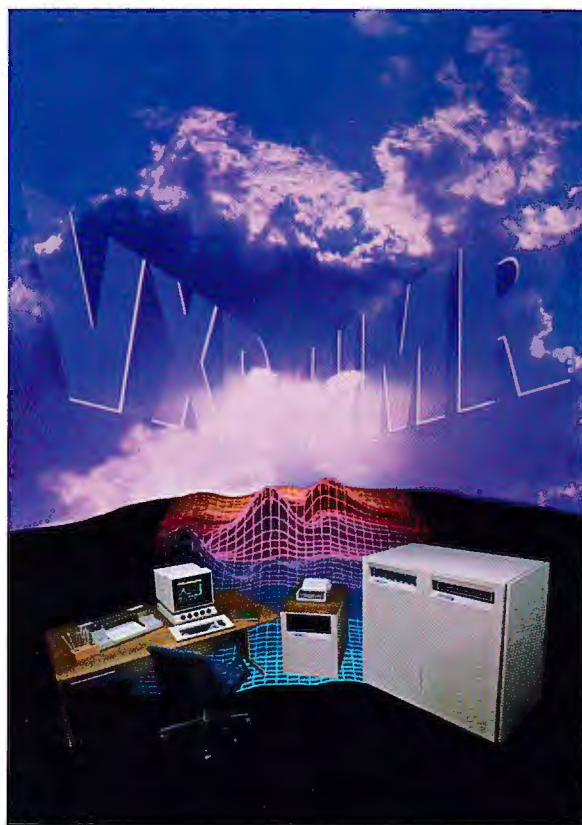
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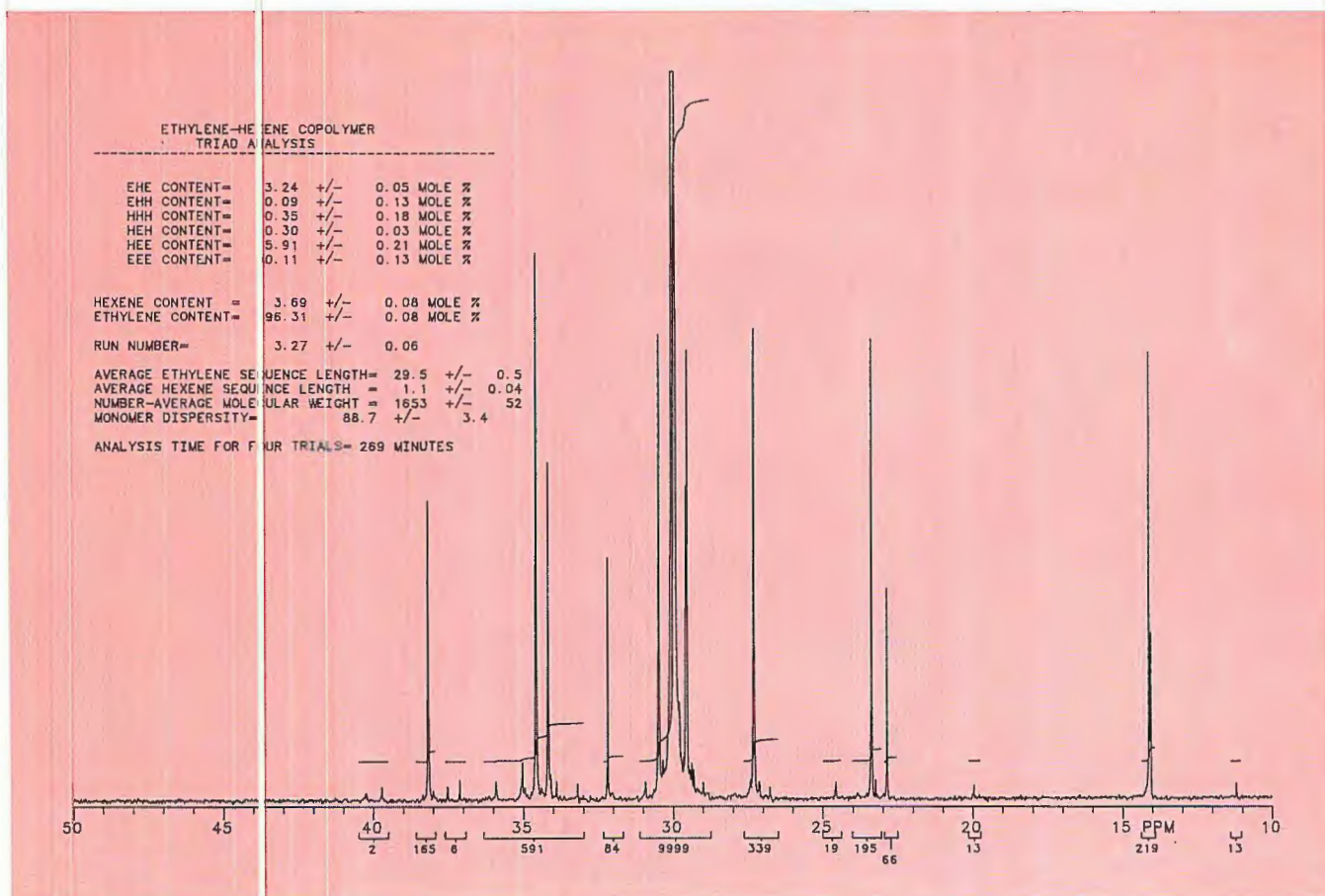


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Department of Medicinal Chemistry

Dear Barry:

It was good to have seen you at the EAS last week. As you know, in the past few years the EAS has offered an exciting NMR program, due largely to the efforts of Gwen Chmurny. The EAS NMR Symposium is held in the Fall thereby offering a welcome relief to those of us who are unable to get a complete annual dose of NMR at the ENC.

The 1986 EAS will have another fine program in NMR and, with the departure of the FACSS meeting to other quarters, it will be the only major Fall NMR meeting on the East Coast. The 1986 meeting will also have, for the first time, a poster session which I am co-chairing with Dr. Walter Boyko of Villanova University. We would like to extend an invitation to your readers to submit papers for this poster session on any topic in NMR. We would also like to point out that this poster session will constitute the entire first day (Monday) of the NMR Symposium.

One caution: the 1986 EAS will be almost six weeks earlier than the 1985 meeting. Hence, the deadline for submission of papers has been moved up to February 15, 1986. The details of all this can be found in the eyecatcher below.

NMR POSTER SESSION
for the 1986
SILVER JUBILEE CELEBRATION
of the
EASTERN ANALYTICAL SYMPOSIUM
October 6 - 10, 1986

For details, contact:

Andy
Dr. Andy Evans
Berlex Laboratories
110 E. Hanover Avenue
Cedar Knolls, NJ 07927
201/540-8700 x302

or

Dr. Walter Boyko
Villanova University
Department of Chemistry
Villanova PA 19085
215/645-4871

Deadline for Receipt of Papers
February 15, 1986

CALIFORNIA INSTITUTE OF TECHNOLOGY

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
THE CHEMICAL LABORATORIES

November 6, 1985

Mail Code 164-30

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843Re: ^{13}C CP-MAS studies of brominated
polyacetylene analogs

Dear Barry,

We would like to initiate a subscription to the TAMU newsletter with an account of some preliminary ^{13}C CP-MAS results on the chemistry of an insoluble polymer system obtained in collaboration with Dr. Dan Sandman (GTE Laboratories, Waltham, MA). The bromination of the polyacetylene-like compound DCH (poly-dicarbazole-hexadi-yne) is a topochemical solid-state reaction which occurs with preservation of the crystal structure, but which results in marked changes of physico-chemical properties. At present the nature of this chemical process is unknown since both reactant and product are completely insoluble.

We have used ^{13}C CP-MAS in order to learn where bromine ends up in the structure. Our ^{13}C data were taken at 50.366 MHz on a home-built solid state spectrometer using a high power double-tuned magic angle spinning probe from Doty Scientific. Standard cross-polarization methods including magnetization flipback and dipolar dephasing delays were used with spinning speeds of 3-5 kHz and decoupling power of 12-16 gauss. Figure 1 shows the spectra at various stages of bromination. The peak assignments were aided by running the respective spectra of carbazole, 3,6-dibromocarbazole, 1,3,6,8-tetrabromocarbazole and 3,3',6,6'-tetra-bromo dicarbazole-hexa-2,4-diyne. In the spectra of these model compounds the brominated C-atoms could not be detected at all while the peaks of the adjacent C-atoms were very broad and unresolved. This is presumably due to the strong dipolar coupling to the $^{79,81}\text{Br}$ nuclei, which experience strong electric quadrupole interactions (NQCC ca. 200 MHz). Under such conditions the corresponding peaks in the MAS spectrum are expected to consist of broad powder patterns with complex shapes¹. Even the linewidths of more remote C-atoms are affected by this mechanism.

Inspection of Figure 1 shows that the attack of bromine on the polymer structure results in a non-selective broadening of all peaks. Chemical shift changes suggest that the aromatic moiety is brominated at the C-3 position, but the triple bond and the double bond also appear

to be brominated to some degree at an uptake level of 3.8 Br/repeat unit. Higher bromine uptake levels do not result in further bromination of the carbazole moiety, but rather in an attack of the double and triple bonds of the polymer. Preliminary work on DCH exposed to nitric acid fumes indicates that this reaction is governed by similar principles.

It is clear that the ^{13}C CP-MAS can provide new information about the chemical reactivity of this solid polymer, despite the broadening arising from the quadrupole bromine nuclei.

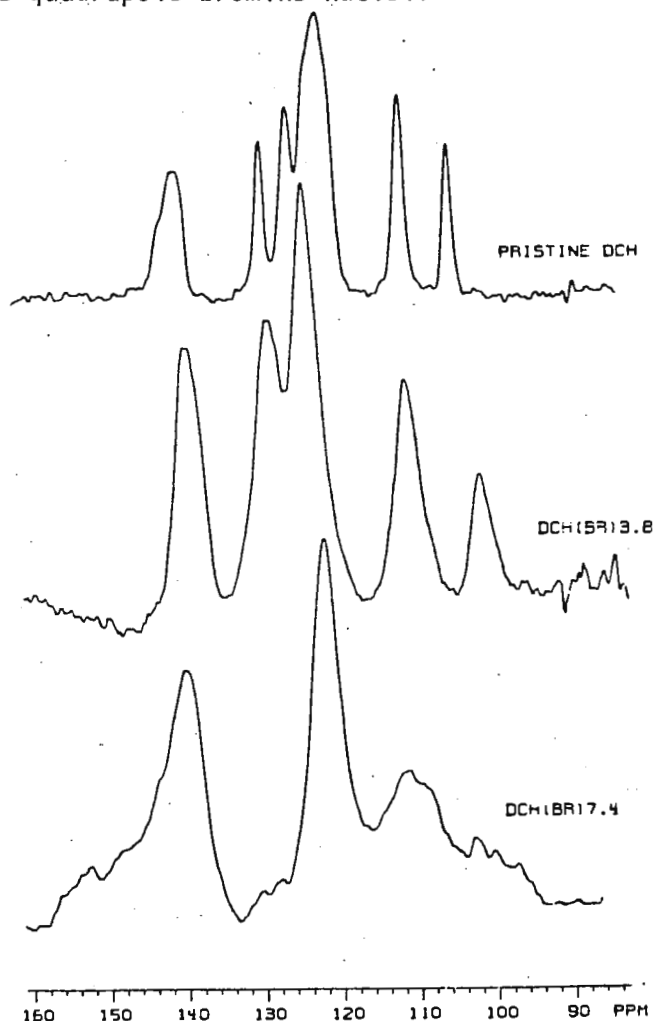
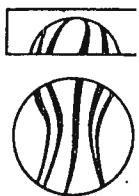


Figure 1. ^{13}C CP-MAS spectra of brominated DCH

Sincerely yours,

James Yesinowski H. Eckert

James P. Yesinowski and Hellmut Eckert
Southern California Regional NMR Facility



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From the School of Pharmaceutical Chemistry

November 4, 1985

Professor B L Shapiro
Department of Chemistry
Texas A+M University
COLLEGE STATION
TX 77843
U S A

Dear Barry

DEPT in Proteins

We are using NMR to examine interactions of thyroid hormones with one of their transport proteins, thyroxine binding prealbumin (TBPA). Part of that study involves ^{13}C NMR analyses of the protein and the protein-hormone complex. TBPA is a relatively large protein by NMR standards (54,000 molecular weight), and hence peak broadening and overlap present a problem for spectral assignments. We have found, however, that the DEPT spectral editing technique^{1,2} is extremely valuable in simplifying protein spectra. The lower trace in Figure 1 shows the (Waltz decoupled) ^{13}C spectrum of TBPA and the upper three traces the DEPT subspectra.

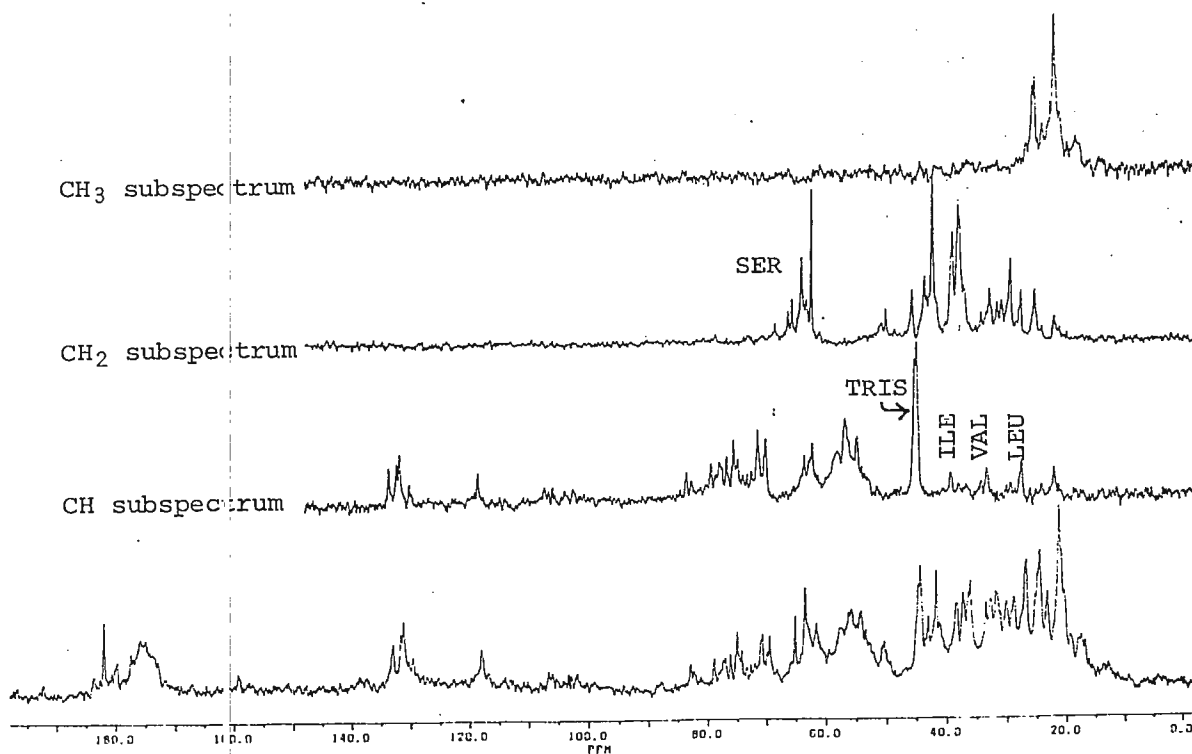


Figure 1 DEPT subspectra of TBPA

Many resonances, including serine CH₂'s and valine CH's which were previously buried under peaks of other multiplicity, become resolved.

A number of other projects in our lab related to NMR in drug design also require well resolved protein ¹³C spectra and the DEPT technique has proven to be generally applicable. Figure 2 shows subspectra for insulin where the spectral simplification is even more striking than for TBPA.

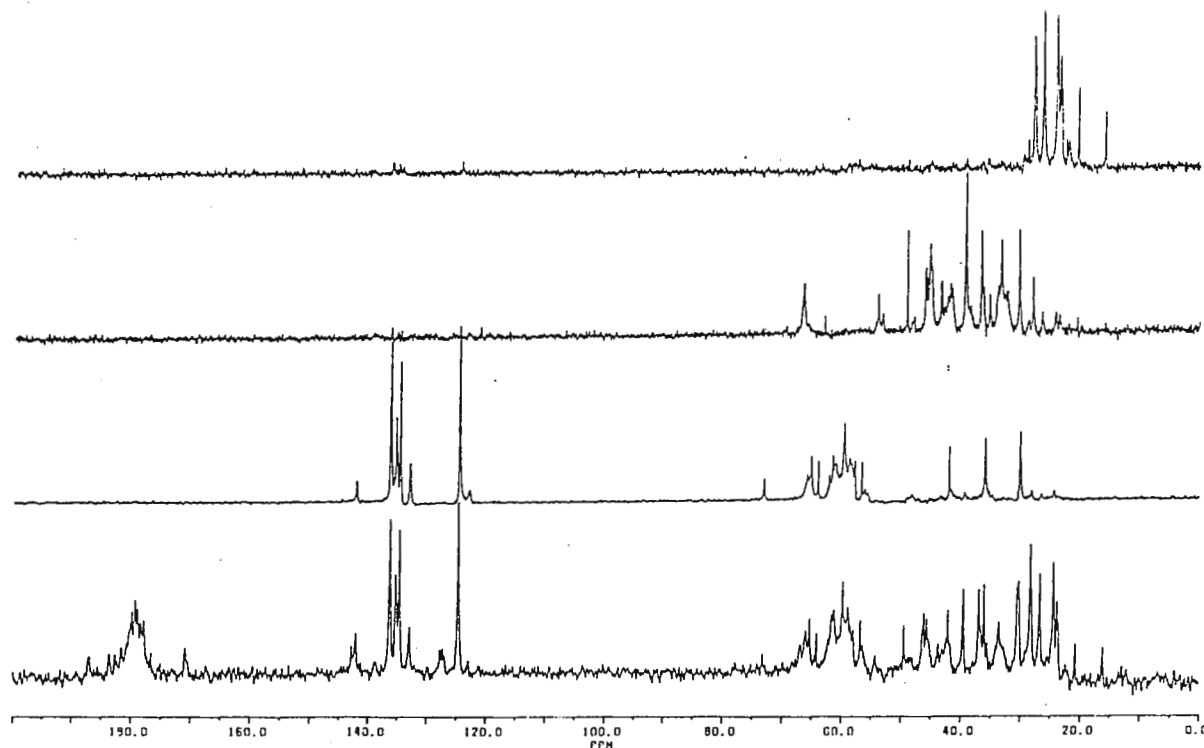


Figure 2 DEPT subspectra of insulin

The three subspectra were generated from an overnight run on our Bruker AM300WB spectrometer.

Please credit this contribution to Ian Rae's account.

Best wishes,

David Craik

Jon Hall

Kerry Higgins

References

1. D.M. Doddrell, D.J. Pegg and M.R. Bendall, J. Magn. Reson., 48, 323 (1982)
2. D.M. Doddrell, D.J. Pegg and M.R. Bendall, J. Chem. Phys., 77, 2745 (1982)

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November 7, 1985

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

More on Radiation Damping

Dear Barry:

Shortly before the August issue arrived we experienced problems due to radiation damping on our AM-500. Trying to shim the magnet with the proton probe in place we couldn't get good-line shape using the usual CHCl_3 resonance. The line width at half height would not go below about 0.8 Hz. The sealed sample also contains TMS.

Out of curiosity we changed the observe window to the TMS signal and found it to be only about 0.20 Hz! wide. We de-tuned the probe until the FID of the CHCl_3 signal no longer improved. Without any further changes the homogeneity appeared much improved. The CHCl_3 width at 0.55% height decreased from about 10 Hz to below 6 Hz; spinning side bands decreased as well.

Most surprising though was the decrease of the TMS line width to about 0.15 Hz! After ejecting the sample we looked at the label and realized that instead of the usual 15% CHCl_3 it contain 50% CHCl_3 and 2% TMS.

On a high sensitivity probe (S/N on 0.1% EB >300:1) radiation damping can be observed at concentration levels which could be considered "low". Spinning side bands may appear to be larger (they aren't damped as much).

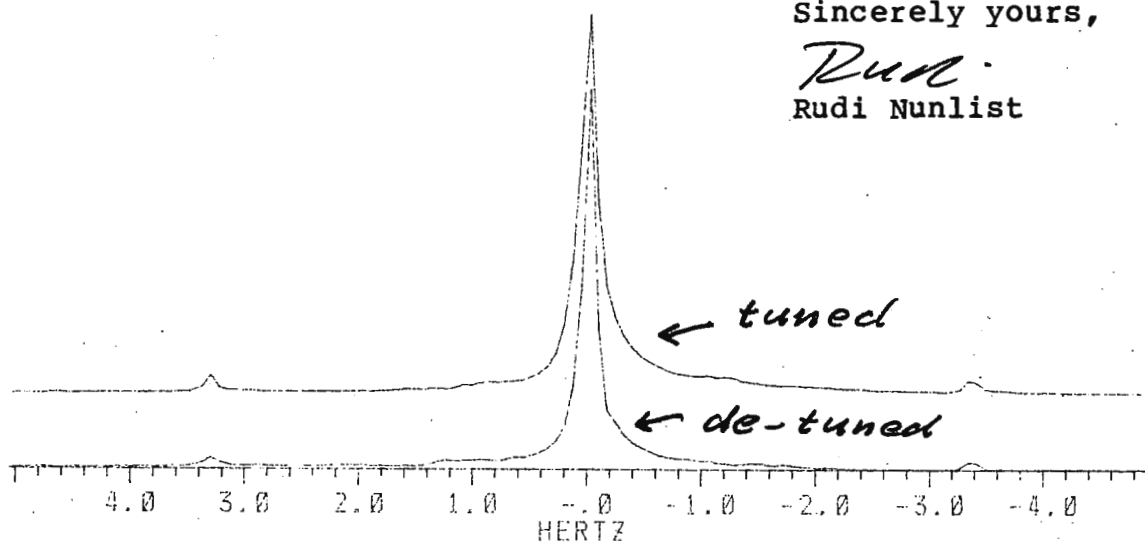
We also looked at the potential problem at lower fields. Three instruments are equipped with ^{13}C / ^{31}P and ^1H switchable

probes. On the 180 we have a 10 mm probe, on the 200 and 300 we use 5 mm probes. The standard samples we use contain 60% C_6D_6 , 1% TMP and 38% dioxane to check s/n on both carbon and phosphorus. We found it to be difficult to shim on the dioxane FID at 300 MHz and on the 10 mm probe at 180 MLT. De-tuning the 180 MHz probe resulted in instant improvement as well. To shim the magnet for 10 mm probes by observing protons on the decoupling coil may need to be done at very low concentration if the results are to be meaningful.

Sincerely yours,

Rudi

Rudi Nunlist



Prof. Dr. GERHARD HÄGELE
Institut für Anorganische Chemie
und Strukturchemie I
der Universität Düsseldorf

4000 Düsseldorf, den 25.10.1985
Universitätsstr. 1/26.42.U1.32
Telefon 0211 - 311-2288/2287
Telex 8 587 348 uni d

Data Transmission from a Bruker AM-200
to an IBM PC.

Dear Professor Shapiro,

indeed we got some information for the TAMU letter - thanks for the reminder. A few weeks ago we succeeded in a very easy way of DATA TRANSMISSION from our Bruker AM200 - spectrometer to a commercial IBM-PC via serial interface.

Since we are interested in spectra ready made for publications - like those normally plotted after successful machine-sessions - we found a way to direct data which primary were bound for the digital plotter onto an IBM-PC. The usual "CA"-command of Bruker's DISNMR - program switches the output-channel for plotter-information from the digital plotter to the serial interface. Afterwards the data transmission can be started by the usual plot-commands (e.g. "PX"). So the only things required - besides the PC - are an appropriate transmission cable and a (short) computer-program to make the PC receive and store the incoming data. We found out the transmission parameters required on the PC and condensed them to a BASIC - program called HERMES. (These parameters can be found together with our pin-connection of the transmission cable at the appendices to this letter.)

The data received contain the original lineshape (accompanied by all other plotter-information; e.g. axis etc.) coded as pen-movement commands for the digital plotter. Using the well documented Bruker manual for our Watanabe WX4636 plotter we wrote programs that act on the data received with several purposes. We just finished a program MIKEPLOT which yields ink-plots in various layouts on a PC-connected Calcomp M84 DINA4-plotter. A second program PCPREP to extract the lineshape-data in terms of frequency/intensity units is in progress.

This informations should point out an easy way of data-transmission usefull to everyone working on an AM200 because NO SPECIAL MANIPULATIONS are required on the spectrometer itself. Since DISNMR supports FULL TIMESHARING it is possible to transmit data besides all other actions of the AM200 spectrometer (e.g. measuring in job 1, plotting in job 2 and transmitting in job 3).

The original programs will be available on request from the authors.

Your sincerely

M. Grzonka

(M.Grzonka)

G. Hägele

(Prof. G.Hägele)

Appendix A: Transmission Parameters for Self-Programmers

```

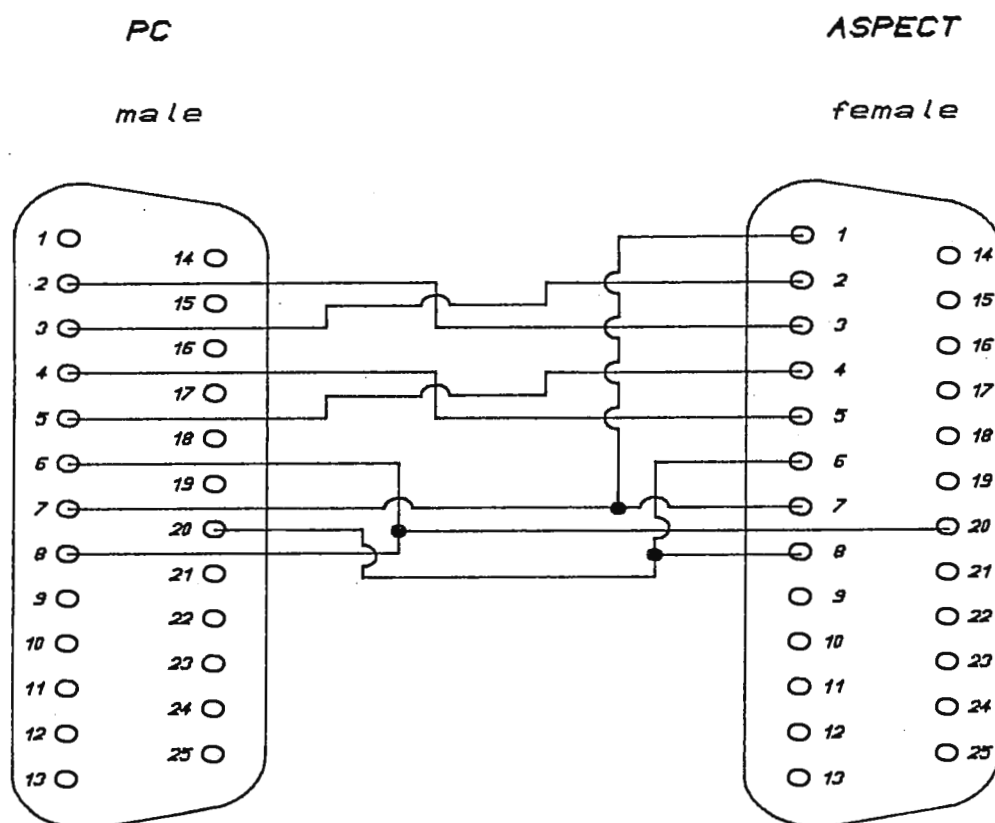
transmission speed: 9600 baud
parity              : none
data bits           : 8
stop bits           : 1

code                : ASCII
  
```

The transmission is done in blocs of 64 bytes. Every TWO bytes are logically corresponding to ONE plotter command or ONE integer digit. The chr\$(128) character (hex=08) in the first byte of these groups of two indicates a plotter command.

Appendix B: Pin Connection on the Transmission Cable

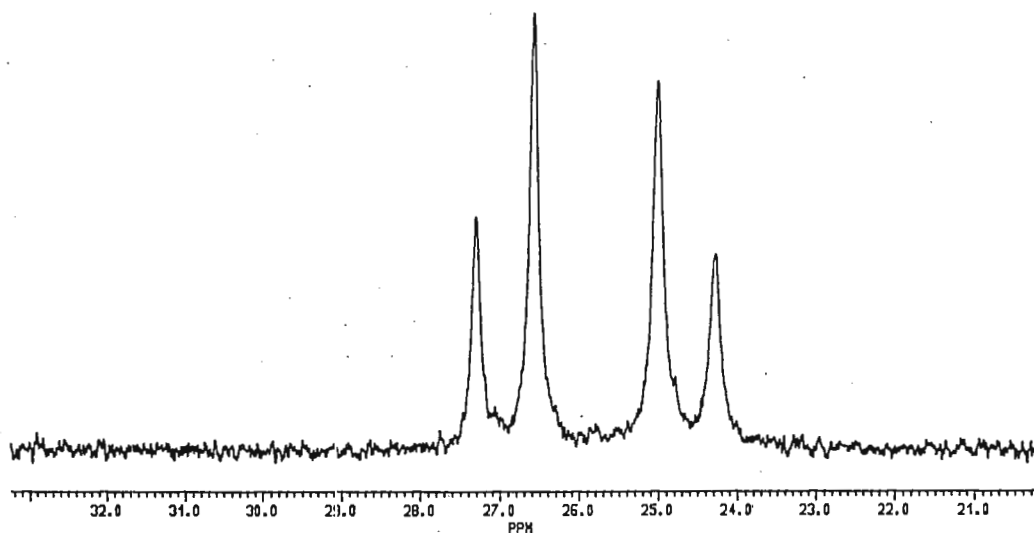
(you may use a standard - cable for transmission between serial RS232 interfaces instead)



Minimum Pin-Connection for the
ASPECT 3000 / IBM-PC Line

Appendix C: Sample Ink-Plots from MIKEPLOT

a) Plot similar to Bruker Layout



Parameter-Liste :

DM1

DATE 15-10-85

SF 81.015

SY 81.026

O1 -8646.000

SI 16384

TD 16384

SW 2415.459

HZ/PT .295

PW 8.0

RD 0.0

AD 3.391

RG 100

NS 68

TE 297

FW 3100

Q2 3800.000

DP 12H 88

LB 1.000

GB 0.0

CX 30.00

CY 0.0

F1 33.238PPM

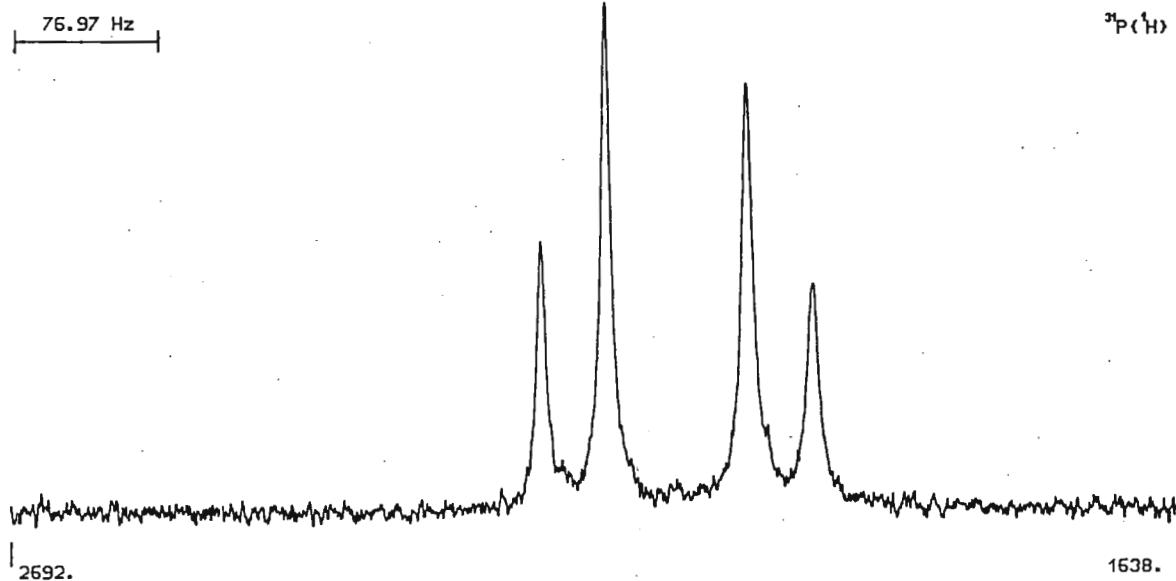
F2 20.223PPM

HZ/CM 35.147

PPM/CM .434

SR -10802.41

b) Same Lineshape in our "PUBLICATION" - Format



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Manning Park, Billerica, MA 01821
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Rheinstetten 4, West Germany



NMR Systems designed to solve problems.

Peter Stilbs
Institute of Physical Chemistry
Uppsala University
Box 532
S-75121 Uppsala , Sweden

Tel: ***46-18-183646

Uppsala 13 November 1985

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

Re: Spectral densities of motion from spin relaxation at different magnetic fields.

Dear Barry;

Thank you for the reminder which arrived today; we actually started writing this letter yesterday...

It is by now fair to state that various relaxation rate measurements have become a standard tool in NMR. If we restrict ourselves to systems that show no static interactions in NMR-spectra, one problem in the interpretation of relaxation rates is that one seeks the correlation functions for molecular motion but that the relaxation experiment gives a linear combination of the Fourier transform of the correlation function at but a few frequencies. In the extreme-narrowing regime, one can at best obtain an effective correlation time for non-rigid molecules. The situation is brighter if there is a frequency dependence in the relaxation times and one can then test detailed motional models.

A class of systems that has motions that are well "tuned" to NMR frequencies is isotropic aqueous surfactant systems, i.e. simple micellar and microemulsion systems. In general, they are systems of high concentration of simple molecules that can be isotopically labelled with e.g. deuterium quite easily. We show in figures 1a and 1b two examples of field-dependent spin-lattice and spin-spin relaxation rates for a micellar and microemulsion system that contain a specifically deuterated surfactant. The solid lines represent the fits of a particular motional model, the so-called "two-step" model to the experimental data. The data at the lower field strengths have been obtained by simply lowering the magnetic field of a Bruker CXP spectrometer that normally operates at 2.1 Tesla (13 MHz deuterium frequency).

Finally, we would like to point out that the spectral densities can be determined over a wide frequency interval without the need for any motional model. This can be done for example, if one can lower the field to a value where T_1 equals T_2 , as in Figure 1a or by analysing the bandshape of ^{13}C nuclei with directly bonded ^2H -s (at essentially complete enrichment), as has been suggested by the Volds.² If one has the relaxation rate value at say ω , one simply measures the spin relaxation at twice that frequency (2ω) which gives the spectral density at 4ω , and then one measures at 4ω and so on. One example of this procedure is shown in Figure 2 for the case of spherical micelles.

Please credit this contribution to Peter Stilbs subscription.

Yours Sincerely

Olle Söderman *Peter Stilbs* *Ulf Henriksson*
 /Olle Söderman/ /Peter Stilbs/ /Ulf Henriksson/

1. B. Halle and H. Wennerström, J. Chem. Phys., 75 (1981) 1928
2. J. Martin, R.L. Vold and R.R. Vold, J. Magn. Resonance, 51 (1983) 164

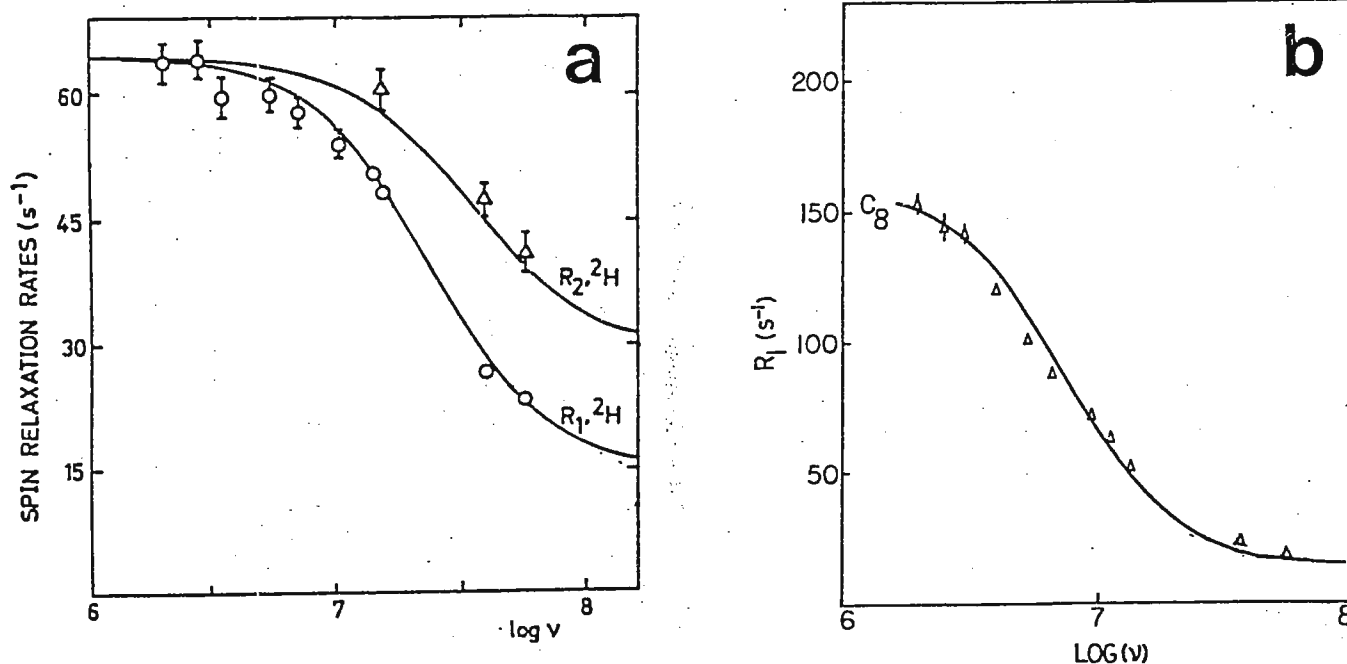


Fig. 1. ^2H R_1 and R_2 for a micellar (30% dodecyltrimethylammonium chloride) system (a) and ^2H R_1 for a microemulsion composed of H_2O / sodium dodecylsulphate/ toluene/ octanol. The solid lines are the prediction of the "two-step" model.

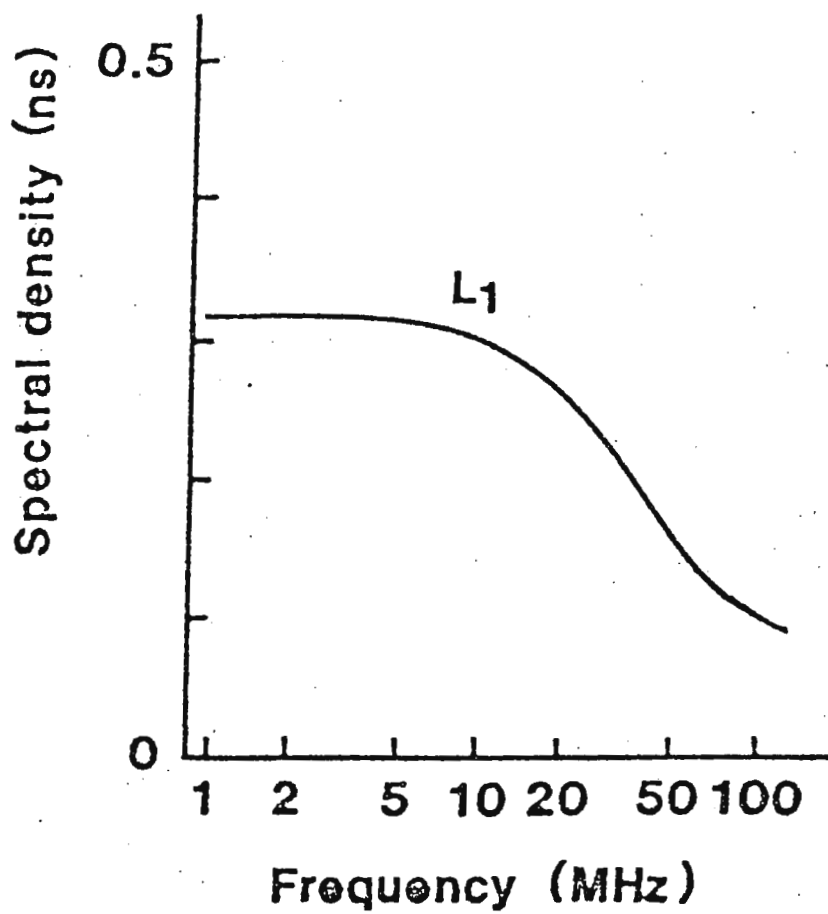


Fig. 2. The "model-free" spectral density for the micellar system in Figure 1a.

JOB OPENING-INSTRUMENTATION SPECIALIST

About half of the candidate's time will be spent overseeing (with assistance from electronics shop personnel) the operation and maintenance of 7 high-resolution supercon spectrometers and 1 solids spectrometer. The remainder of the time will be devoted to design and implementation of equipment for new NMR experiments in solids and liquids. Interested persons should write or call P. Mark Henrichs, Research Laboratories, Eastman Kodak Company, Rochester, New York, 14650, (716) 477-6229.

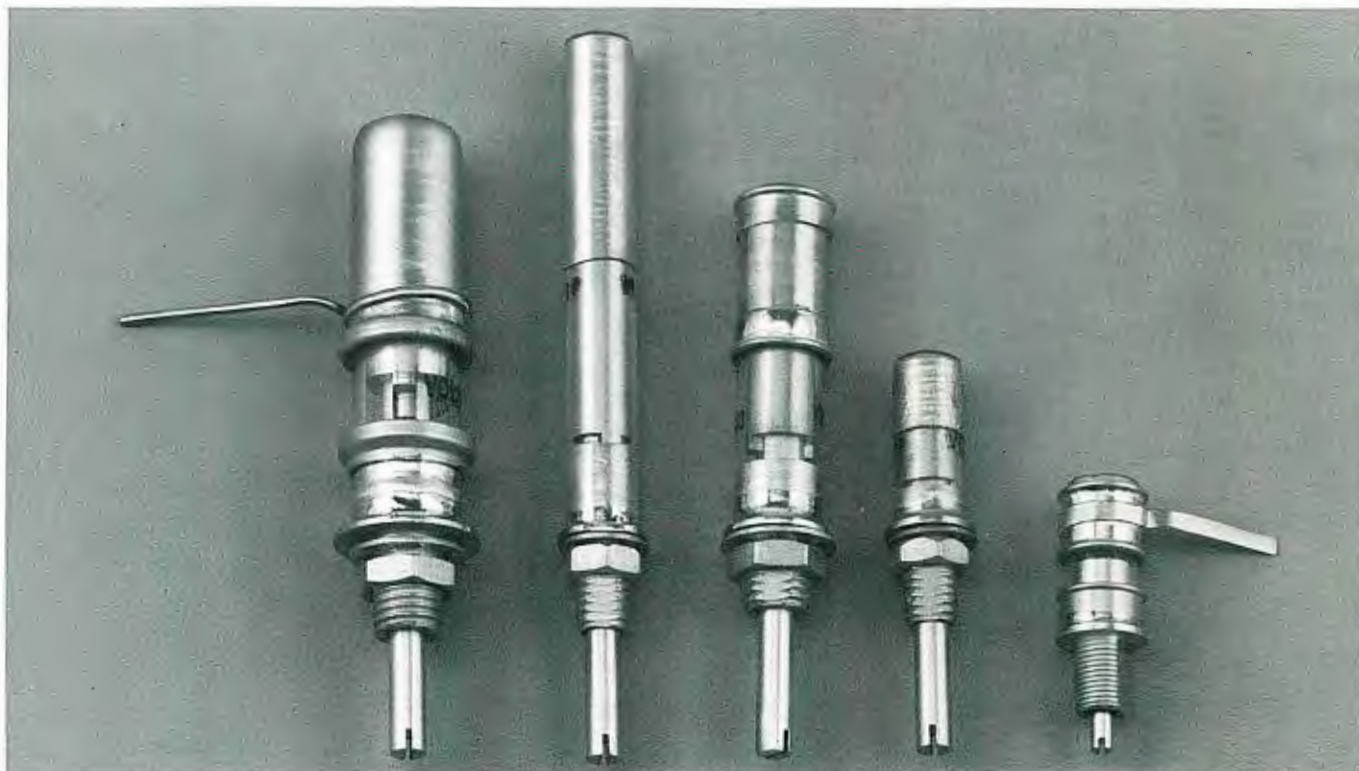
XII International Conference on Magnetic Resonance in Biological Systems, Todtmoos, West Germany, September 8-12, 1986.

The conference will be held in a small beautiful village in the Black Forest. A variety of plenary and special subject lectures, as well as lectures chosen from poster submissions will be given on subjects such as protein structure and function, nucleic acid-protein interactions, biological membranes, in vivo NMR, NMR imaging, ESR, and new techniques. Enquiries should be addressed to Professor Dr. H. Rüterjans, Institut für Biophysikalische Chemie, J.W. Goethe Universität, Universitätsklinikum, Haus 75A, Theodor Stern Kai 7-15, D-6000 Frankfurt am Main 70, Germany.



Non-Magnetic Precision Trimmer Capacitors

FOR NMR SPECTROMETERS AND MR IMAGING EQUIPMENT



Voltronics Corporation has produced non-magnetic trimmer capacitors for over 20 years. The increasing applications have impelled the company to mount an active, continuing engineering effort in this field. The capacitors listed in this catalog are the most popular. However, if you require something special, please call the factory or your local sales representative. Each of these parts was designed to meet a specific application.

Non-magnetic Properties

The severe requirement for non-magnetic properties is such that in a 14,000 Gauss field the capacitors must not distort the useable field by more than one part per 600 million. To achieve this, no materials or platings exhibiting measurable magnetism, such as stainless steel or nickel, are used. Commercial brass is unacceptable. Typical magnetic susceptibility is 40×10^{-6} CGS units. Voltronics' strict traceability system and its testing for minute magnetism insure this essential parameter.

Non-rotating Piston Trimmer Design

The capacitors have Voltronics' unique non-rotating piston design which offers 100% tuning linearity without reversals, high Q, long life, and low internal inductance. The internal bushing arms which prevent rotation also wipe on the moving piston to form a low resistance contact which can carry several amperes of RF current. **No current flows along the tuning screw as in all other trimmer capacitor designs!**

The capacitors are internally O-ring sealed so that they can withstand immersion in flux and cleaning solvents without leaking.

Dielectric

There are four choices of dielectric material: annular band glass, embedded band glass, quartz, and sapphire. Annular band glass consists of a tube of glass with metallized bands on the outside. Embedded band glass is the same as annular band with a metallic electrode embedded inside to decrease the effective dielectric thickness and thus increase capacitance. This also lowers the voltage rating. Quartz has the best voltage rating and has the highest Q. Sapphire's high dielectric constant combined with a high Q and voltage rating make it the best overall dielectric, but also the most expensive.

Voltage Ratings

All ratings are in D.C. RF voltage ratings are dependent on many factors including frequency, continuous wave (CW) or pulse use, and the RF current. The usual RF failure mode in CW application is a thermal breakdown inside the dielectric. However, in pulse applications the heat often does not build up and parts can withstand higher current levels. Breakdowns tend to occur in the air gap without permanent damage. Care in rounding corners and the addition of corona rings can help. Most applications are different and we cannot duplicate them here in our testing. Note the comparative data in the box on page 2.

FIG. 1

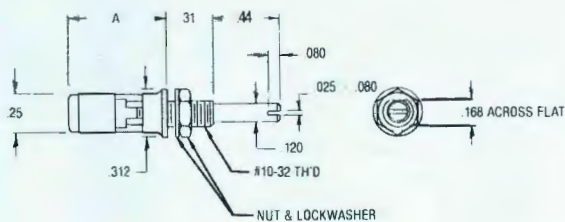


FIG. 2

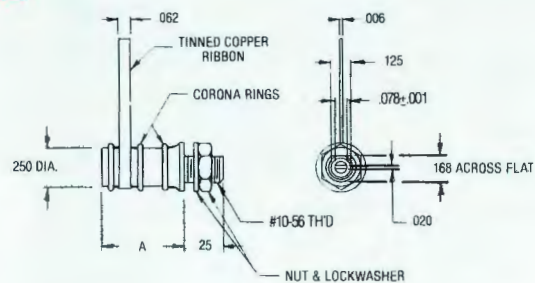


FIG. 3

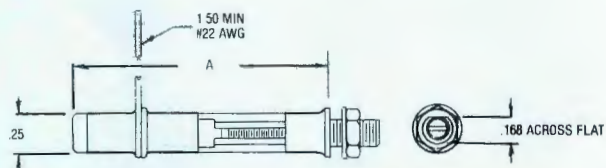


FIG. 4

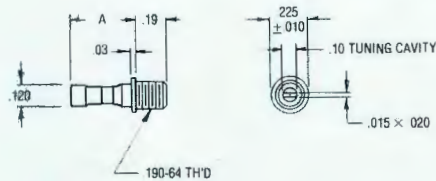


FIG. 5

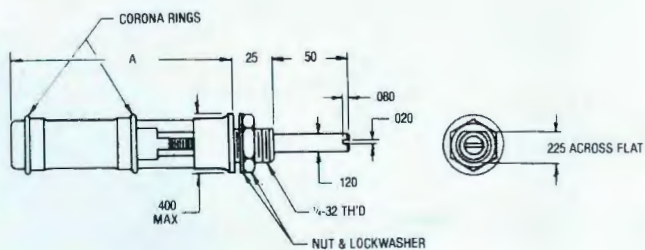


FIG. 6

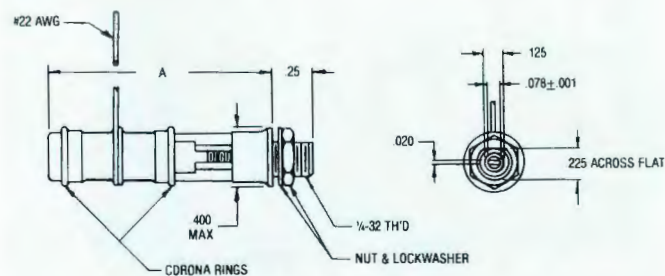
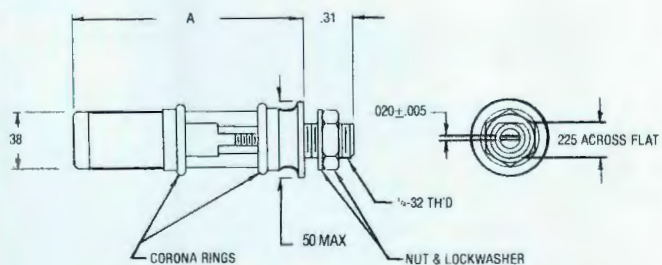


FIG. 7



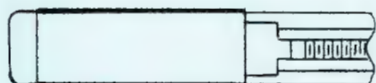
| IN | | MM | | IN | | MM |
|-------|---|------|--|-------|---|-------|
| 0.001 | — | 0.03 | | 0.300 | — | 7.62 |
| 0.005 | — | 0.13 | | 0.310 | — | 7.87 |
| 0.006 | — | 0.15 | | 0.312 | — | 7.92 |
| 0.015 | — | 0.38 | | 0.323 | — | 8.20 |
| 0.020 | — | 0.51 | | 0.380 | — | 9.65 |
| 0.025 | — | 0.64 | | 0.400 | — | 10.16 |
| 0.030 | — | 0.76 | | 0.420 | — | 10.67 |
| 0.036 | — | 0.91 | | 0.430 | — | 10.92 |
| 0.060 | — | 1.52 | | 0.440 | — | 11.18 |
| 0.062 | — | 1.57 | | 0.500 | — | 12.70 |
| 0.078 | — | 1.98 | | 0.531 | — | 13.49 |
| 0.080 | — | 2.03 | | 0.630 | — | 16.00 |
| 0.090 | — | 2.29 | | 0.960 | — | 24.38 |
| 0.100 | — | 2.54 | | 1.000 | — | 25.40 |
| 0.120 | — | 3.05 | | 1.020 | — | 25.91 |
| 0.125 | — | 3.18 | | 1.218 | — | 30.94 |
| 0.168 | — | 4.27 | | 1.300 | — | 33.02 |
| 0.190 | — | 4.83 | | 1.380 | — | 35.05 |
| 0.225 | — | 5.72 | | 1.500 | — | 38.10 |
| 0.235 | — | 5.97 | | 1.670 | — | 42.42 |
| 0.250 | — | 6.35 | | 1.760 | — | 44.70 |
| 0.281 | — | 7.14 | | | | |

Non-Magnetic Precision Trimmer Capacitors

| Type | Capacitance (pF) | | Q 20 MHz | DCWV | Dielectric | Non-Rotating Piston | Figure | "A" Dim. |
|----------|------------------|------------|-------------|------|------------|------------------------|---------------------------------|-----------|
| | From Below | To Above | | | | | | |
| V2105 | 0.4 | 3.5 | 2000 | 1250 | Quartz | Yes | 1 | 0.63 |
| V2098 | 0.35 | 3.5 | 3000 | 3000 | Quartz | No | 2 | 0.53 |
| NMQM6G | 1.0 | 6.0 | 2000 | 1250 | Quartz | Yes | 3 | 0.63 |
| V5172 | 0.8 | 8.0 | 2000 | 500 | Sapphire | No | 4 | 0.42 max |
| V2102 | 0.8 | 10.8 | 2000 | 3000 | Quartz | Yes | 5 | 1.218 max |
| V2010 | 0.8 | 10.0 | 2000 | 3000 | Quartz | Yes | 6 | 1.218 max |
| V2002A | 0.9 | 12.0 | 2000 | 6000 | Quartz | Yes | 7 | 1.50 max |
| V2002B | 0.9 | 12.0 | 2000 | 6000 | Quartz | Yes | 7 with extended shaft option | 1.50 max |
| V1631 | 0.7 | 18.0 | 550 | 750 | Glass | No | 8 | 1.02 |
| NMQM22G | 1.0 | 22.0 | 2000 | 1250 | Quartz | Yes | 3 | 1.67 |
| V2101 | 5.0 ± 1.5 | 25.0 ± 2.0 | 2000 | 3000 | Quartz | Yes | 5 | 1.50 max |
| V2066 | 0.8 | 38.0 | 500 | 1250 | Glass | Yes | 9 | 1.67 |
| NMTM38G | 1.0 | 38.0 | 500 | 1250 | Glass | Yes | 3 | 1.67 |
| V2050 | 1.0 | 40.0 | 2000 | 2500 | Sapphire | Yes | 10 | 1.30 |
| NMTM120C | 2.0 | 120.0 | 350 | 1000 | Glass | Yes | 11 | 1.76 |

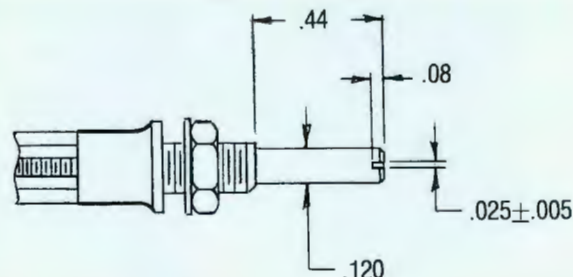
No Lead Option

Any part shown with leads can be furnished without them by adding "NL" to the part number (ex. V2098NL). You can solder directly to the dielectric, but care is required because the glass or quartz can be cracked by severe mechanical or thermal shock.



Extended Shaft Option

An extended shaft is available with any Voltronics precision trimmer with a non-rotating piston because the tuning screw only rotates and does not move in and out. This is convenient when remotely tuning long probes. To specify an extended shaft unit, add "E" to the type number (ex. NMTM120CE).



GENERAL SPECIFICATIONS

(where not specified with type numbers)

Linearity

±1% with no capacitance reversals

Insulation Resistance

10⁹ Megohms at 25°C to 125°C

Turning Torque

0.5 to 5 inch ounces

Life

Over 10,000 cycles

Temperature Coefficient

-100 to +500 ppm/°C

Dielectric Withstanding Voltage

Twice DC working voltage (listed with each part)

Capacitance Tuning Range

From below minimum to above maximum value listed for each part.
Capacitance measured at 1 MHz on Boonton Electronics 75A-S9 bridge using Voltronics V1265 guarded test jig.

Temperature Range

-55°C to 125°C

Drawing Tolerances (where not specified)

Decimal: XXX ± .016"
XX ± .03"

COMPARATIVE DATA

VOLTRONICS NON-ROTATING TRIMMER CAPACITORS VS. A COMPETITIVE ROTATING STYLE

The following data was compiled by an independent NMR research lab:

| | Voltronics Non-rotating V2002A | Competitive Rotating Style |
|--|---|------------------------------------|
| Peak RF Breakdown Voltage 50 MHz 200 MHz | 3.7 KV 3.2 KV | 2.5 KV 1.9 KV |
| Q at 200 MHz | over 450 (max sensitivity of system) | substantially less |
| Magnetism | no measureable field distortion within one cm of sample | unuseable within 7 cm of sample |

Technical drawing of a cable tie assembly. The side view shows a cable tie with a length dimension 'A' and a minimum length of 1.50 MIN #22 AWG. The assembly includes a nut and lockwasher. Dimensions include .25, .323, .96 MAX, .060, .020, #4-48 TH'D, and 1/4-32 TH'D. The end view shows a diameter of .225 ACROSS FLAT.

Technical drawing of a wire assembly. The drawing shows a side view and a cross-sectional view. The side view includes dimensions: .25, .30, .31, .125, .020, 1.0 MIN, .281, .138, .235, and .036. Labels include: #22 AWG, #20 AWG, #64 (.036) 4 HOLES, and .036. The cross-sectional view shows a circular wire with four holes.

Technical drawing of a bolt and nut assembly. The bolt is shown in a side view with dimensions: .25 (head diameter), .31 (head length), .44 (shank diameter), .08 (shank length), .025 (thread pitch), .120 (thread length), and .31 (nut length). The nut is shown in a top view with a dimension of .167 ACROSS FLAT. The assembly is labeled "NUT & LOCKWASHER".

QUANTITY

| QUANTITY | | | | | |
|----------|-------|-------|-------|-------|---------|
| 1—4 | 5—9 | 10—24 | 25—49 | 50—99 | 100—299 |
| \$ 75 | \$ 66 | \$ 60 | \$ 54 | \$ 48 | \$ 43 |
| 100 | 88 | 80 | 72 | 64 | 56 |
| 81 | 71 | 65 | 59 | 52 | 46 |
| 88 | 77 | 70 | 63 | 56 | 49 |
| 48 | 44 | 40 | 36 | 32 | 28 |
| 116 | 102 | 93 | 84 | 74 | 65 |
| 116 | 102 | 93 | 84 | 74 | 65 |
| 98 | 86 | 78 | 70 | 62 | 55 |
| 225 | 198 | 180 | 162 | 144 | 126 |
| 84 | 74 | 67 | 60 | 54 | 47 |
| 73 | 64 | 58 | 52 | 46 | 41 |
| 114 | 100 | 91 | 82 | 73 | 64 |
| 101 | 89 | 81 | 73 | 65 | 57 |
| 79 | 69 | 63 | 57 | 50 | 44 |
| 56 | 49 | 45 | 41 | 36 | 32 |

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SURCHARGES (If applicable. Don't apply to those parts which include these features.)

| | | | | | | |
|--------------------------|---|---|-----------|---|---|---|
| "E" Extended Metal Shaft | 4 | 3 | 3 | 3 | 2 | 2 |
| "NL" No Lead | | | No Charge | | | |

Voltronics
CORPORATION

UNIVERSITÉ DE LAUSANNE

INSTITUT DE CHIMIE ORGANIQUE

Rue de la Barre 2 — 1005 Lausanne, Switzerland
Téléphone (021) 44 42 50

19 November 1985

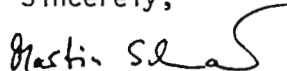
Professor Bernhard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

INEPT in ^{17}O NMR

Dear Professor Shapiro,

^{17}O NMR spectroscopy has undergone a dramatic development in recent years and may now be considered as a routine method¹⁾. There are, however, almost no experimental methods available to perform an assignment of the spectra. Usually specific enrichment, chemical shift - structure relationships etc. are employed. To overcome this problem we have used the INEPT sequence to distinguish between protonated and non - protonated oxygens. With an average coupling constant $^1J(^{17}\text{O}, \text{H})$ of 85Hz, the value of 0.0056 J^{-1} for the interpulse delay $\tau^2)$ and the addition of 0.01 M $\text{Cr}(\text{acac})_3$ to shorten the proton T_1 's we obtained good INEPT spectra of simple alcohols (^{17}O in natural abundance) within a few minutes. When trying to determine the coupling constant from the separation of the two INEPT lines it is to be realised that this distance is usually larger than the actual coupling constant. A fitting of the experimental spectrum with two lorentzian lines by a least squares procedure provided the desired results. Fig. 1 shows a typical spectrum. To study further the influence of the linewidth on the apparent coupling constant \tilde{J} in an INEPT spectrum we calculated some spectra. Fig. 2 shows the results and Fig. 3 the functional dependance of \tilde{J} on the linewidth $\Delta\nu_{1/2}$. As a general rule one can say that only for $J > \Delta\nu_{1/2}$ \tilde{J} corresponds to the true coupling constant J .

Sincerely,



Dr. Martin Schumacher

P.S. Please credit this contribution to the account of Prof. A. Merbach

- 1) J. P. Kinzinger in "NMR of Newly Accessible Nuclei", P. Lazlo, Ed., Academic Press, New York, Vol. 2, p. 75 (1983)
- 2) D. T. Pegg et al., J. Magn. Reson. 44, 32 (1981)

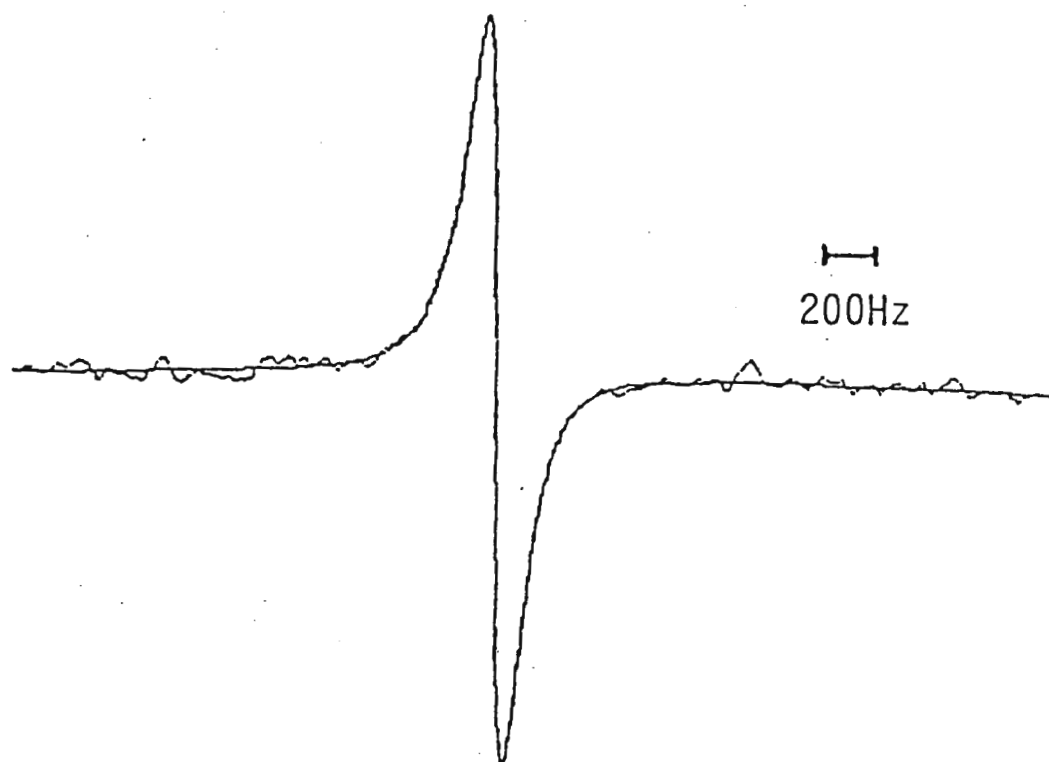


Fig. 1 Experimental ^{17}O NMR spectrum of neat ethanol (LB = 50Hz) with superimposed simulated spectrum

Measured: $\Delta\nu_{1/2} = 173\text{Hz}$, $\tilde{J} = 142\text{Hz}$

Calculated: $\Delta\nu_{1/2} = 175\text{Hz}$, $J = 81\text{Hz}$

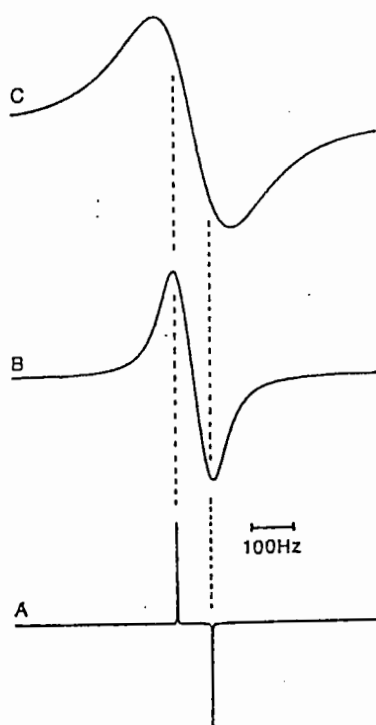


Fig. 2 Calculated INEPT spectra

- A $\Delta\nu_{1/2} = 1\text{Hz}$
- B $\Delta\nu_{1/2} = 100\text{Hz}$
- C $\Delta\nu_{1/2} = 300\text{Hz}$

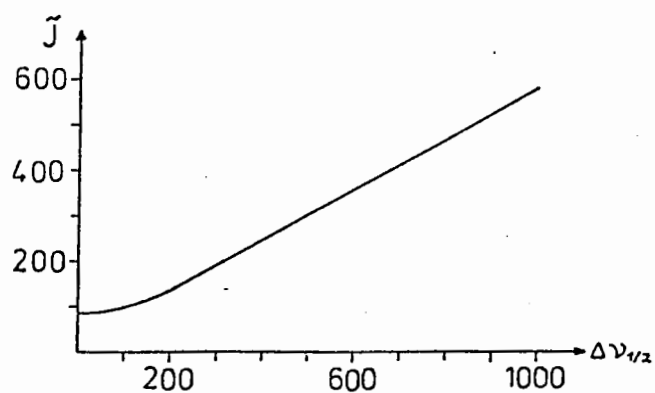


Fig. 3 Dependence of the apparent coupling constant \tilde{J} on the linewidth $\Delta\nu_{1/2}$; $J = 85\text{Hz}$

Texas A&M University NMR Newsletter - Book Reviews

Book Review Editor - W. B. Smith, Texas Christian University, Fort Worth, Texas.

"Solid State Nuclear Magnetic Resonance of Fossil Fuels:
An Experimental Approach"

by
David E. Axelson

Multiscience Publications, Ltd., P.O. Box 1464, Station B,
Montreal Quebec, Canada H3B 3L2. 1985; 226 pages;
\$56.00 plus postage and handling.

This handy book would be better subtitled "Everything You Ever Wanted to Know about Quantitative NMR but Were Afraid to Ask." Quantifying high resolution solid state NMR data on fossil fuels is perhaps the most difficult task facing today's NMR spectroscopist. Axelson uses the problems inherent to fossil fuel work as effective examples for a concise but comprehensive treatment of a multitude of effects that could contribute to errors in carbon counting.

The book begins with a brief introduction to coal structure that reviews the complex nature of these materials and defines such terms as "rank," lipinites," and "macerals." There is a short chapter on the fundamentals of solid state NMR, followed by one on relaxation processes and the pulse sequences used to measure them. Next comes a chapter on quantitative analysis, in which results from fossil fuel studies are interwoven with those of model polymers. Further chapters deal with artifacts, line broadening mechanisms, and methods for resolution enhancement. The final chapter provides a general survey of the CPMAS literature on fossil fuels.

The index is complete and the presentation is organized. The book could have benefited from a careful editing, perhaps catching the typo in the first sentence of the first paragraph of the Foreword, perhaps removing the overabundance of commas (count 'em - six in one sentence in Chapter 2!), and maybe evening out some of the "down-home" phraseology ("...this is no excuse for ignoring the true potential of the solid state NMR techniques..."). Overall the book is well done and contains many helpful tables. The literature is covered through the end of 1984.

This is a very useful book for several reasons. First, most of the fossil fuel literature has been published in Fuel, a journal that is not routinely perused by most chemists. This book serves to focus, organize, and review the many excellent CPMAS papers that have appeared in Fuel and in other petrochemical journals. Many of the techniques and considerations in these papers are relevant to CPMAS analysis of other materials, and these methods are summarized in the book.

In addition, this book deals with many practical and experimental issues facing the NMR spectroscopist. Acoustic ringing, baseline roll, digitization errors, and magic angle missetting are among the numerous topics that Axelson addresses and illustrates with abundant diagrams. There is even a section on troubleshooting.

Finally, the book does an excellent job of summarizing those considerations necessary for obtaining quantitative CPMAS results.

This book is an excellent reference volume, not only for those involved in fossil fuel characterization, but for any user of high resolution solid state NMR spectroscopy.

L.W. Jelinski
AT&T Bell Laboratories
Murray Hill, New Jersey

國立清華大學
NATIONAL TSING HUA UNIVERSITY

HSINCHU, TAIWAN 300

REPUBLIC OF CHINA

DEPARTMENT OF CHEMISTRY

CHEMISTRY BUILDING

November 14, 1985

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX77843

¹H NMR Assignment of Aromatic Region for Cardiotoxin I (Naja
Naja Atra) by phase sensitive 2D experiments

Dear prof. Shapiro:

This contribution is to begin our subscription to the TAMUNMR newsletter.

The phase sensitive 2D experiment have been developed and demonstrated recently that it has several advantages compared with that of absolute value mode. We obtained phase sensitive mode 2D experiments with time proportional phase increment (TPPI) approach. Combining scalar (COSY) and NOE (NOESY) connectivity, we are able to assign all the aromatic proton resonances of cardiotoxin I (Naja Naja Atra).

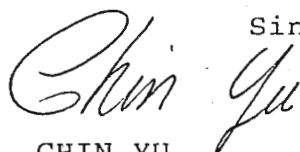
Shown in the Figure is a combination plot of two phase sensitive spectra (DQF-COSY/NOESY) of a 20 mM cardiotoxin I in D₂O. Double quantum filtering technique was applied to remove the solvent peak (HOD) and isolated methyl groups. Spectrum(a) showed the slice at the position labeled an arrow(+) in DQF-COSY spectrum. The anti-phase fine structure of cross peaks in such experiment is clearly observed. Spectrum(b) is conventional 1D reference with resolution enhancement with sine bell window function.

In phase sensitive NOESY spectrum, the diagonal and cross peaks are both negative (negative NOEs, $\omega_C^2 \tau_C^2 \gg 1$). With these two phase sensitive spectra, we assigned the aromatic proton resonances of cardiotosin I as showed on top of spectrum (b).

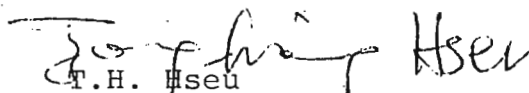
The phase sensitive DQF-COSY and NOESY experiments were recorded on our Bruker AM-400 spectrometer equipped with an Aspect-3000 computer and an array processor. Data were collected as 2Kx1K. A shifted sine bell (45°) window function was applied on both dimensions, and the spectra were not symmetrized.

Please credit this letter to Chin Yu's account.

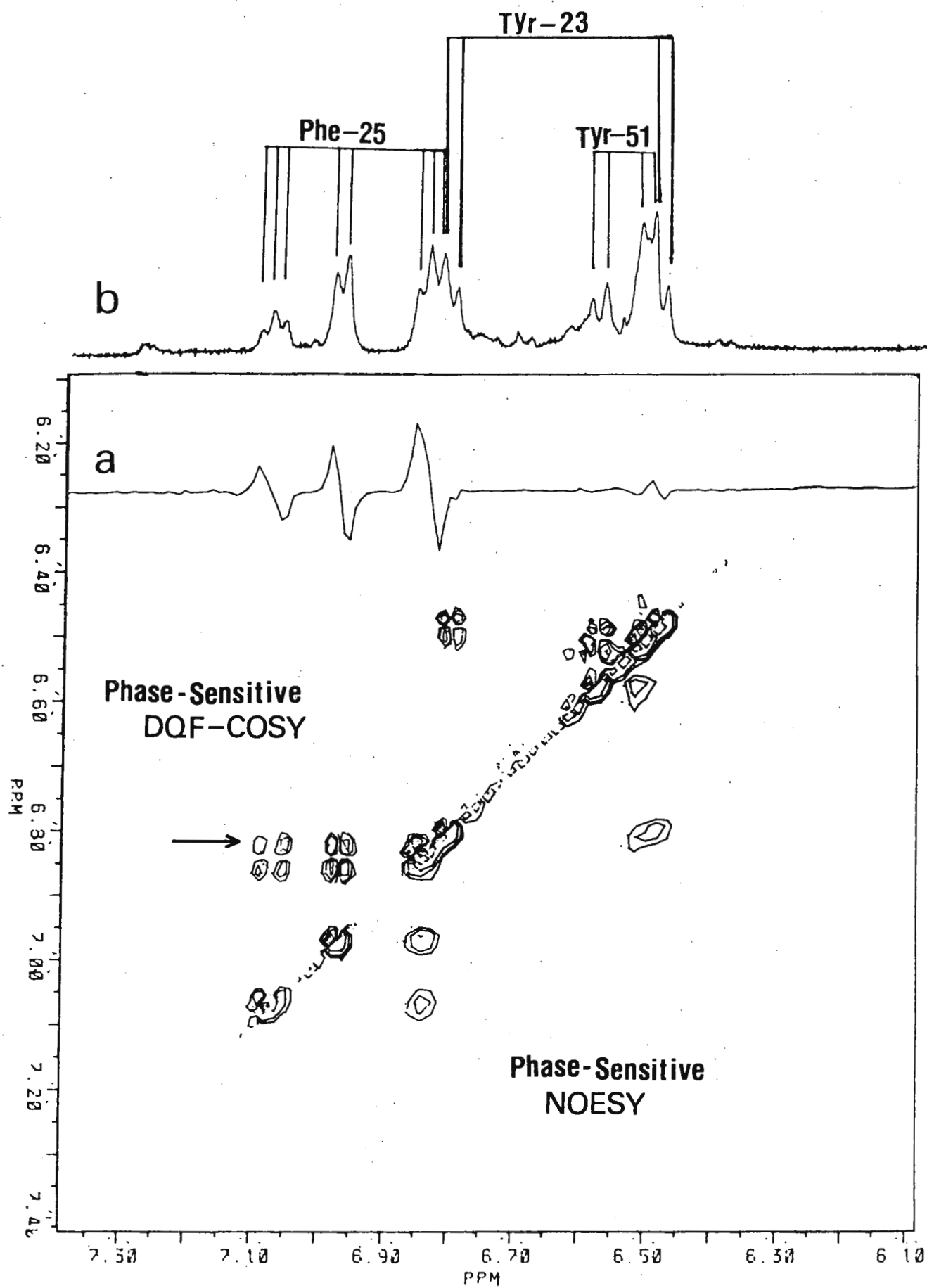
Sincerely,



CHIN YU
Associate professor
of Chemistry



T.H. Hsueh
Chairman
Institute of Life Science





Rensselaer Polytechnic Institute Troy, New York 12180-3590

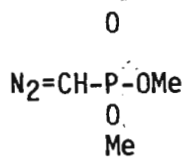
November 7, 1985

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

Title: Interesting Shifts and ^{31}P Couplings from 2D ^1H - ^{13}C Correlated Spectrum

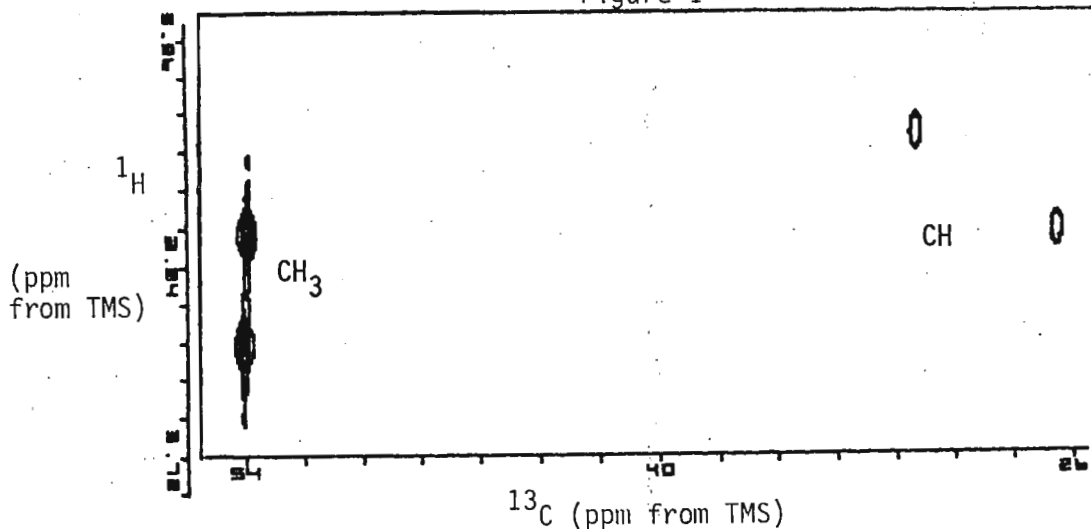
Dear Barry:

Shown in Figure 1 is a two-dimensional proton-carbon correlated spectrum of the compound:



The correlated spectrum was obtained to help resolve the proton spectrum which was somewhat overlapped in CDCl_3 and as a double check on the unusual chemical shift assignments of the methoxy carbons relative to the CH resonance. In the process, all four phosphorous couplings can be resolved, the most difficult being the $J_{\text{C}-\text{P}} = 5 \text{ Hz}$ of the methoxy carbons which needed extreme expansion (see Figure 2) to discern. The relative angles of the resonances in the contour plot would also indicate that the ^{31}P coupling to the methyls is opposite in sign to that of the methine. The other coupling constants are $^3J_{\text{H}(\text{CH}_3)-\text{P}} = 12 \text{ Hz}$, $^1J_{\text{C}(\text{CH})-\text{P}} = 231 \text{ Hz}$ and $^2J_{\text{H}(\text{CH})-\text{P}} = 11 \text{ Hz}$.

Figure 1



(continued on page 49)

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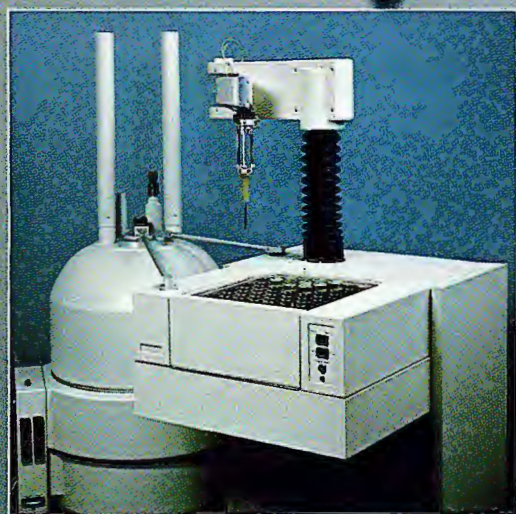


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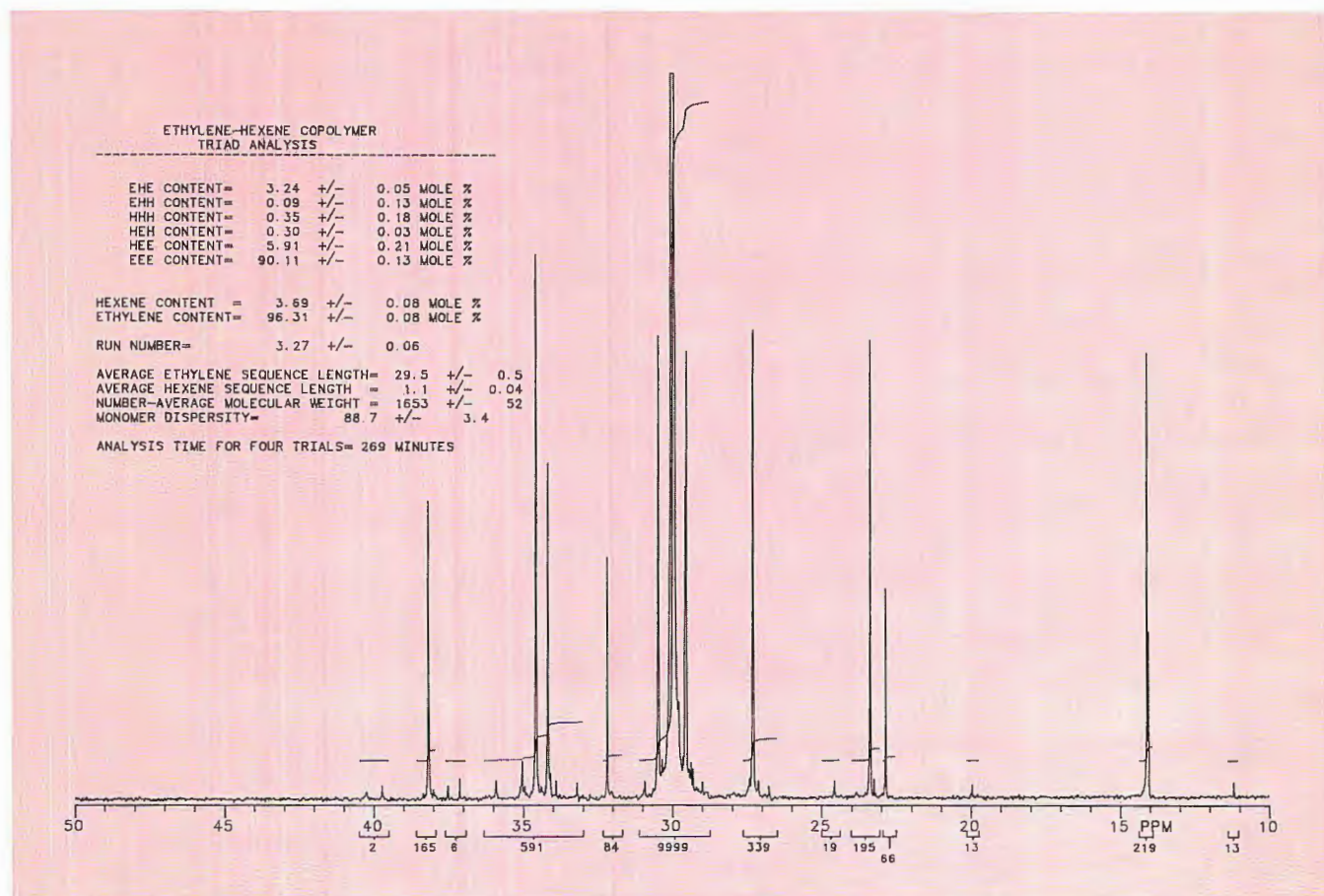
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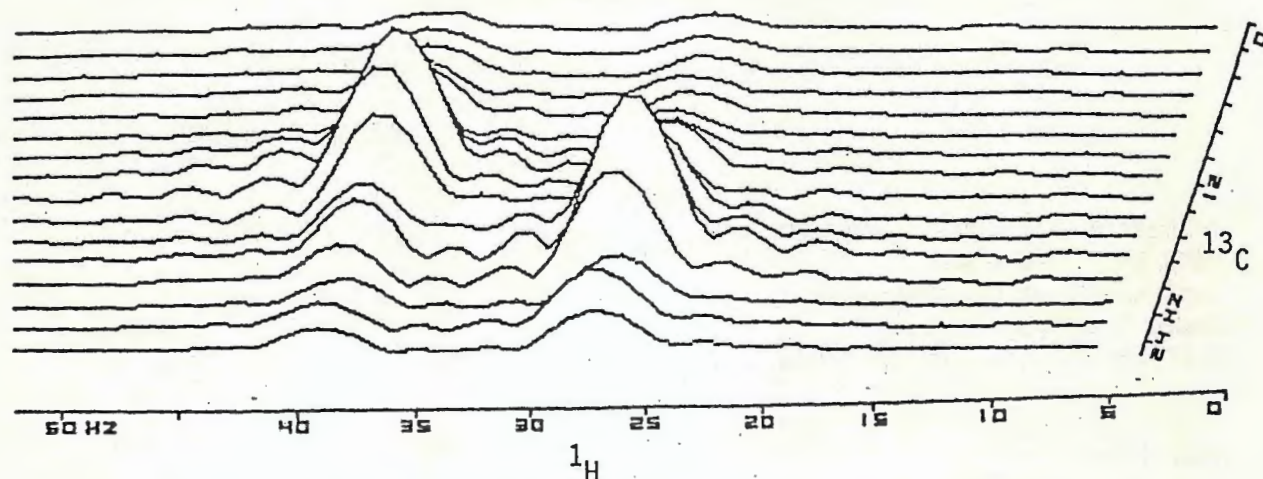
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(continued from page 46)

Figure 2



The two-dimensional data was collected using a standard heteronuclear correlated pulse sequence on our Varian XL-200. We collected 128 incremented carbon spectra of 100 acquisitions each, assuming a J_{CH} of 165 Hz. The acquisition time was 0.6 sec, and the respective carbon and proton spectral widths were 1700 and 400 Hz. The final array was 2048 x 1024 points.

Sincerely yours,

Herb Schwartz *Eric Yau*

Herbert M. Schwartz and Eric Yau

HMS:sd



TOWSON STATE UNIVERSITY

TOWSON, MARYLAND, 21204

Department of Chemistry

(301) 321-3058

22 October 1985

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

Dear Barry:

Water Suppression Techniques for a JEOL FX-90Q

Our research is directed at the modes of binding to DNA exhibited by various intercalating acridine dyes, measured by $^1\text{H-NMR}$. The solutions of DNA-acridine dye complexes are of necessity very dilute, and even though we are using D_2O as the solvent, the residual water peak is intense enough to cause a dynamic range problem. Of the solvent suppression techniques in the literature, the most promising is P.J. HORE's $133\bar{1}$ pulse sequence (1):

$$\begin{aligned} \alpha(X)-T-3\alpha(-X)-T-3\alpha(X)-T-\alpha(-X) \text{ ACQ}+ \\ \alpha(-X)-T-3\alpha(X)-T-3\alpha(-X)-T-\alpha(X) \text{ ACQ}- \end{aligned}$$

Where α is the pulse width and T the pulse interval. The second part of the sequence corrects any imperfections in the 180° transmitter phases. The transmitter phases are cycled 90° every two scans as in the CYCLOPS method (2), and the acquisition pattern is cycled in the same manner. The following overall sequence results:

$$\begin{aligned} \alpha(X)-T-3\alpha(-X)-T-3\alpha(X)-T-\alpha(-X) \text{ ACQ } 0^\circ \\ \alpha(-X)-T-3\alpha(X)-T-3\alpha(-X)-T-\alpha(X) \text{ ACQ } 180^\circ \\ \alpha(Y)-T-3\alpha(-Y)-T-3\alpha(Y)-T-\alpha(-Y) \text{ ACQ } 90^\circ \\ \alpha(-Y)-T-3\alpha(Y)-T-3\alpha(-Y)-T-\alpha(Y) \text{ ACQ } 270^\circ \\ \alpha(-X)-T-3\alpha(X)-T-3\alpha(-X)-T-\alpha(X) \text{ ACQ } 180^\circ \\ \alpha(X)-T-3\alpha(-X)-T-3\alpha(X)-T-\alpha(-X) \text{ ACQ } 0^\circ \\ \alpha(-Y)-T-3\alpha(Y)-T-3\alpha(-Y)-T-\alpha(Y) \text{ ACQ } 270^\circ \\ \alpha(Y)-T-3\alpha(-Y)-T-3\alpha(Y)-T-\alpha(-Y) \text{ ACQ } 90^\circ \end{aligned}$$

The optimum α is a pulse width chosen such that 64α is a multiple of 2π . The transmitter offset is aimed at the frequency ν of the water signal, and the ideal T is $1/2\nu$. This pulse sequence has suppressed the HOD peak as much as 1000-fold, without significant spectral distortion. However, our JEOL FX-90Q "cyclopses" every acquisition and cannot be programmed to cycle transmitter phases every two acquisitions, without violating the JEOL software. A program that explicitly commanded

each phase shift would exceed the 64 address capacity of the PG 200 pulse programmer. Thus, we tried a simpler version, which uses the $1\bar{3}3\bar{1}$ sequence and a ($0^\circ, 90^\circ, 180^\circ, 270^\circ$) acquisition pattern, but omits the 180° phase correction. This program produces less than 100-fold suppression. Next we attempted a sequence closer to Hore's in effect:

$$\begin{aligned} \alpha(X) - T - 3\alpha(-X) - T - 3\alpha(X) - T - \alpha(-X) & \text{ ACQ } 0^\circ \\ \alpha(Y) - T - 3\alpha(-Y) - T - 3\alpha(Y) - T - \alpha(-Y) & \text{ ACQ } 90^\circ \\ \alpha(-X) - T - 3\alpha(X) - T - 3\alpha(-X) - T - \alpha(X) & \text{ ACQ } 180^\circ \\ \alpha(-Y) - T - 3\alpha(Y) - T - 3\alpha(-Y) - T - \alpha(Y) & \text{ ACQ } 270^\circ \end{aligned}$$

Followed by the phase correcting sequence:

$$\begin{aligned} \alpha(-X) - T - 3\alpha(X) - T - 3\alpha(-X) - T - \alpha(X) & \text{ ACQ } 180^\circ \\ \alpha(-Y) - T - 3\alpha(Y) - T - 3\alpha(-Y) - T - \alpha(Y) & \text{ ACQ } 270^\circ \\ \alpha(X) - T - 3\alpha(-X) - T - 3\alpha(X) - T - \alpha(-X) & \text{ ACQ } 0^\circ \\ \alpha(Y) - T - 3\alpha(-Y) - T - 3\alpha(Y) - T - \alpha(-Y) & \text{ ACQ } 90^\circ \end{aligned}$$

Although the 180° phase corrections, are still not programmed on alternate scans, this version has attained 930-fold suppression. The parameters were optimized as follows: 360° corresponds to $104 \mu\text{s}$ on our instrument, so $1.625 \mu\text{s}$ is the smallest ideal pulsewidth α . $1.600 \mu\text{s}$ is the closest to this that we are able to set on our instrument. Although theoretically T should be 1.18 ms , we have found that a sharp maximum in suppression is reached at $T = 1.249 \text{ ms}$ when $\alpha = 1.6 \mu\text{s}$. There is some distortion, however. We will soon acquire an attenuator, and possibly it will enable us to make finer adjustments in α which will result in less distortion.

Any suggestions for improving the program would be appreciated. We acknowledge the technical assistance and helpful discussions provided by Dr. Thomas Martin. We also wish to thank Dr. Eugene Mazzola, and Dr. William Bearden for help and advice.

Yours Sincerely

Richard S. Preisler

Richard S. Preisler

Eileen Katsimpiris

Eileen Katsimpiris

REFERENCES.

1. P.J. HORE, J. Magn. Reson. 54, 146 (1983).
2. D.I. HOULT, R.E. RICHARDS, Proc. R. Soc. London Ser. A 344, 311 (1975)

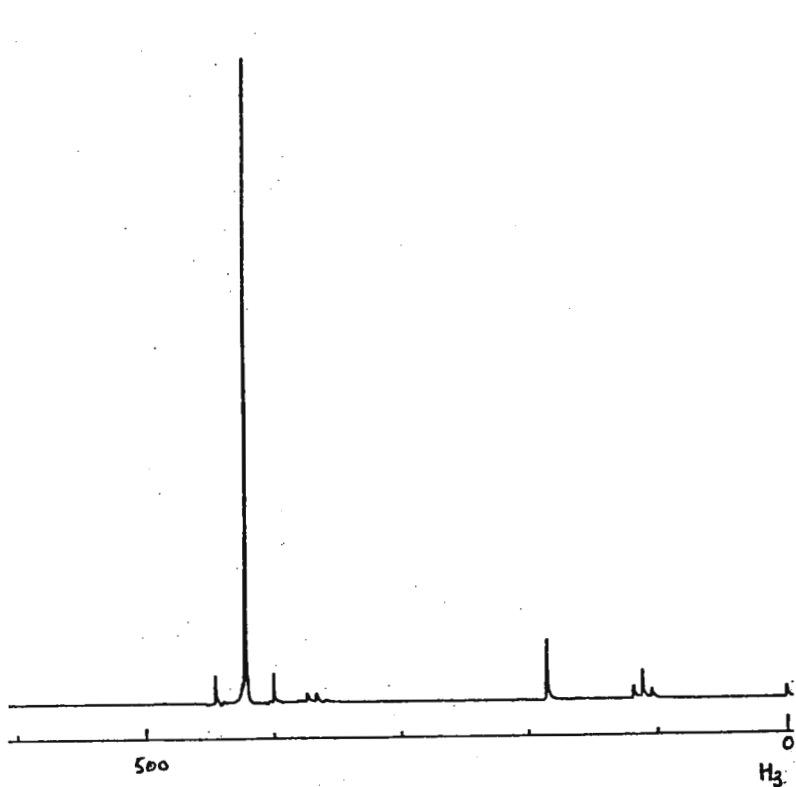


Figure 1. Single pulse spectrum of Ethyl Acetate 15% by volume in H_2O 20%, D_2O 65%.

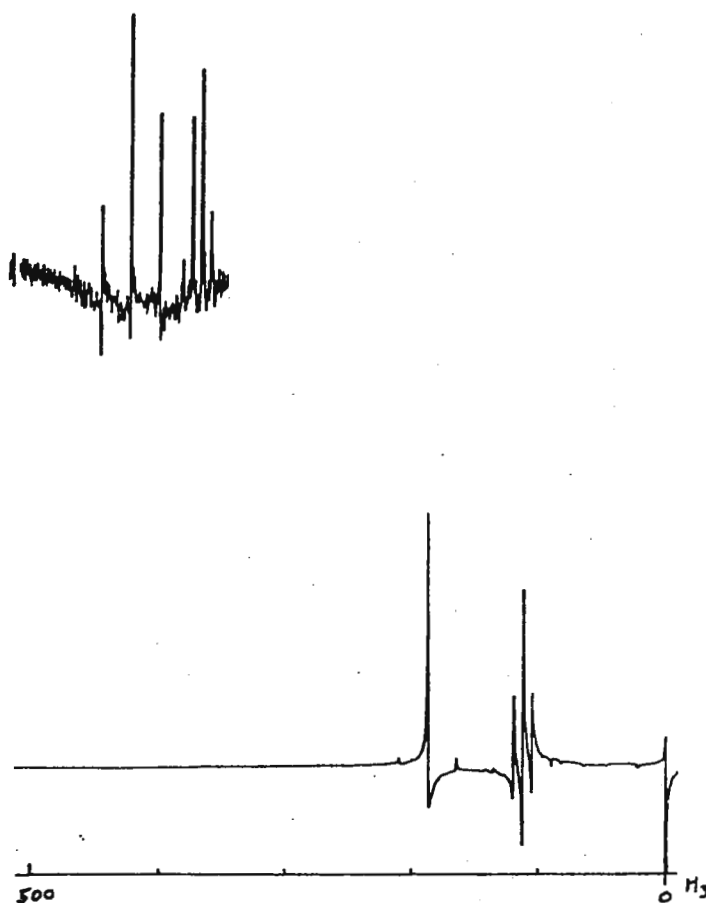


Figure 2. Water suppressed spectrum, same sample.

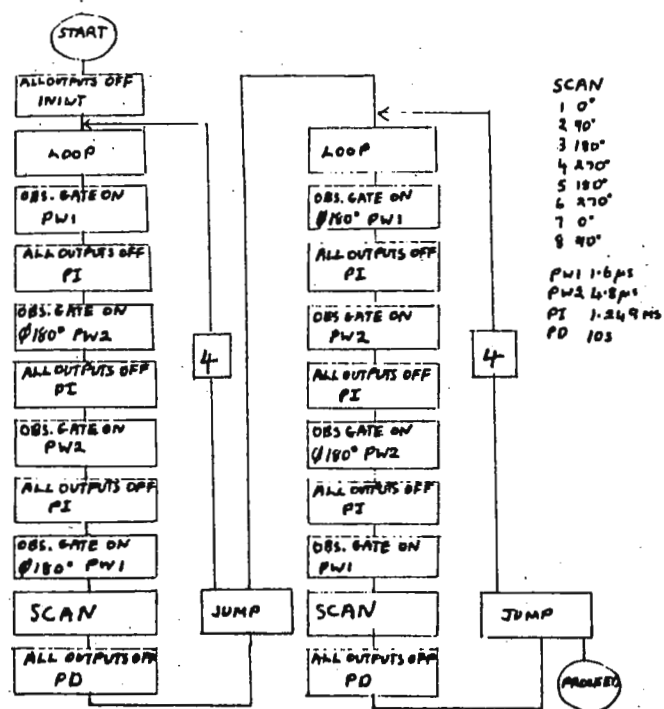
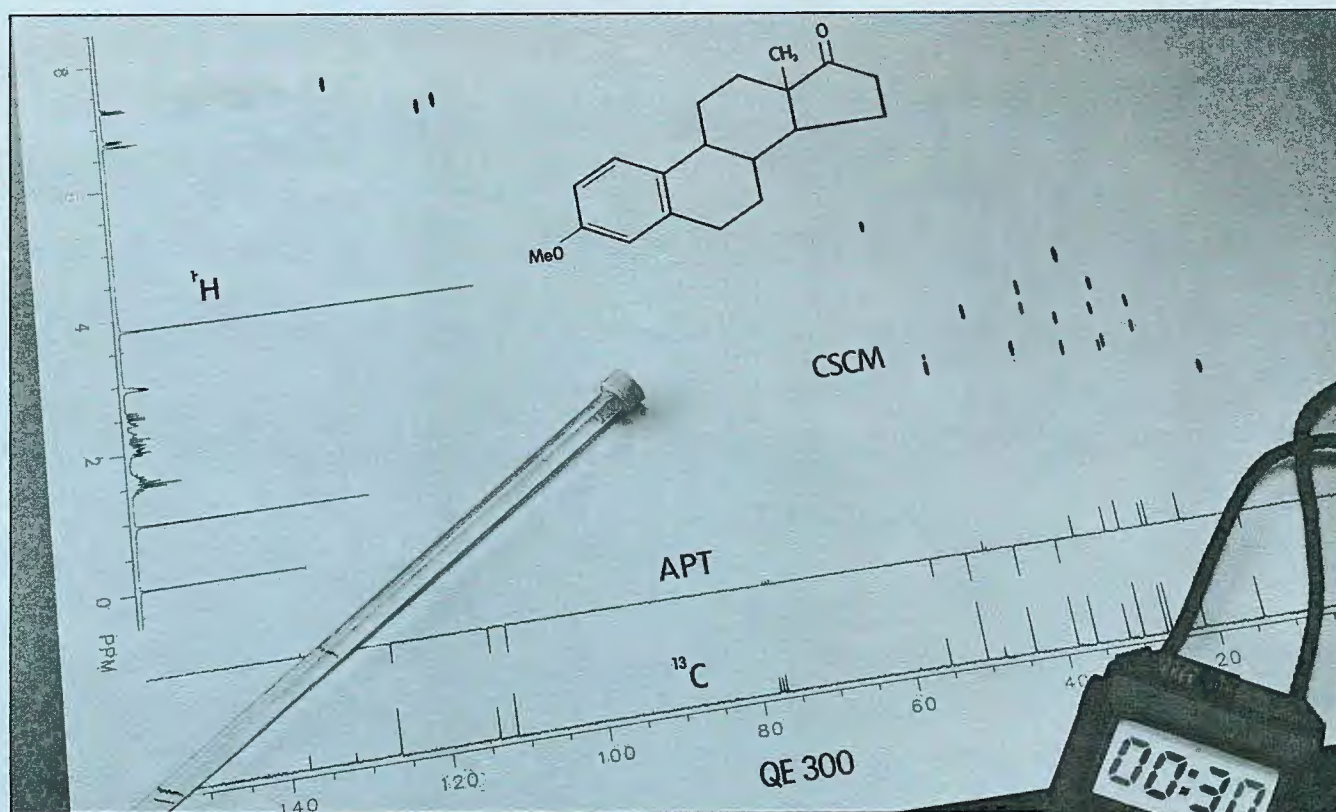


Figure 3. Flow chart of our ^{133}I program. Transmitter phases are CYCLOPED automatically 90° every Scan by the FX-90Q.



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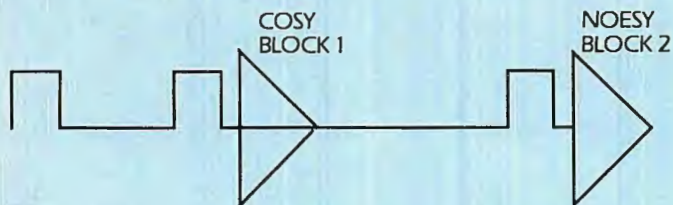
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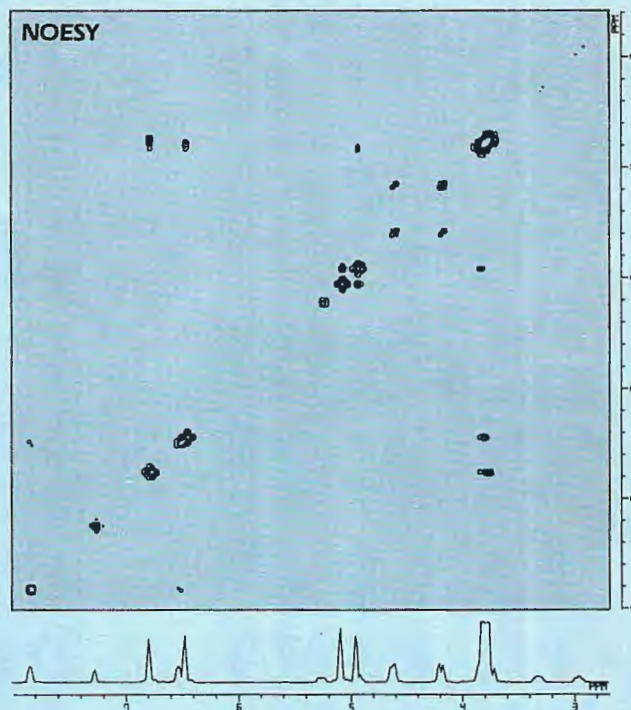
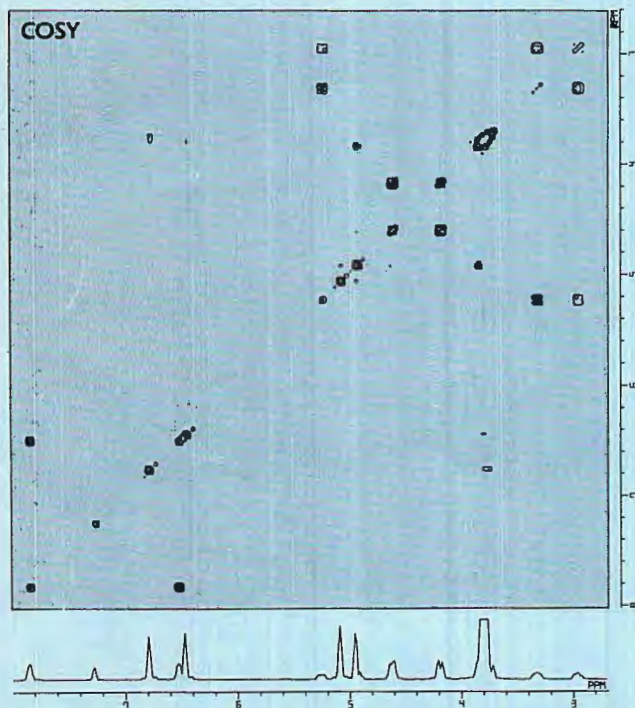
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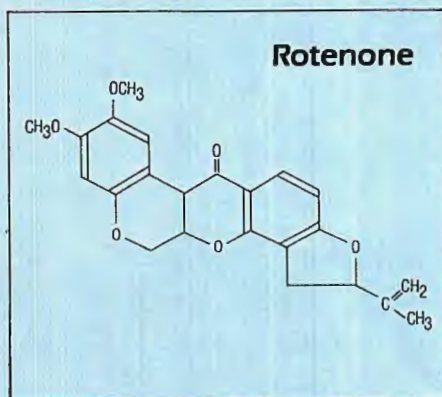


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