TEXAS A&M UNIVERSITY

NMR NEWSLETTER

NO. 330

MARCH 1986

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Wilmad Glass Company, Inc. . . . inside front cover

FORTHCOMING NMR MEETINGS (Additional listings are solicited)

8th Rocky Mountain Regional Meeting - June 8-12, 1986; Denver Convention Complex; Denver, Colorado; Meeting Chairman: William E. Beard, USDA-ARS, P.O. Box E, Ft. Collins, Colorado 80522.

4th International Symposium on NMR Spectroscopy - June 16-20, 1986; Tabor, Czechoslovakia; Chairman: Dr. Petr Trska, NMR Laboratory, Institute of Chemical Technology, Suchbatarova 5, CS-166 28 Prague 6, Czechoslovakia.

Scuola Internazionale di Fisica E. Fermi: The Physics of NMR Spectroscopy in Biology and Medicine - June 24-July 4, 1986; Varenna, Italy; Chairman: Professor B. Maraviglia, Dipartimento di Fisica, Universita degli Studi, "La Sapienza," P. le Aldo Moro, I-00185 Roma, Italy.

International Society of Magnetic Resonance (ISMAR), 9th Meeting - June 29-July 5, 1986; Hotel Gloria; Rio de Janeiro, Brazil. Chairman: N.V. Vugman, Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.

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.

28th Rocky Mountain Conference - August 3-7, 1986; Radisson Hotel; Denver, Colorado; Conference Chairman: R. Barkley, CIRES, University of Colorado, Boulder, Colorado 80309, (303) 492-1158. Abstract Deadline: March 21, 1986. NMR Chairmen: J. Haw, Dept. of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966, and F. Miknis, Western Research Institute, Box 3395, University Station, Laramie, Wyoming 82071, (307) 721-2307.

XXIII Congress Ampere on Magnetic Resonance - September 15-19, 1986; Rome, Italy; XXIII Congress Ampere, Dipartimento di Fisica, Universita de Roma, "La Sapienza," P. le Aldo Moro 5, I-00185 Roma, Italy.

Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XIII) - September 28-October 3, 1986; St. Louis, Missouri; Program Manager: Dr. Sydney Fleming, FACSS (Titles), 24 Crestfield Road, Wilmington, Delaware 19810.

1986 Eastern Analytical Symposium - October 20-24, 1986; Hilton Hotel, New York; see Newsletter No. 329, p. 23 and Newsletter No. 325, p. 27.

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. 332 (May) ---------- 25 April 1986

No. 333 (June) ---------- 30 May 1986

Universität Bern

Institut für organische Chemie

CH-3012 Bern, Freiestrasse 3
Telefon 031 65 43 11

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

6.1.1986

HETERO-NOE-DIFFERENCE SPECTRA

Dear Professor Shapiro

in the course of developping and optimizing new techniques for the elucidation of unknown structures we recognized the great value of heteronuclear NOE experiments. Confronted with the problem to connect molecular fragments of known structures (COSY, C-H-COSY, ...) separated by quaternary carbons, the NOE's measured for these quaternary barriers can be very helpful. Applying the cycling scheme recently proposed for the homonuclear case [1], we could improve the selectivity dramatically [2]. NOE's are detected most conveniently using the difference (FID, spectra) technique. The optimization of the experiment with respect to selectivity and sensitivity is one important point - the presentation of aesthetic spectra is another.

In case a) the number of entries in the individual frequency lists used for the irradiation of the selected protons is different. Therefore different decoupler offsets are used for broadband decoupling in the acquisition part of the individual spectra. This leads to a bad suppression of the signals of proton bearing carbons in the difference spectra and more severe eventually to distorted intensities for the quaternary signals.

In case b) the number of frequency entries in the individual lists is the same (or a multiple) and moreover the value of the last entry used for broadband decoupling during acquisition is the same for all spectra. This leads to the excellent suppression of most of the proton bearing carbons.

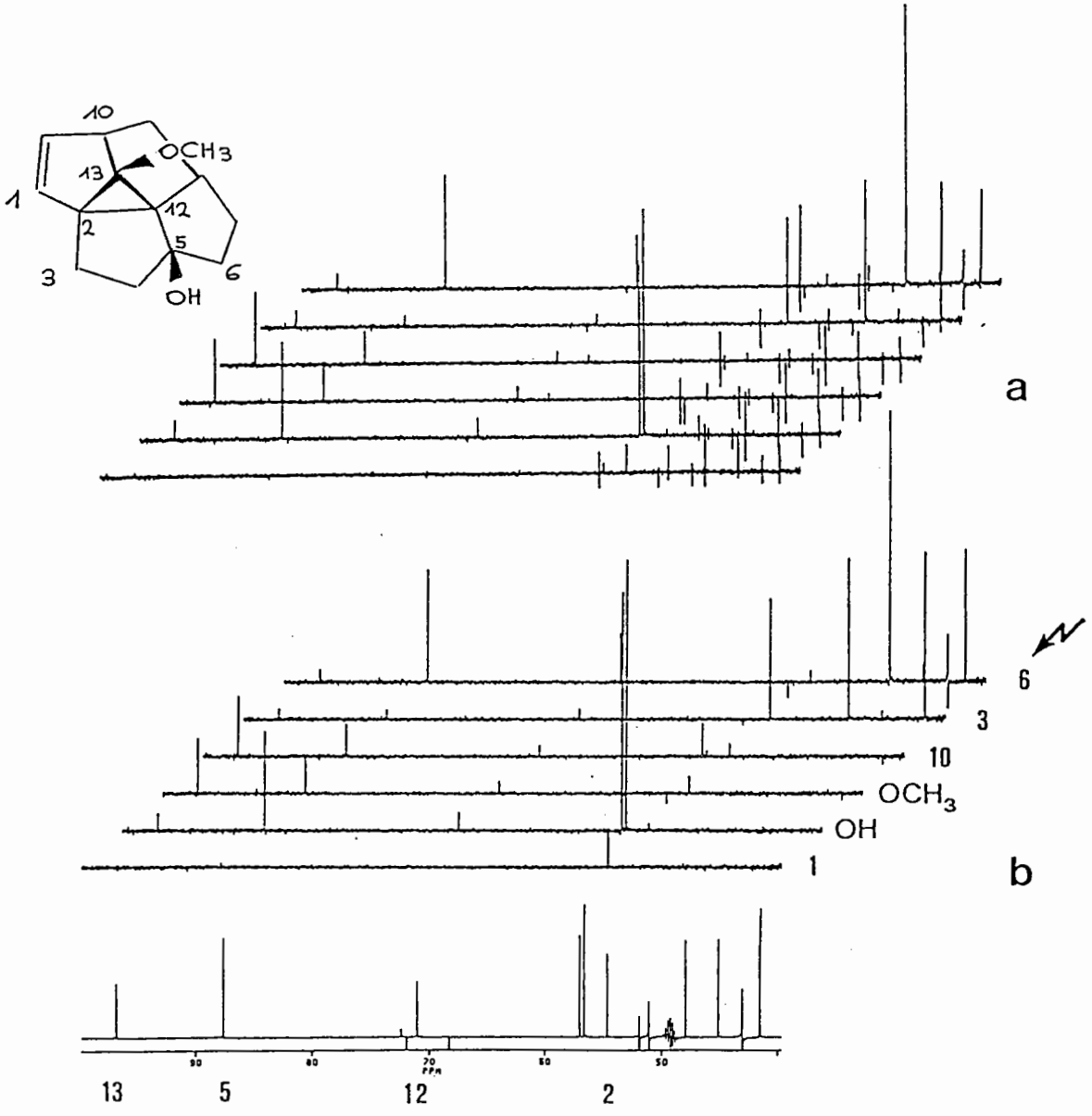
The residual (absorptive) signals of some non-quaternary carbons are caused by the simultaneous irradiation of one of the corresponding satellite signals and the selected proton multiplet which accidentely have the same proton resonance frequency. This generates NOE not only for quaternary but also for some non-quaternary carbons.

Sincerely yours

Dr. P. Bigler

1 D. Neuhaus, J. Magn. Reson. 53 (1983) 109

2 P. Bigler, M. Kamber, Angew. Chem. Int. Ed. 24,(1985) 705



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PRAHA 6 - SUCHDOL

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

January 27, 1986

re: Faster plotting of symmetrical 2D contour maps

Dear Barry,

plotting COSY spectra of large spin systems is very time consuming on XL-200 equipped with Nicolet Zeta plotter (e.g. the contour plot of a tetrasaccharide takes 2 hours). Almost half of this time is vasted since the contour is symmetrical around the main diagonal. Simple modification of the Varian provided DRXCON program allows plotting of either upper or lower triangular half of the data matrix which both contain the same information.

Plotting only one half of the data matrix saves not only the plotting time but also reduces the requirements on the size of PLOTSPOOL (on V77-200 systems) so the software disk need not be reconfigurated for most of the 2D plots. The plot in Fig. 1 was complete in 8 min and 15 sec. only while the standard full plot of the same size took 16 min.

Details of program modification are available upon request.

Sincerely yours,

Jan

Jan Schraml

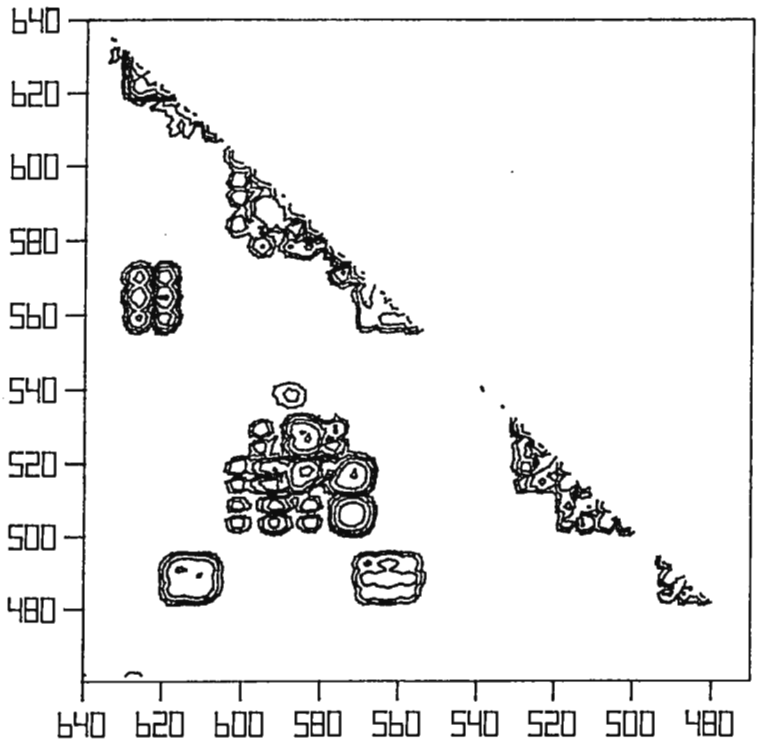

Fig. 1

National Chemical Research Laboratory
CSIR, P O Box 395, Pretoria 0001, Republic of South Africa

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Dr P L Wessels, Structural Chemistry Division, NCRL, P O Box 395, Pretoria 0001, Republic of South Africa.

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, february 3, 1986.

Title: The ABC case revisited.

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

Dear professor Shapiro:

Even since my good old times in Uppsala University (Sweden) with the late Ragnar Hoffman (did you ever meet him?) I was intrigued by the apparent simplicity of the ABC case. The Hamiltonian looks so simple! It should be possible to calculate somehow the spin-spin and shielding constants directly from the Hamiltonian, without calculating the spectrum! We have the invariant properties of the matrices to play with or, if you wish, the Vieta relations between the roots and the coefficients of the characteristic equations.

During my last vacations I was able to put this into a set of six equations (two lineal, two quadratic and two cubic) only to find out that I rediscovered Whitman's equations (D.R. Whitman, J.Mol.Spectr. vol 10, page 250, 1963). The only question now was how to solve these equations, since Whitman did not give an answer to this.

Modern computer technology gave me an answer. The solution is not difficult and a short note on the subject is due to appear shortly in the Journal of Magnetic Resonance. For the eventually interested reader a listing of the program (in HP-basic language) is available on request.

Yours, sincerily

Dr. V.J. Kowalewski.

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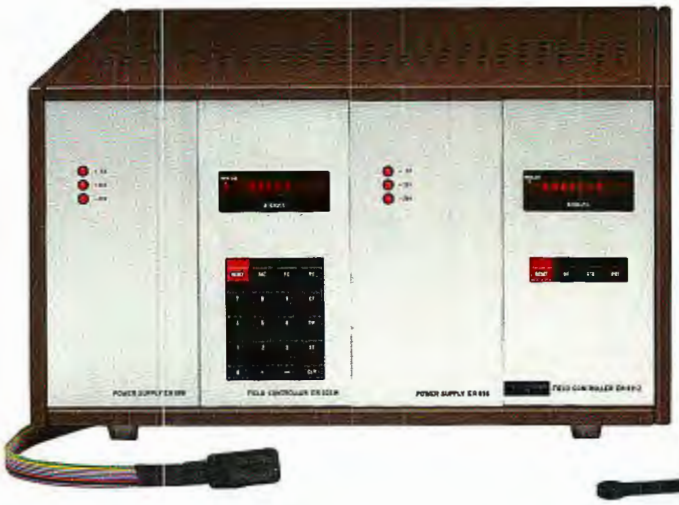

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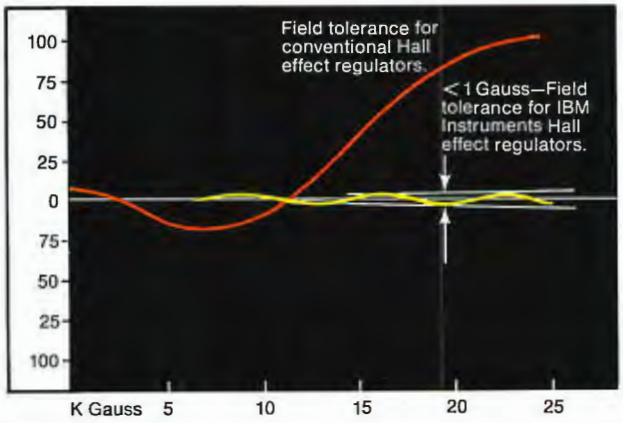

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February 22, 1986

Professor B.L. Shapiro
Editor, TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Temperature Dependence of Relative LIS

Dear Barry:

Milan Hajek (Prague Institute of Chemical Technology) and I have been working jointly on the problem of binuclear shift reagents over the last few years. During his visit to U.S.F. in 1983-84 we generated sufficient data that we are still discovering an occasional tidbit of new information. This is illustrated by some data we recently analyzed for the temperature dependence of the relative induced shifts for the cyclohexene-AgYb(fod)$_4$ system.

Table. Temperature Dependence of LIS for Cyclohexene-AgYb(fod)$_4$

T, °C	H-1, H-2	H-3, H-6	H-4, H-5
30	1.00	0.59	0.46
10	1.00	0.60	0.45
0	1.00	0.60	0.48
-10	1.00	0.61	0.49
-20	1.00	0.61	0.49
-30	1.00	0.61	0.50
-40	1.00	0.63	0.51
-50	1.00	0.63	0.52

[a]AgYb(fod)$_4$ induced shifts; [b]LIS normalized to H-1, H-2.

Joop Peters and I reported last year (TAMU Newsletter 319-26) that a temperature dependence of the relative LIS is observed when there is a significant contact contribution to the total induced shift. The relative shifts reported here for cyclohexene are essentially constant (standard deviations are 2-3%), and this provides further support for our arguments that the LIS induced by binuclear shift reagents are largely, if not entirely, pseudocontact in origin (D.J. Raber and M. Hajek, Magn. Reson. Chem., in press).

Sincerely,

Douglas J. Raber

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State University of Utrecht

Institute of Molecular Biology

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The Netherlands
Telephone 030 - 532995

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

Date January 28, 1986
Your reference
Our reference
Subject

Cardiotoxicity of the anti-cancer drug adriamycin as expressed in ^{31}P NMR spectra of rat heart

Dear Prof. Shapiro,

During the last three years I have been involved in research on the mechanism of action of the anti-tumor drug adriamycin. Although this drug is very popular in routine clinical practice, its use is restricted by a specific, dose-dependent heart toxicity. In the course of studies, aimed at elucidating the molecular mechanisms responsible for this cardiotoxicity, I have carried out ^{31}P NMR experiments on the effects of adriamycin (ADM) on the energy metabolism of rat heart in vivo (in collaboration with Dr. W.P. Aue and Prof.dr. J. Seelig, Basel). Despite considerable progress in the field of localized in vivo NMR spectrometry during the last couple of years, it is still extremely difficult to acquire high resolution spectra of deeply buried organs in small animals via an entirely non-invasive approach. For this reason, we decided to focus on the heart of the rat by surgically implanting a small solenoidal coil around it. By this choice of the experimental approach, we obviously gave up the claim of non-invasiveness of NMR. More importantly, however, it enabled NMR signal to be picked up from the organ of interest exclusively without significant contamination with spurious signals from surrounding tissue.

Figure 1 shows a series of ^{31}P NMR spectra (approx. 6 min each) acquired before and after injection of 25 mg ADM/kg at t=0. Spectra were collected at 32.4 MHz on a Bruker BNT-80 system. Clearly, only phosphocreatine (PCr) levels are significantly affected. Fig. 2 is a compilation of the data obtained on the dos-dependency of the acute effects of the drug on the PCr levels of rat heart (as % of control peak intensities before drug administration). Increasing loads of ADM lead to a progressive depletion of PCr. Although the above ADM-induced effects may not seem to be dramatic (the highest dose removes 20% of the PCr), it should be realized that we are looking at the consequences of a single injection. ^{31}P NMR data on the cardiac energy status of rats treated

with multiple doses of ADM during a period of 2 weeks demonstrated a progressive decline in the PCr/ATP peak ratio (not shown).

In summary, both the acute and chronic cardiotoxicity induced by adriamycin are accompanied by a dose- (and time-)dependent decrease in the concentration of high-energy phosphates (esp. PCr) in rat heart.

Sincerely yours,

Klaas Nicolay

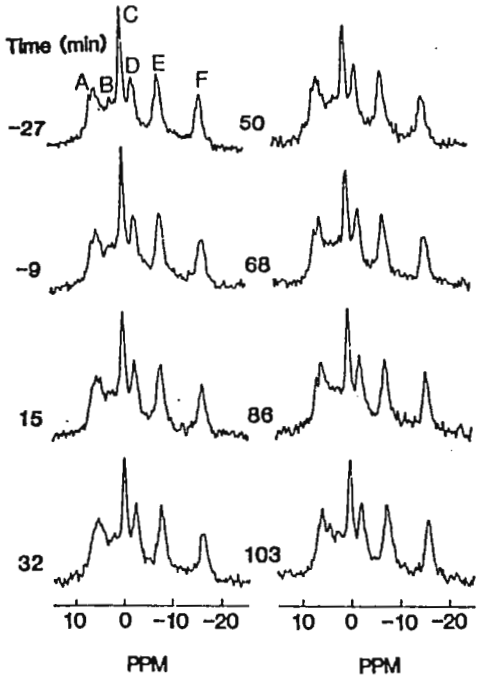

Fig. 1: Acute effects of ADM on ^{31}P NMR spectra of rat heart in vivo. Peak assignments: A, phosphomonoesters; B, phosphodiesters; C, PCr; D, E and F, γ-, α- and β-ATP, resp.

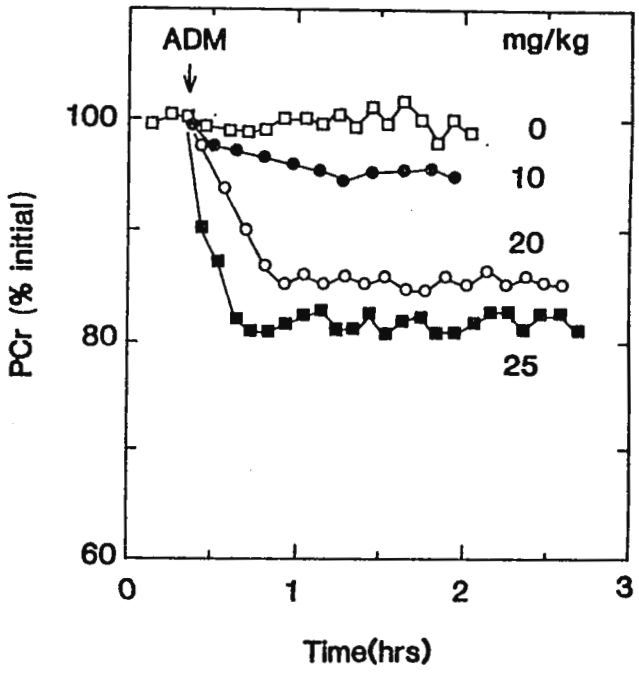

Fig. 2: Dose- and time-dependence of acute effects of ADM on cardiac PCr levels.

Please credit this contribution to the account of Dr. M.J.A. de Bie (University of Utrecht, The Netherlands).

330-12

MASSACHUSETTS GENERAL HOSPITAL ∞ HARVARD MEDICAL SCHOOL

Please reply to

Massachusetts General Hospital
Boston, Massachusetts 02114

NMR LABORATORY
(617) 726-3081

February 6, 1986

Ernst Angle Enhancement in Spin Echo Sequences

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

Dear Barry,

In our preliminary attempts at imaging a solid object using NMR, we unwittingly encountered a problem incorporating Ernst angle (1) enhancement of the signal-to-noise ratio into our pulse sequence. Our one-dimensional spatially resolved experiment used a standard spin echo RF sequence with high power proton decoupling, and short, intense phase-encoding gradient pulses.

Since the recycle delays normally required are quite long - about 20 to 60 seconds - we tried to use smaller flip angles in place of the nineties, together with shortening the recycle delay. The resultant fading signal forced a few moments of deep reflection - culminating in the marvelous insight (doubtless having been achieved independently by others) that the desired increase in overall signal-to-noise enhancement is predicated on leaving some residual magnetization along the positive z-direction. The 180-degree pulse, of course, inverts that magnetization, and makes the steady-state response of the spin system even weaker than using 90-degree pulses at the faster repetition rate.

There are several escapes from this dilemma. One can add a 180-degree flipback pulse (2) at the end of the signal acquisition, which restores the z-component of magnetization to its proper place. This did indeed allow a significant increase in overall signal-to-noise ratio in a fixed total

time. Alternatively, one can use for the first pulse, instead of a flip angle given by

$$\cos \alpha = e^{-\text{recycle}/T_1},$$

the supplement of that angle. Finally, one can, at least in the case of certain imaging applications, produce one's echoes by gradient reversals instead of RF pulses. Such gradient echoes coupled with small flip angles have been recently reported from several sources (3), although we have neither read nor heard about explicit considerations of Ernstian-type enhancement when spin echoes are part of the experiment. A short manuscript is in preparation.

These measurements were performed at the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology. JLA expresses his gratitude to Bob Griffin for some financial support and much tolerance received while on (what became permanent) sabbatical from the University of Cincinnati.

Dan Raleigh

Daniel P. Raleigh,
MIT

Jerry Ackerman

Jerome L. (The Other?)
Ackerman, MGH

1. R.R. Ernst and W.A. Anderson, Rev. Sci. Instr. 37, 93 (1966).

2. J. Tegenfeldt and U. Haeberlen, J. Magn. Reson. 36, 453 (1979).

3. For example, P. van der Meulen, J.P. Groen and J.J.M. Cuppen, Magn. Reson. Imaging 3, 297 (1985).

330-14

TH Delft

Delft University of Technology

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

Your reference and date | Our reference | Office telephone (015) 78 5879 | Date 30.01.1986

Subject | Sub-division

Dear Professor Shapiro,

Aluminum(III) complexes as studied with multinuclear NMR

We are studying mixtures of polyhydroxycarboxylates with aluminum(III) because they appear to be much better calcium(II) sequestering agents than analogous mixtures with borate. Motekaitis and Martell (ref. 1) have performed potentiometric studies on aluminum(III) complexes with polyhydroxycarboxylates. The structures of several of the complexes they present seem rather far fetched to us. Their suggestion that "C-13 and H-1 NMR should provide additional microscopic structural information" turns out to be very optimistic.
On stereochemical principles we predict 13 different complexes for D-tartrato-aluminum(III) (coordination number 6) resulting in 36 carboxylate and 36 hydroxyl C-13 NMR signals. The concentrations of the various complexes depends on the aluminum(III):ligand ratio and the pD of the solution. Ionization of α-hydroxylgroups or hydration water complicates the pictures even more.
For an aqueous solution of 0.5 M aluminum(III) nitrate and 0.5 M glucaric acid at pD 7.2 we observed an incredibly large number of C-13 NMR signals (Fig. 1) indicating the complexity of this problem. Thus we may say that conclusions concerning the structure of complexes which are obtained from potentiometric studies should be considered with great care (or even with suspicion).
Further studies to elucidate some of these structures using multinuclear NMR are in progress.

Sincerely yours,

F. Bleichrodt* M. van Duin

Please credit this contribution to the account of our J.A. Peters.

ref. 1 R.J. Motekaitis, A.E. Martell, Inorg. Chem. 23, 18 (1984)

*present adress: DSM, Research and Patents, Geleen, The Netherlands

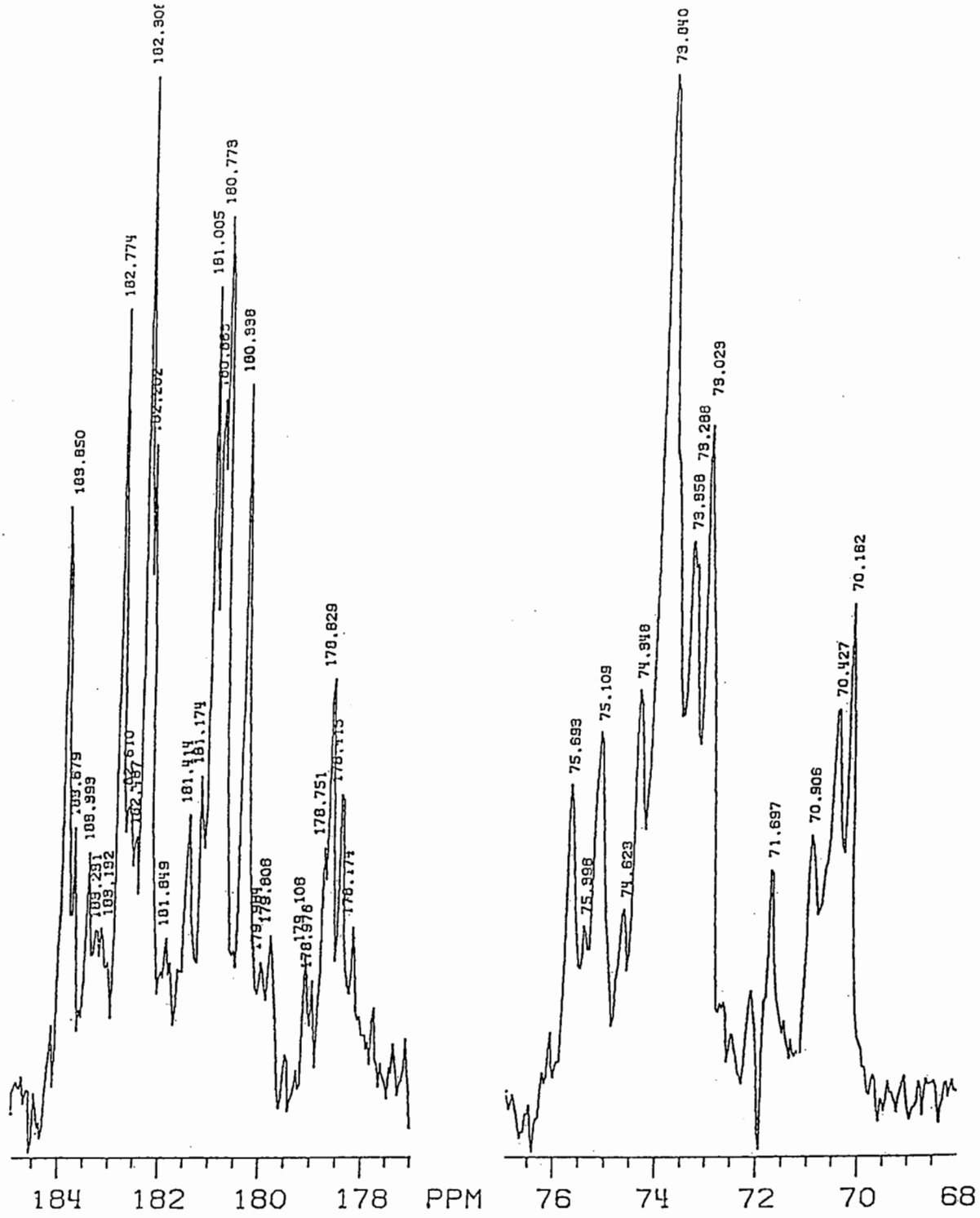

Fig. 1 50.3 MHz C-13 NMR spectrum of an aqueous solution of 0.5 M aluminium(III) and 0.5 M glucaric acid at pD 7.2 (recorded on a Nicolet NT-200 WB, 580 acquisitions, delay time 10.0 s and H-1 decoupled)

TEXAS A&M UNIVERSITY
DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843-3255

February 21, 1986

Dear Professor Shapiro:

Aluminum complexes as studied by potentiometry

The letter by Bleichrodt and Van Duin (ref.1), citing the complexity of their C-13 NMR spectra, makes the following three points relative to our previous potentiometric study (ref.2) on this system: 1, that our suggestion for further studies by other methods, in particular C-13 and H-1 NMR, to provide additional microscopic detail "turns out to be very optimistic"; 2, that the number of stereochemical aluminum(III) tartrate complex isomers possible, coupled with the added number of Al(III) tartrate complexes formed by ligand hydroxyl dissociations, would lead to some 72 distinct C-13 NMR signals resulting in a very complex problem; and 3, that the C-13 NMR (shown as Fig.1 in their letter) of a 1:1 Al(III)-glucaric acid system at pD 7.2 is so complex that conclusions concerning structure of complexes which are obtained from potentiometry should be considered with great care and, parenthetically, even with suspicion. We offer the following points to show the scope and limitations of the potentiometric method, as well as some of the reasons why the system reported by Bleichrodt and Van Duin cannot be compared with the potentiometric results.

The potentiometric method employed in the manner reported (ref.1) measures proton dissociation equilibria and stoichiometries of proton dissociation reactions, which in turn lead to the determination of metal-ligand interactions. It does not determine structures of complexes in solution, but it does indicate metal ion-ligand coordinate bonding modes, and approximate geometric arrangements of ligand donor groups may sometimes be inferred from what is known about coordination requirements of the metal ion and steric restrictions of the ligand. Thus the term "structure" should be avoided in interpreting potentiometric data, lest it be taken too seriously by non-specialists in the field.

It is usually not possible to compare NMR data measured at high concentration (0.5 M in this case) with the results of potentiometric measurements at ~0.001 M. For a bifunctional ligand such as glucaric acid the concentrations of polynuclear species (with the carboxylate functions coordinated to two different metal ions) increases as the square of the concentration. If intermediate hydroxyl groups are also involved in metal ion coordination the concentration of polynuclear species would increase with a higher power of the concentration of reaction species. The pH of 7.2 selected for NMR measurements is unfortunate because it is above the cut-off value cited in ref.2 where hydrolysis of the Al(III)-glucaric acid complex begins. Under these conditions one would expect partial hydrolysis of the Al(III) (i.e., hydroxo complexes are formed), thus leading to more cross linking. Valid comparisons between two types of measurements of complex systems can be made only by careful control of ionic strength, temperature, pH and other factors that affect the equilibrium such as concentrations and molar ratios of the components. Variations of these conditions within allowable limits are necessary to determine the various species present.

The use of NMR for the determination of the donor groups bound to a metal ion (by measuring chemical shifts of neighboring groups) is a valuable technique, a fact that is attested to by over a hundred publications in the field.

Sincerely yours,

R. J. Motekaitis A. E. Martell

ref.1 F. Bleichrodt and M. Van Duin, TAMU NMR Newsletter, March, 1986.

ref.2 R. J. Motekaitis and A. E. Martell, Inorg. Chem. 23, 18 (1984).

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February 12, 1986

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

^{13}C CP/MAS of Carbanions.

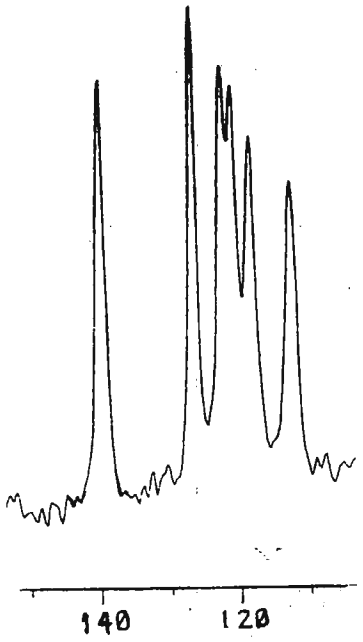
Dear Barry,

Except for changing my address on the writing paper for some months, I will report on a preliminary ^{13}C CP/MAS spectrum of fluorenyl lithium that was obtained on our MSL-100 just before I left. As shown below, the ^{13}C spectrum (r.t., obtained from a THF solution) looks very much like the solution spectrum obtained at contact ion-pair condition, i.e. in diethyl ether (DEE) solution. But it differs significantly from the spectrum obtained in THF, orin better solvating media (U. Edlund, OMR 12, 661 (1979)). As expected, the external cation solvation in DEE will not majorly affect the anion-cation interaction. Consequently, the charge distribution will be very similar to that present in the solid state. No dipolar broadening due to the coupling to the quadrupolar ^{7}Li nucleus is obvious at room temperature. Unfortunately, the Delrin signal masks the expected shift range for the C-9 signal so we can not say if this is true for this carbon as well. But this was just a first shot.

Best regards,

Ulf Edlund
Visiting Professor

UE:sf



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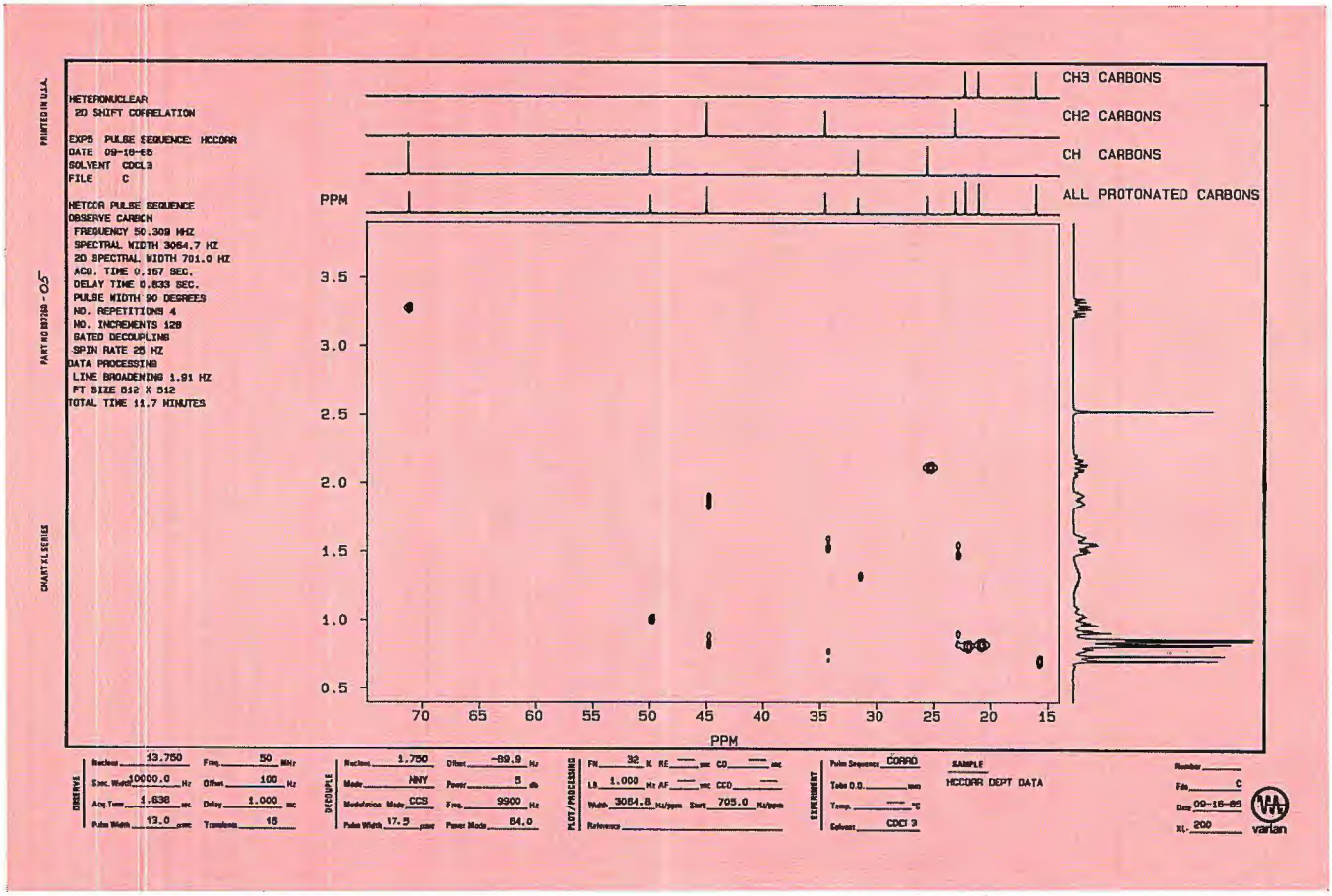

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Ottawa, Canada
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January 29, 1986

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

Dear Barry:

Title: Spectral simplification using selective pulses.

A recent article (1) on the minimisation of Bloch-Siegert shifts when performing spin decoupling difference spectroscopy prompted us to write about the use of selective pulses to obtain similar information. The pink slips that we received also aided and abetted in this.

The technique is a combination of two published ones (2,3). The basic pulse sequence is

$$90^\circ_x - \tau - 90^\circ_y \; 90^\circ_y - \tau \quad \text{acq } (+)$$

$$90^\circ_x - \tau - 90^\circ_y \; 90^\circ_{-y} - \tau \quad \text{acq } (-)$$

Protons coupled to that inverted by the 180° pulse are refocussed. All others are not and are therefore subtracted. The final spectrum consists of the resonances for the inverted proton and those to which it is coupled. The addition of a 90°_y pulse after the second delay (immediately prior to data acquisition) results in coherence transfer to protons coupled to those which are coupled to that inverted. This is a 1-D selective relay experiment. The advantage of this technique is that there are no Bloch-Siegert shifts. The disadvantage is that all proton resonances contain anti-phase components. However, with judicious choice of data massaging parameters, followed by a magnitude calculation, one can obtain spectra with resolution at least as good as that from a straight FT of the normal spectrum.

The normal spectrum of the lactose derivative shown is the bottom spectrum. The sample is a diastereotopic mixture. The H-3 proton overlaps both H-3' and H-4' and therefore cannot be observed. The middle spectrum is that obtained using the basic pulse sequence

with H-1 inverted. The top spectrum is that obtained when the additional 90°_{y} pulse is added. This spectrum permits the observation of H-3. The small peaks that occur in both spectra correspond to the glycerol moiety since its methine proton overlaps H-1. For both these spectra a τ value of 40 milliseconds was used and the decoupler was used to generate the 180° selective pulse (90° pulse length of 60 milliseconds.)

Best regards,

Harold C. Jarrell Ian C.P. Smith John K, Saunders

References

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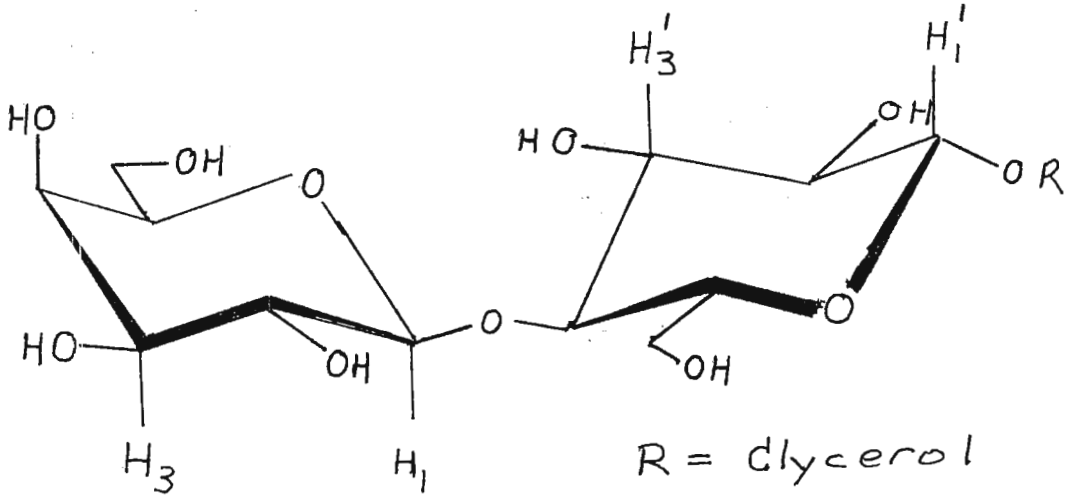

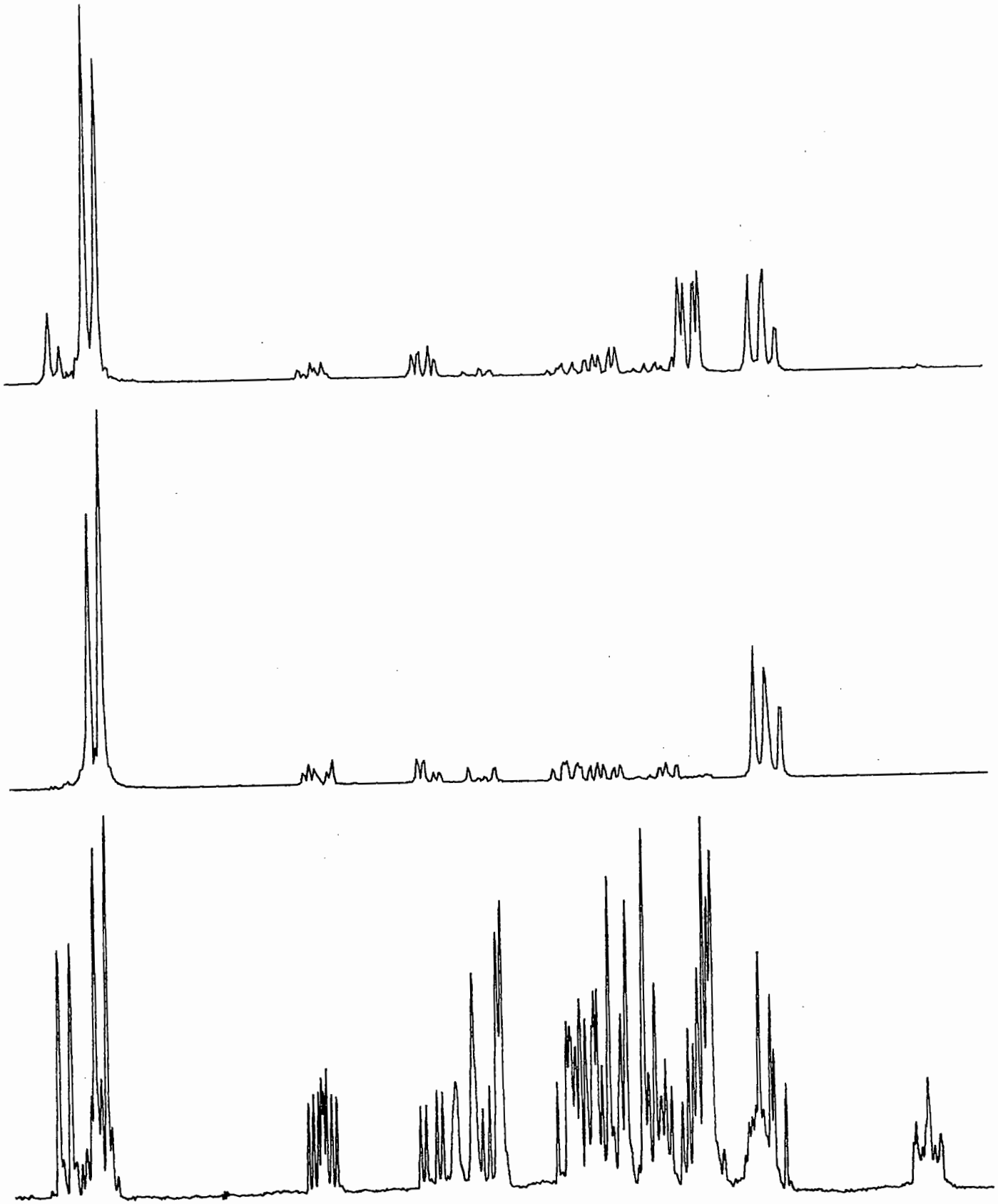

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Drexel University
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Department of Chemistry
(215) 895-2638, 2639

February 10, 1986

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

POOR MAN'S IMAGING ON THE FX-90Q

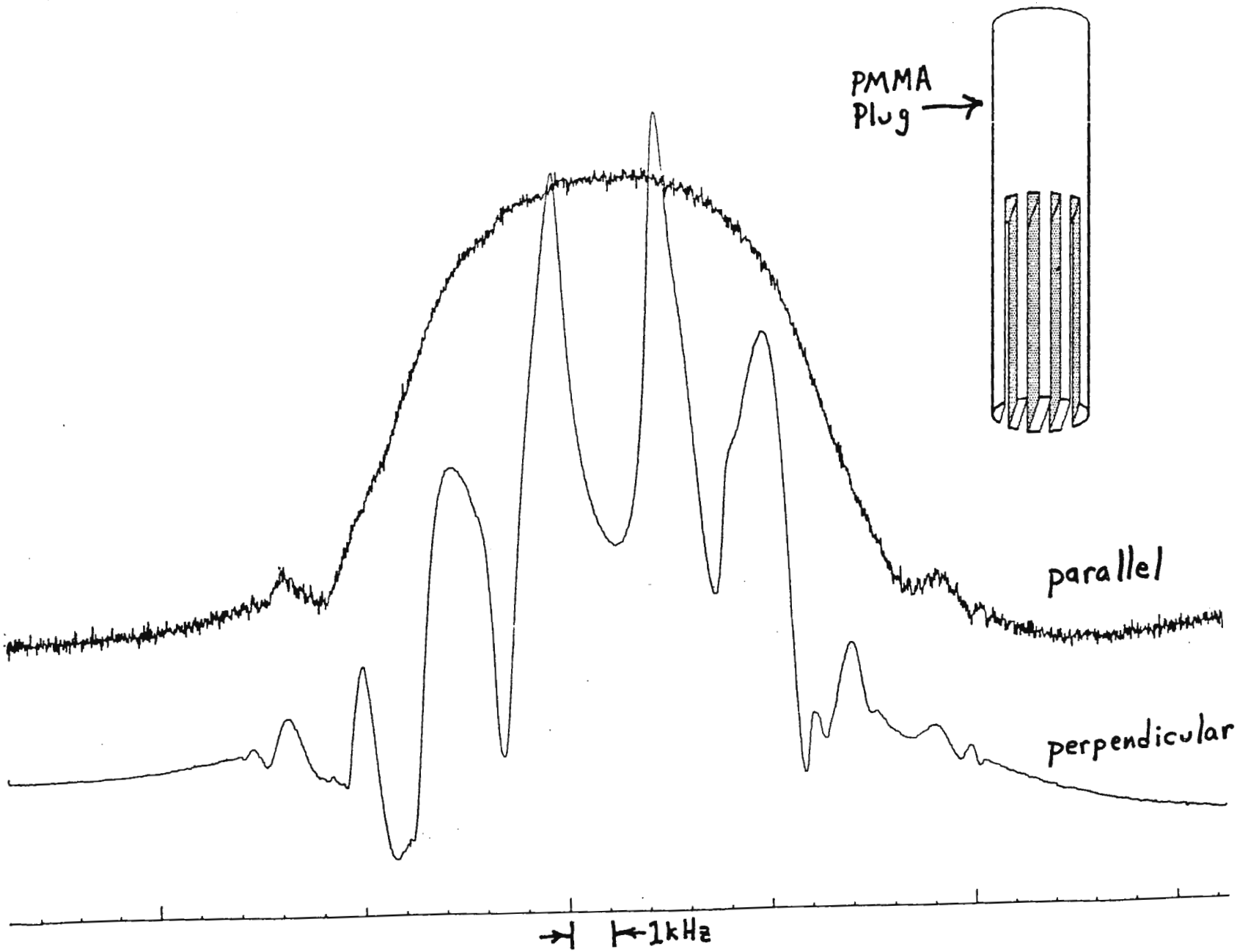
Dear Barry;

In response to your latest reminder, we report a technique which allows us to do low resolution NMR imaging with a commercial spectrometer. On our JOEL FX-90 spectrometer, the pulsed field gradient (standard homospoil unit) has been used to generate the spatial resolution required for one dimensional imaging experiments. A single 90° pulse is used in combination with the field gradient during data accusition. The available field gradient of 0.05 T/m gives us a spatial resolution for protons of ca. 1.3 kHz/mm. Therefore, it is possible to generate a one dimensional image of a sample contained in a 10 mm sample tube within a 15 kHz window. PMMA plugs were cut to fit into 10 mm sample tubes to test the resolution of the technique. The details of the plugs are shown in the figure. The plugs were then placed in sample tubes containing water for imaging. The images shown in the figure correspond to different orientations of the plug; with the cuts oriented perpendicular and parallel to the field gradient. The spectra yielded the expected one dimensional images though the spatial resolution was limited to ca. 1 mm. In the future we expect to interface the spectrometer computer with a main frame computer. This will enable us to use image reconstruction techniques to combine several one demensional images taken at different sample orientations to generate a two dimensional image. We also plan to extend this work to solvent diffusion in polymeric solids.

Sincerely,

Steve Frank

Frank D. Blum,
Stephen Pickup


PMMA
Plug
parallel
perpendicular
1kHz

The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

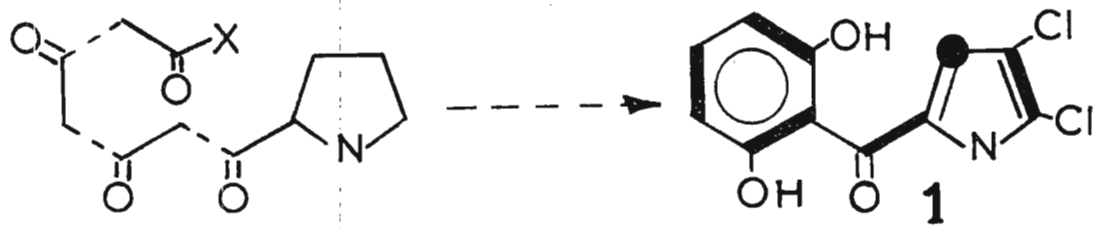
February 11, 1986

An example of acetate incorporation via the TCA cycle

Dear Barry,

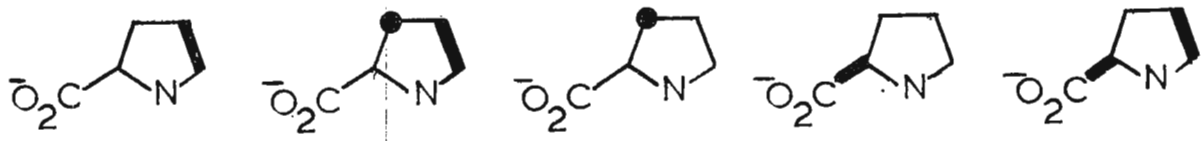
Here is my belated response to your multicolored memo barrage.

An examination of the biosynthesis of pyoluteorin (**1**), a bacterial phytotoxin of several Pseudomonas spp, has recently been completed. This was of interest because its structure suggested its origin from a tetraketide having proline (or equivalent) as the starter unit and incorporation experiments with [1,2-$^{13}C_2$]acetate have confirmed that such an intermediate from the tricarboxylic acid (TCA) cycle is involved.



1

The ^{13}C spectrum of enriched-**1**, initially obtained in acetone-d_6 did not provide all of the required data because of broadening of the ortho pattern and overlap of the para-C and C-2 absorptions. Consequently the solvent was changed to CD_3OD but the sample was not examined for several days at which time it was evident that not only were the C-2 and para patterns overlapped but the latter revealed that partial exchange had occurred at the meta positions. This sample was again examined a few weeks later from which it was clear that further H/D exchange had occurred. To get a spectrum in which each pattern was clearly resolved, the enriched-**1** was converted to its O,O-diacetate and examined in $CDCl_3$ solution giving the spectrum shown in Fig. 1. From this spectrum it is apparent that C-4, -5 and the aryl carbons are more highly enriched than C-1, -2 and -3 and the latter lacks the prominent satellites exhibited in each of the other patterns. The enrichment levels were found to be (±0.1): aryl carbons, 2.8%; C-4, -5, 2.2%; C-1, -2, -3, 0.6%. These values are averaged from measurements in all spectra except for the meta-carbons, for which a reliable value was only available from the acetone solution. In the first two turns the TCA cycle generates proline entities with the labelling patterns:



Thus, the observed enrichment levels are entirely consistent with the original premise utilizing proline (or equivalent) from the 1st and 2nd turns of the TCA cycle. The fact that inadvertent exchange occurred in CD_3OD was a small disadvantage but did not affect collection of the requisite data. Only a few other examples of acetate incorporation via the TCA cycle have been reported.[1]

Perhaps, this will reinstate my TAMU newsletter "subscription".

Sincerely,

J.B. Stothers,

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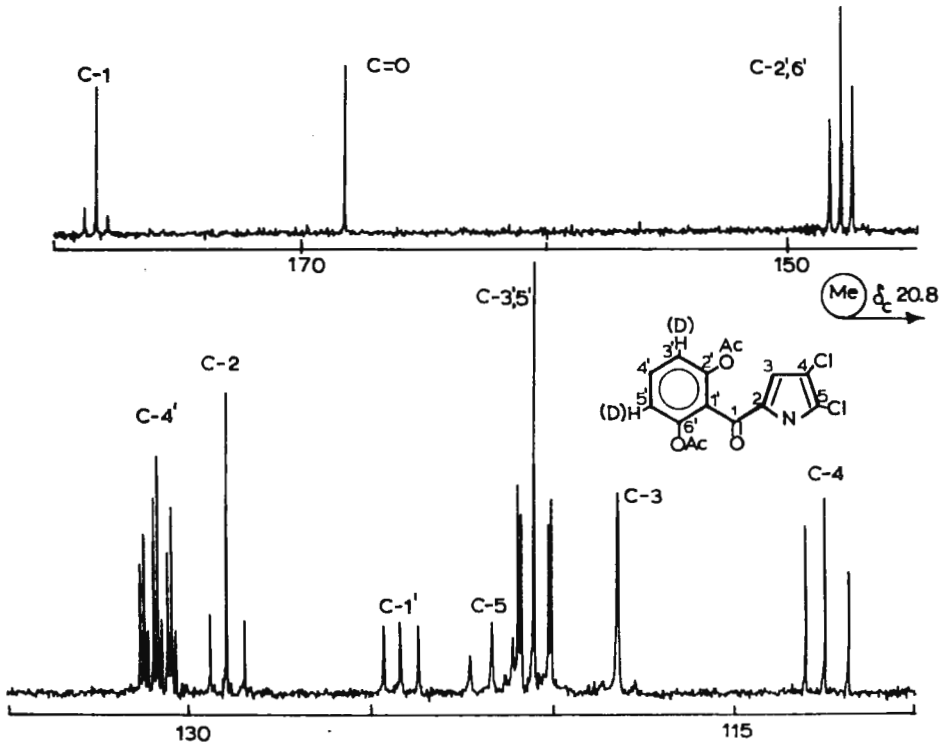

Figure 1

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Your file Votre référence

Our file Notre référence

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

Feb. 12, 1986

Cross Polarization - Induced Explosive Decomposition of Certain Electrically Conducting Polymers

Dear Prof. Shapiro,

In order to initiate my subscription to the TAMUNMR Newsletter, I would like to share a recent experience that indicates that nmr is not the safe profession that I had anticipated it would be. It is already well known that sample - induced rotor failures may arise from chemical interactions due primarily to the presence of liquids or surfactants in the sample.[1] However, we appear to have encountered an even more hazardous situation in solid state nmr studies of certain electrically conducting polymers, including polythiophene, polypyrrole, and copolymers of thiophene and pyrrole.

The polymers were synthesized electrochemically on a conducting glass electrode (a 2.0 cm^2 sheet coated with Sb doped SnO_2) with a 4 cm^2 Pt flag electrode used as a cathode.[2-6] The electrolyte was tetrabutylammonium perchlorate in acetonitrile. Other common electrolytes include : $AgClO_4$, $LiClO_4$, $AgBF_4$, KBF_4, $NaBF_4$, etc.[3] The polymers were mechanically removed from the anode , washed and dried. A Bruker CXP200 nmr spectrometer operating at 50.3 MHz for ^{13}C observation was used. Relevant experimental conditions were as follows: 90° pulse width 5 μs, 1 ms contact time, 50 ms dipolar decoupling (at 12G) and 5 s recycle delay.

In attempting nmr analysis of these polymers the first cross polarization sequence in each case was immediately followed by the catastrophic failure of the boron nitride rotor. The disintegration of the rotor resulted in the tachometer/strobe light attachment being blown apart, as was the coil. The upper section of the probe was blackened and the entire probe required extensive and careful cleaning before re-use. The extent of the damage was fortuitously minimized to some extent by the nature of the Bruker probe design, but more serious consequences could be envisioned for different probe designs where more critical and/or expensive components might be subjected to the full force of the rotor disintegration. This phenomenon has been subsequently confirmed as arising from the extremely violent, explosive decomposition of the polymers themselves as a consequence of the application of the high power decoupling (representing several hundred watts of rf power). The effects noted above resulted from the detonation of as little as 30 - 50 mg of polymer.

It is important to note that prior to our attempts at nmr analysis the differential scanning calorimetry (DSC) analysis of these polymers was

undertaken (heating rate of 20°C/minute over the range 50°C to 450°C) with no abnormal effects noted.

It has been previously reported that polythiophene perchlorate films were not stable even in vacuum or inert atmospheres.[3] A well washed and dried film burned itself out in the absence of oxygen, this phenomenon being attributed to electrostatic sparking, when films were suddenly shocked and touched each other.[3] Furthermore, a study of conducting polymers by Devreux et al[7] included perchlorate derivatives, but employed relatively low power decoupling fields (6G) as compared with the present experimental conditions. We conclude that, at the very least, all perchlorate derivatives of these electrically conducting polymers be treated with extreme care.

This experience prompts us to make several suggestions regarding preliminary testing of polymers that may conceivably behave similarly. While it is suggested that preliminary DSC and/or thermogravimetric analysis (TGA) experiments at high heating rates (and to high temperature) be performed on suspicious samples (thus sacrificing someone else's equipment, however), the failure of this screening process in the present case indicates that secondary measures be considered. In particular, we suggest two possibilities. First, we have found that these samples could be detonated by the application of a spark from a solid state piezoelectric gas igniter. Second, it is possible, albeit less desirable, to pulse a small sample in the probe while outside the magnet. This sample should not be in a rotor, but some other suitable temporary sample holder open to the air.

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Sincerely,

David Axelson

Dr.David E.Axelson

Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74078

2/13/86

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

Title: HETCOR 2-D Analysis of 3,6-Dibenzylhexahydro-8a-methoxy-5H-4a,8-(methano-selenomethano)-2H-pyrido[3,4-e]-1,3-oxazine

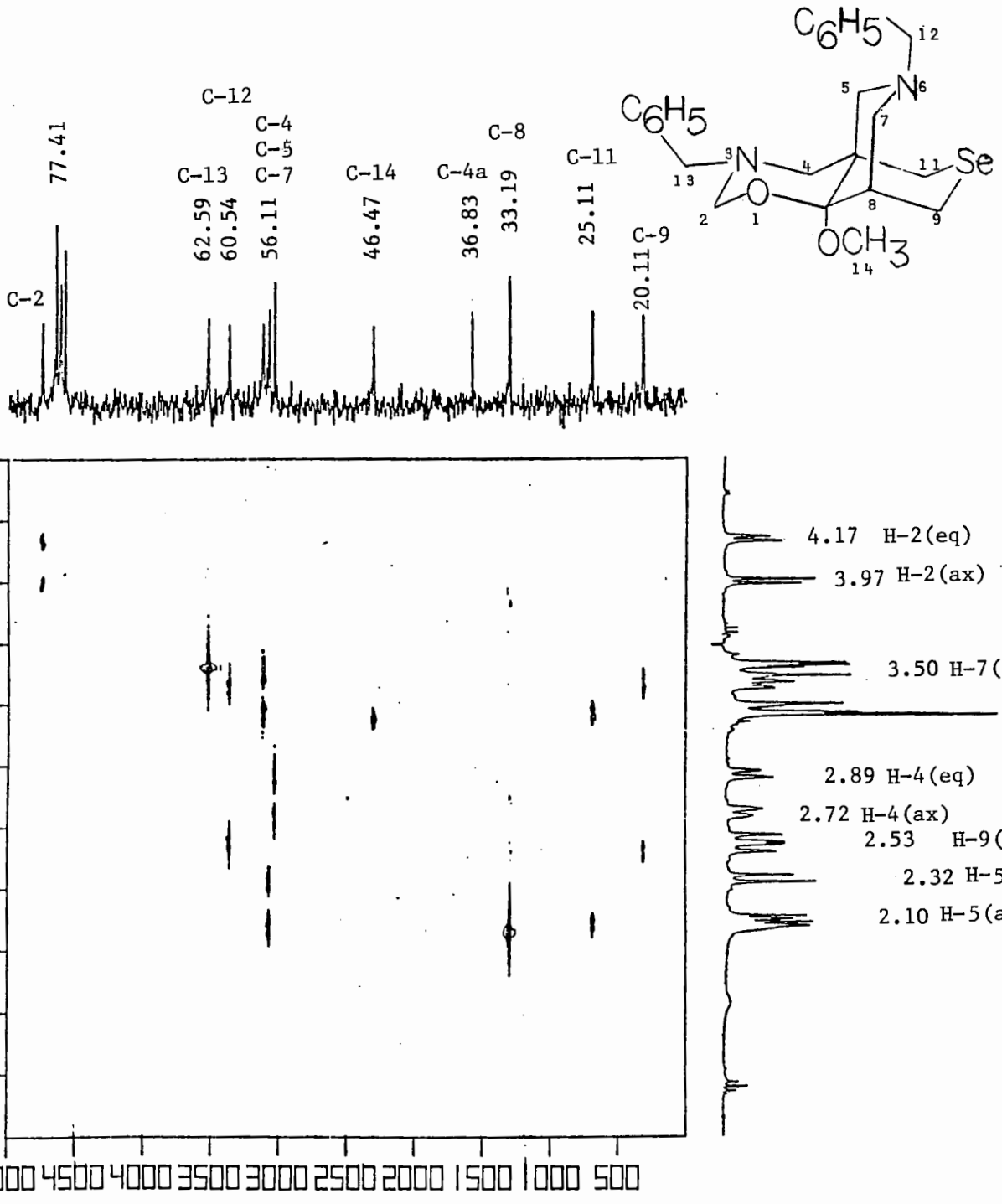
Dear Barry:

We have been able to isolate a rather complex, tricyclic system from some of our recent work with selenane derivatives. The title compound was found to have a complex ^{1}H NMR spectrum as can be seen from the enclosed printout but the ^{13}C spectrum did appear somewhat cleaner. In any event, it was not possible by only a perusal to assign any signals and a HETCOR 2-D plot was originated. As can be seen from the accompanying 2-D plot, it is easy to correlate ^{1}H signals with the corresponding ^{13}C signals for most of the atoms involved. This is a classic case of the utility of HETCOR 2-D plots for unraveling such complex structures. We know the structure is the correct one from a very recent X-ray diffraction analysis of a single crystal but we had predicted this structure in advance. It is rare for such predictions to come true for so complex a material but this did. We trust this meets the contribution required by the TAMU NMR newsletter.
Best regards.

Sincerely yours,

Darrell

K. Darrell Berlin
Regents Professor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36.83
33.19
25.11
20.11
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4.17 H-2(eq)
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3.50 H-7(eq)
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2.89 H-4(eq)
2.72 H-4(ax)
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January 28, 1985

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

Software Enhancements for the BNC-28 Computer

Dear Barry:

Our Bruker WP-80 spectrometer is equipped with a BNC-28 computer. Since this computer (as well as the spectrometer) has performed so consistently reliably over the past 9 years we have been reluctant to replace it with an Aspect-2000. The software, however, has a number of inconveniences, not the least of which is the absence of a horizontal ppm scale on the plotted spectra. We have written a software overlay for FTNMR version #71125 which rectifies this deficiency with two new commands. The first, **TX**, asks for the major and minor ppm tic spacings, and the second, **PT**, plots both the major and minor tic marks in a single pass. Our overlay also modifies the **F** (cursor hardcopy) subcommand of the **C** (cursor) routine so that the cursor ppm as well as frequency values are printed. Finally, the assign cursor (**EP,C,A**) routine and the set right and left limits (**SL** or **EP,F**) routine for plotting and peak printout accept the more convenient ppm rather than frequency units.

We would be happy to make this paper tape overlay available upon request to anyone who still posses a BNC-28 relic.

Sincerely,

Sam Kaplan

Samuel Kaplan
(716) 422-4784

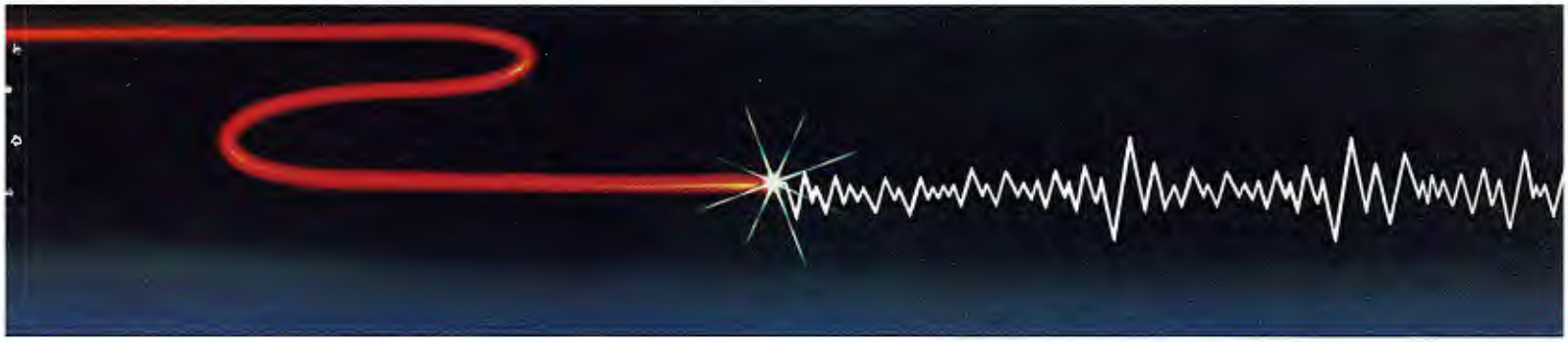
8th European Experimental NMR Conference

This meeting is held every two years and is devoted to the experimental aspects of nuclear magnetic resonance spectroscopy. This year the scientific program will cover biomedical NMR, two-dimensional spectroscopy, high resolution NMR in the solid state, the study of atomic motion in solids, stochastic NMR, quantitative measurements, the prospects for very high magnetic fields, magnetic resonance imaging, and in vivo NMR. The 8th EENC will be held near Spa, a resort in the East of Belgium, June 3-6th 1986. Participants will be housed in the Hotel Sol Cress where all the scientific sessions will be held. There will be invited lectures, poster sessions and a scientific instrument exhibition. The Conference Secretary is

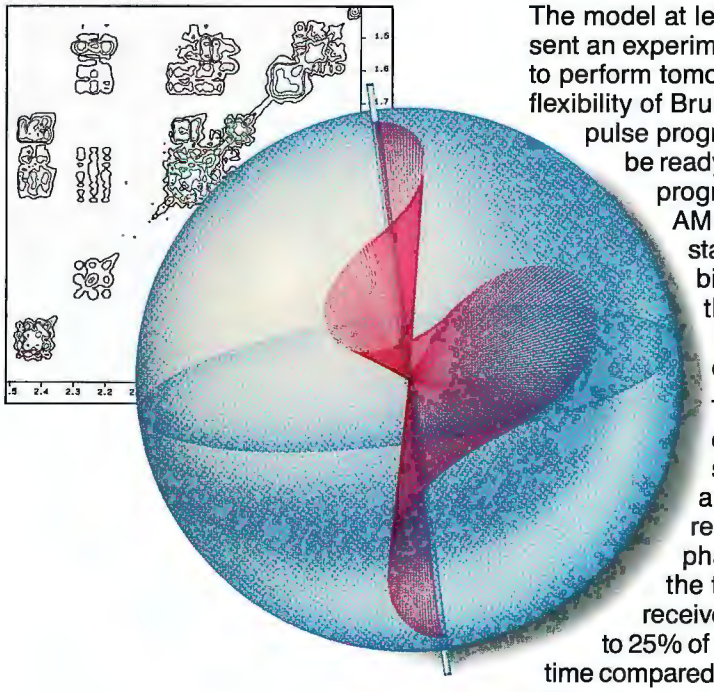
Professor J. Reisse,
8th E.E.N.C.,
Université Libre de Bruxelles,
Chimie Organique E.P. (CP 165),
50, Avenue F.D. Roosevelt,
B-1050 Bruxelles,
Belgium.

Registrations should be received by 1st May 1986.

The NMR evolution continues:



COSY3 spectrum, 512W x 512W. The experiment time, incl. transform, was less than 15 minutes!



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February 7, 1986

Professor Bernard L. Shapiro
Chemistry Department
Texas A and M University
College Station, Texas 77843-3255

Re: Replacement EPR Microwave Diode

Dear Professor Shapiro:

Since our Varian EPR is no longer being manufactured and spare parts are becoming increasingly difficult to get, we are establishing a stock of spare parts to help us keep our instrument in service. Some components are no longer available (sample cavity) and some soon won't be (hall probe), and most parts seem to be very expensive.

A replacement microwave detector diode for the E-102E X-band bridge from Varian costs $495.00 and has an 8 month delivery time. Both prices, time and money, seemed excessive so we began a search for an alternate source. We have uncovered a standard manufactured device which comes as a complete package with connectors identical to the Varian diode so that it can be replaced as easily as the original part. Our initial tests, using the weak pitch sample, show the performance to be equal to the original diode.

The packaged shottky diode (Part #2086-6010-13) is available from MA/COM Omni Spectra, Inc., 21 Continental Blvd., Merrimack, NH 03054 at a cost of $149.80, and a field replaceable diode for this package costs a mere $30.00 (Part #9999-4050-00).

We would appreciate hearing from others that may have identified alternate sources for replacement parts.

Sincerely yours,

Robert W. Dykstra

RWD/m

330-36

THE UNIVERSITY OF ILLINOIS AT CHICAGO

Department of Physiology and Biophysics (M/C 901)
Box 6998, Chicago, Illinois 60680
(312) 996-7620

February 14, 1986

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

A Solids, Coordinate-Generating Subroutine

Dear Dr. Shapiro:

During different calculations concerning interpretation of the nmr results in solids, we have developed and tested simple, but very useful subroutine which generate x,y,z coordinates of atoms within the symmetric block of unit cells.

The input data are the relative x/A, y/B, and z/C coordinates of atoms in one unit cell. Generated coordinates give the block of unit cells (NC * NC * NC) with atoms' numbering starting at the most inner (central) unit cell. Such arrangement of atoms is very convenient for calculation of different types of lattice sums.

The enclosed listing of the program does not require further explanation.

Yours sincerely,

Daniel Fiat

Dr. Daniel Fiat
Professor of Physiology
and Biophysics

R. Goc

Dr. Roman Goc
Visiting Assistant Professor

RG:vr

Enclosure

```
C SUBROUTINE BLK GENERATE X,Y,Z COORDINATES OF ATOMS WITHIN THE SYMMETRIC BLOCK
C                    OF UNIT CELLS.
C  NU - NUMBER OF ATOMS IN UNIT CELL
C  NC - DIMENSION OF REQUIRED BLOCK (3,5,7,9,...)
C  NT - TOTAL NUMBER OF ATOM WITHIN THE BLOCK
C  X, Y, Z - RELATIVE COORDINATES OF ATOMS
      SUBROUTINE BLK
      DIMENSION K(3)
      COMMON /BC1/NU,NC,NT
     */BC4/X(2000), Y(2000), Z(2000)
      NT=NU*NC**3
      NC1=NC-1
      L=1
      K1=1
C STARTS GENERATING COORDINATES FOR SUCCESIVE UNIT CELLS
  40  DO 45 I=1, 3
  45  K(I)=0
      K(L)=1
      DO 50 I1=1, NC1
      NI=NU*K1*I1
      K2=NU*K1
      DO 50 I2=1, K2
      NW=NI+I2
      X(NW)=X(I2)+K(1)*I1
      Y(NW)=Y(I2)+K(2)*I1
  50  Z(NW)=Z(I2)+K(3)*I1
      L=L+1
      IF(L.EQ.4) GO TO 60
      K1=NC*K1
      GO TO 40
C  CALCULATES NEX - NUMBER OF THE  CENTRAL UNIT CELL
  60  NEX=NC/2*(NC**2+NC-1)+NC
C  STARTS RENUMBERING ATOMS - CENTRALL UNIT CELL WILL HAVE ATOMS NO 1,2,...
      DO 70 I=1, NU
      NS=(NEX-1)*NU+I
      XT=X(I)
      YT=Y(I)
      ZT=Z(I)
      X(I)=X(NS)
      Y(I)=Y(NS)
      Z(I)=Z(NS)
      X(NS)=XT
      Y(NS)=YT
  70  Z(NS)=ZT
      RETURN
      END
```

THE UNIVERSITY OF CONNECTICUT

The College of Liberal Arts and Sciences
Department of Chemistry
Box U-60, Room 151
215 Glenbrook Road
Storrs, Connecticut 06268

February 15, 1986

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843-3255

Lone-Pair Orientation and the Magnitude of One-Bond C-H Coupling Adjacent to Heteroatoms

Dear Professor Shapiro:

It has been known for some time that the magnitude of the one bond $^{13}C-^{1}H$ coupling constant for bonds adjacent to heteroatoms such as nitrogen and oxygen is dependent on both substituent electronegativity and the orientation of the C-H bond relative to the non-bonded electrons of the heteroatom.[1] Thus, for example, the magnitude of ^{1}J at the anomeric carbon in pyranosides is diagnostic of configuration at C(1): $^{1}J_{C-H}$ of an axial C-H bond adjacent to an oxygen in a six-membered ring is invariably smaller than $^{1}J_{C-H}$ of an equatorial bond[1,2].

In the course of several mechanistic studies, we have had occasion to determine ^{1}J for C-H bonds adjacent to oxygen atoms in a wide variety of acetals and ortho esters. As expected, the magnitude of $^{1}J_{C-H}$ increases monotonically as the number of oxygen atoms attached to the carbon of interest increases: ^{1}J = 140.3, 162.0, and 187.0 Hz for CH_3OCH_3, $(CH_3O)_2CH_2$, and $(CH_3O)_3CH$, respectively. In addition, the <u>difference</u> in magnitude between an axial C-H bond and an equatorial C-H bond adjacent to oxygen in a six-membered ring remains a fairly constant 10 Hz regardless of substituents on the ring or the number of oxygens attached to the carbon bearing the hydrogen. This useful correlation seems to be confined to the second-row atoms. Indeed,it has been reported that very little, if any, directional sensitivity is observed for ^{1}J of bonds adjacent to sulfur in thio-D-glycosides[2]. For this reason we were somewhat surprised to to find an 8.8 Hz difference

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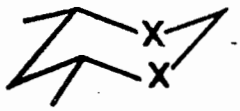
in the magnitude for the two one-bond couplings between C(2) and the axial and equatorial hydrogens in cis-4,6-dimethyl-1,3-dithane. We have been able to assign these couplings on the basis of spin-tickling experiments and, contrary to our expectations, $^{1}J_{C(2)-Hax} > {}^{1}J_{C(2)-Heq}$. This result is, of course, the reverse of the trend observed for ^{1}J adjacent to oxygen (see below).

A larger set of experimental data is needed before any firm conclusions can be drawn from this isolated (albeit surprising) example. The observation suggests that caution should be exercised in extrapolating from literature data on the conformational dependence of ^{1}J derived from studies of systems containing second-row heteroatoms.

Please credit this contribution to Professor Edward T. Samulski's account.



	X = O	X = S
$^{1}J_{C(2)-Hax}$	157.05	153.7
$^{1}J_{C(2)-Heq}$	167.05	144.9

[1]P. E. Hansen, Progr. Nucl. Mag. Reson. Spec., **14**, 175 (1981)
[2]V. S. Rao and A. S. Perlin, Carbohyd. Res., **92**, 141 (1981)

Sincerely,

William F. Bailey

William F. Bailey
Associate Professor

PHILIPPS-UNIVERSITÄT MARBURG

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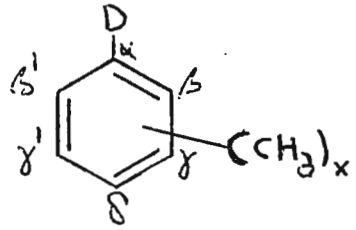
Prof. B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas

An Increment System for Deuterium Isotope Effects

Dear Professor Shapiro,

Although the detailed understanding of deuterium isotope effects on ^{13}C chemical shifts is still far from complete some useful correlations have been worked out recently[1,2].
We want to communicate here a little systematic study, where in a rather restricted, but complete set of compounds - all possible 19 methylated benzenes with one deuterium atom - the deuterium isotope effects have been measured.



We wanted to compare these data with the known methyl group increments[3] on the ^{13}C chemical shifts within the same compounds in order to see to some detail, whether a parallelism exists between these data and the deuterium isotope effects.
Although a quantitative comparison has not yet been worked out, an inspection of the table reveals that there might be incremental behavior of isotope effects over one, two and more bonds depending on number and position of the methyl groups.

Sincerely yours

(Stefan Berger) (Bernd Diehl)

1) Wesener, J. R., Moskau, D., Günther, H., J. Amer. Chem. Soc. 1985, 107, 7307-7311.
2) Künzer, H., Berger, S., ibid. 1985, 107, 2804-2805.
3) Dalling, D. K., Ladner, K. H., Grant, D. M., Woolfenden, W. R., ibid. 1977, 99, 7142-7149.

Table 1. Deuterium Isotope effects on ^{13}C chemical shifts of monodeuterated benzenes[a]

1-deutero-benzene	Ring Carbon Atoms α	ß	ß'	γ	γ'	δ	Methyl Carbon Atoms γ	γ'	δ	δ'	ε
1-deutero-	283	111	111	11	11						
2-methyl	312	86	110		7		61				
3-methyl	280	106	110	11	7	4					
4-methyl	276	110	110	11	11	7					-3
2,3-dimethyl	309	79	112	9	11	6	66		14		
2,4-dimethyl	299	85	109	12	10	9	62				
2,5-dimethyl	304	85	106	2	11	2	63				
2,6-dimethyl	327	83	83	1	1	8	63	63			
3,4-dimethyl	274	104	111	13	8	10					
3,5-dimethyl	279	105	105	10	10						
2,3,4-trimethyl	306	78	112	10	13	10	69		13		
2,3,5-trimethyl	316	80	108	4			64		14		
2,3,6-trimethyl	340	79	87	4		7	65	62	13		
2,4,5-trimethyl	298	87	104		12	10	60				
2,4,6-trimethyl	323	83	83			12	63	63			
3,4,5-trimethyl	276	106	106	10	10	11					
2,3,4,5-tetramethyl	306	79	109		13	11	70		13		
2,3,4,6-tetramethyl	327	77	85	9	2	13	70	62	13		
2,3,5,6-tetramethyl	340	79	79	9	9	13	65	65	12	12	
2,3,4,5,6-pentamethyl	340	79	79	10	10	14	70	70	14	14	

[a]Values in ppb, measured in solutions of unequal amounts of deuterated and undeuterated compounds. α, ß, γ and δ values for carbon atoms clockwise, ß', γ' and δ' values for carbon atoms anticlockweise from the deuterium atom.

UNIVERSITÄT TÜBINGEN
PHYSIKALISCHES INSTITUT
Prof. Dr. O. Lutz

D-7400 TÜBINGEN 1, den 21.02.1986
Morgenstelle
Telefon (0 70 71) 29 67 14

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

H_2O - D_2O - Solvent Isotope Effect on Magnetic Shielding

Dear Barry,

for years we investigated NMR signals of many heteronuclei, often in aqueous solution. We always had a look on the H_2O - D_2O - solvent isotope effect on magnetic shielding for these nuclei. For the definition of δ_{SIE} see the legend of the figure 1, $\nu(D_2O)$ means the Lamor frequency of the nucleus in question in D_2O solution . For a better comparison we have choosen small concentrations, 0.1 molal if possible. In figure 1 results are given for some groups of the Periodic Table.
The following rules can be derived:

Normally, the Larmor frequency of ionic nuclei is smaller in D_2O than in H_2O.

The amount of the SIE increases with the atomic number.

The SIE is small for the alkali and large for the halide nuclei.

But, for IIb-elements the SIE is anormal, that means positiv, but only for the IIb-nuclei in halide salt solutions. For the IIIb-elements the amount of the normal SIE decreases.

We are continuing in the investigation of the SIE through the Periodic Table and we hope to get more insight into the origin of this solvent isotope effect.
Sincerely yours

Otto

(Otto Lutz)

(continued on page 45)

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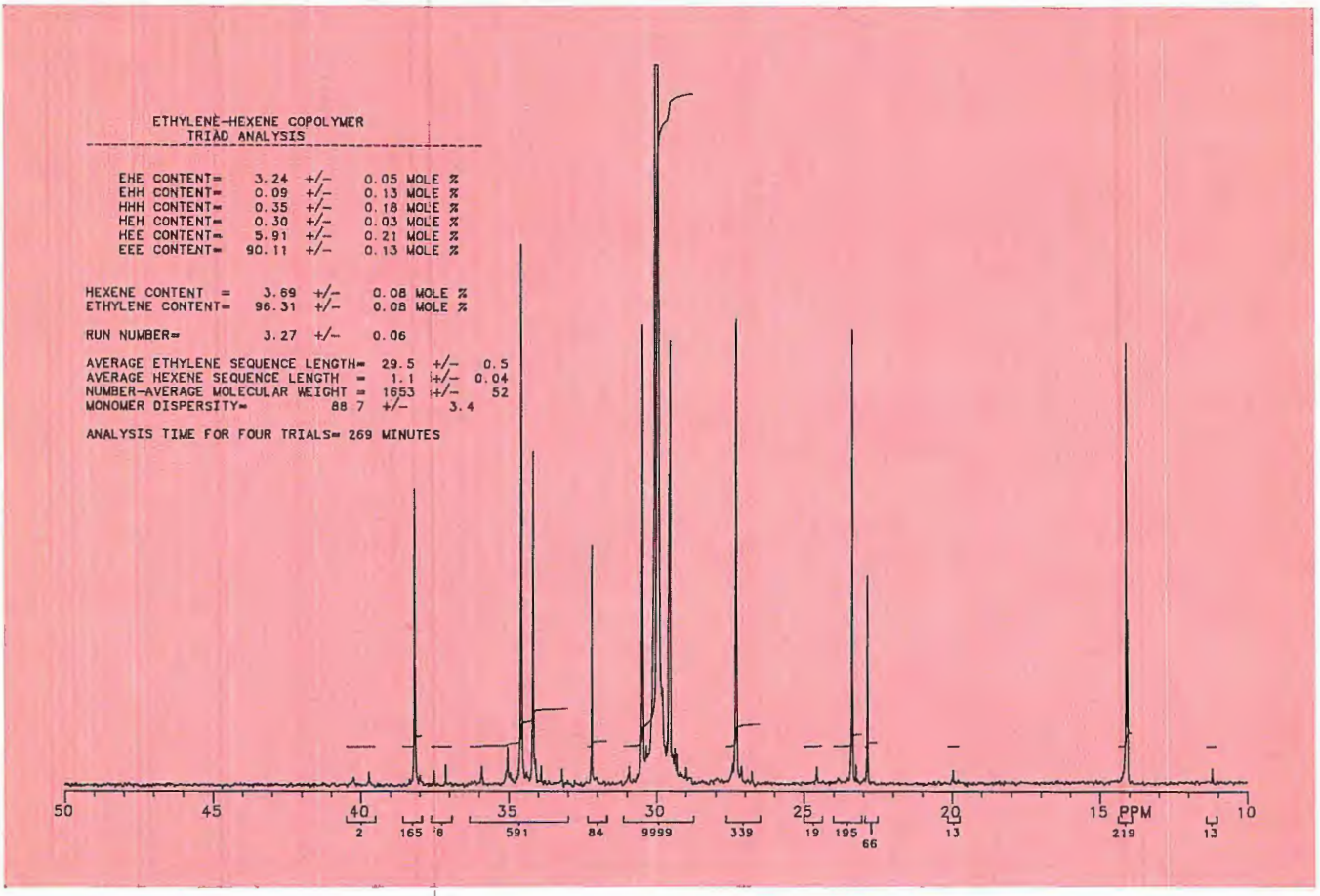

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(continued from page 42)

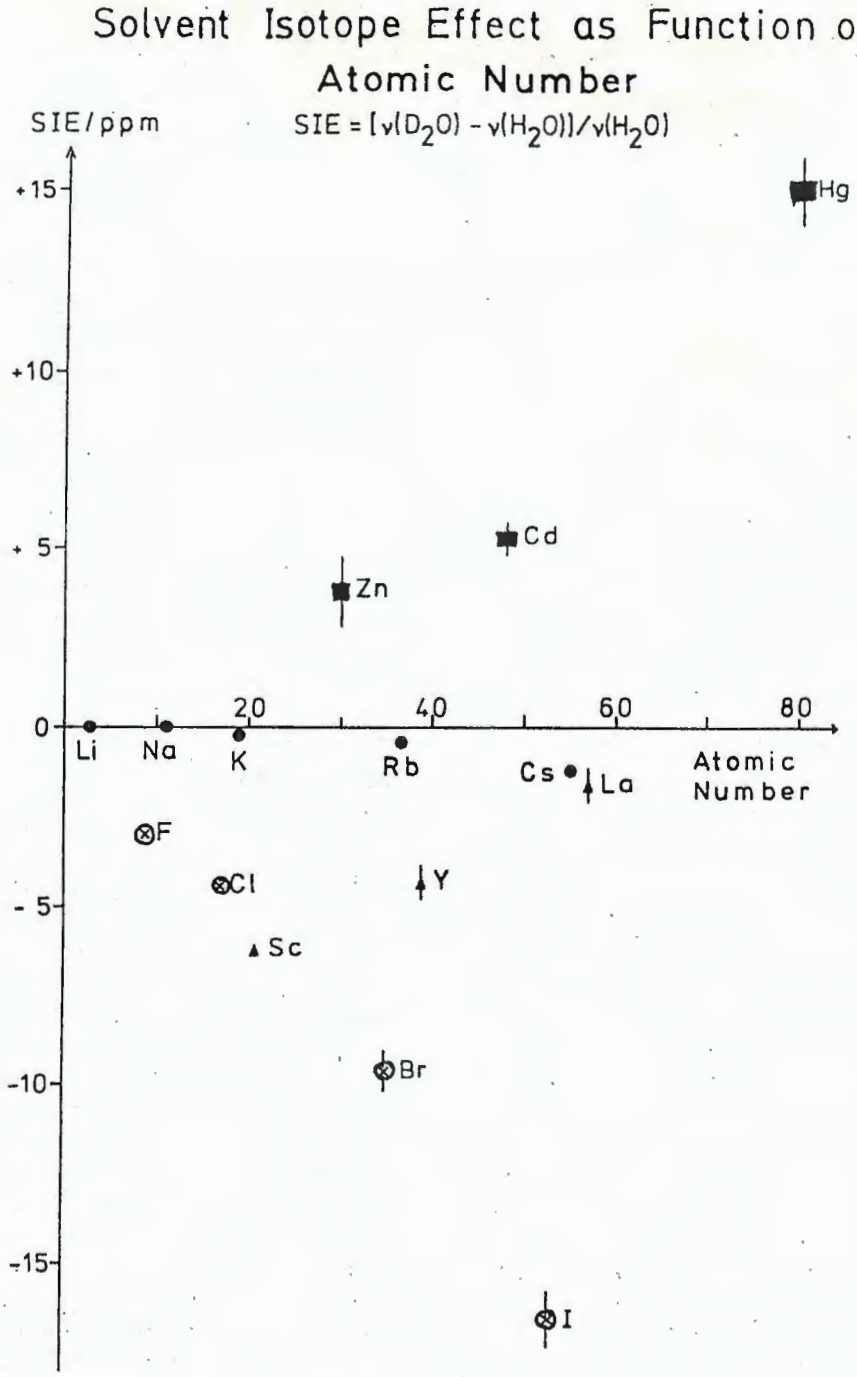

Fig.1: Solvent isotope effect as a function of the atomic number of the nuclei of the different groups. For ^{7}Li, ^{19}F, ^{89}Y data are taken from:

^{7}Li: A. Loewenstein , M. Shporer, Chem. Comm., 214(1968);

^{19}F: C. Deverell, K. Schaumburg. H.J. Bernstein, J. Chem. Phys. 49, 1276(1968);

^{89}Y: C. Hassler, J. Kronenbitter, A. Schwenk, Z. Physik A280, 117(1977)

The other data are taken from investigations of our group during all the years; reference list on request.

NTSU
NORTH TEXAS STATE UNIVERSITY

Department of Chemistry

February 18, 1986

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

Lithium Isotope Shifts

Dear Professor Shapiro:

We were interested in the recent comments in TAMU NMR Newsletter concerning the PERSCI disk drives on JEOL FX spectrometers. We have recently bought reconditioned drives from EF Industries for our FX-90Q. We have had no trouble with these so far and they were cheaper than JEOL's price for a trade.

t-Butyllithium is a tetrahedral tetramer in hydrocarbon solvent. We have found an additional peak 0.02 ppm (0.3 Hz at 13.19 MHz) upfield from t-butyllithium-^{6}Li which has a T_1 relaxation time at 26°C of 111 sec compared to 161 sec for t-butyllithium-^{6}Li. The two peaks have the appropriate larger chemical shift difference at 7.0 T, although we have not measured the relaxation at the higher field strength. Given the reactivity of t-butyllithium, we immediately suspected some contaminant or decomposition product. However, the peak is apparently not due to oxygen contamination and is not consistent with Lewis bases coordinated to the tetramer (typically downfield of the t-butyllithium peak). We think other aggregation states (e.g. dimers) would have a larger chemical shift difference that observed here.

An additional possibility is an isotopically shifted peak due to t-butyllithium containing 3 ^{6}Li nuclei and 1 ^{7}Li nucleus. With the 94.5% isotopic-abundance of ^{6}Li used in this work, the ^{6}Li resonance for the tetramer containing one ^{7}Li nucleus would be 17.5% of the main peak. To our knowledge, this would be the first observation of lithium isotope shifts. More importantly, it helps to explain the origin of the ^{6}Li relaxation which is not well understood. (Wehrli, F.W. J. Magn. Reson. 30, 1978, 193)

Assuming an isotopically shifted peak:

$R_4{}^6Li_4$: $1/T_1^{obs} = 1/T_1^{other} + 3/T_1^{Li\text{-}6} = 1/161$

$R_4{}^6Li_3{}^7Li$: $1/T_1^{obs} = 1/T_1^{other} + 1/T_1^{Li\text{-}7} + 2/T_1^{Li\text{-}6} = 1/111$

Ignoring contributions from the presence of ^{6}Li, $T_1^{Li\text{-}7}$ is 357 sec. This compares remarkably well to the 354 sec calculated

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(817) 565-2713

from data for $^{6}Li_6$ relaxation of t-butyllithium containing natural-abundant ^{6}Li, (Thomas, R. D., Ph.D. Dissertation, Wayne State University, 1981) assuming $T_1^{other} = T_1^{DD}(^{6}Li\text{-}^{1}H)$, which was found to be 118 sec.

$R_4{}^{7}Li_3{}^{6}Li$: $1/T_1^{obs} = 1/T_1^{other} + 3/T_1^{Li\text{-}7} = 1/59$

Apparently interaction with ^{7}Li nuclei plays a significant role in the relaxation of the ^{6}Li nucleus in alkyllithium aggregates. We are currently carrying out isotope experiments to confirm the new peak as the isotopically-shifted tetramer. (If anyone can suggest some "experimental artifact" or other explanation for the observed peak, we would be anxious to hear from you.)

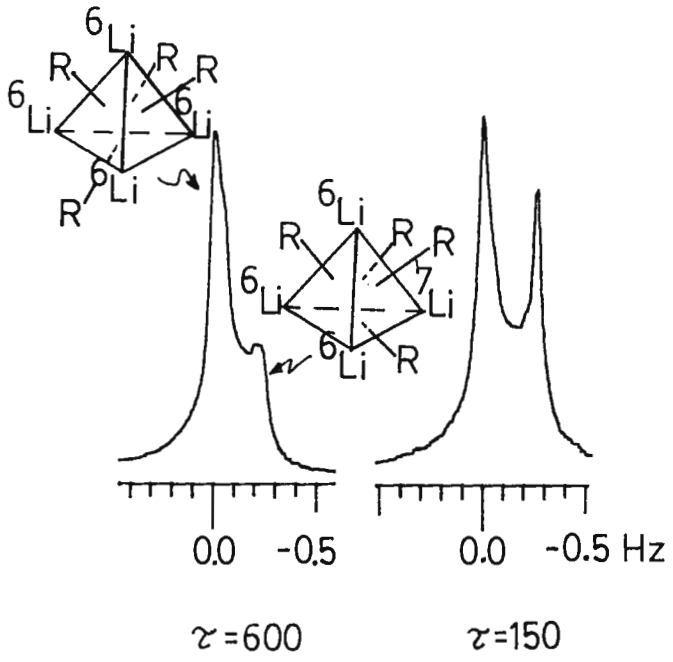
We might add that since there is no 3-parameter fitting routine for the inversion-recovery data as part of the JEOL software, we have modified a Pascal program for the Simplex algorithm (Caceci, M. S.; Cacheris, W. P. Byte 9, 1984, 340-362) to run on our IBM-PC. We then use data generated by the fitting program as input to the program Plotcall, by Golden Software, to produce graphs such as that shown below with a dot matrix printer.

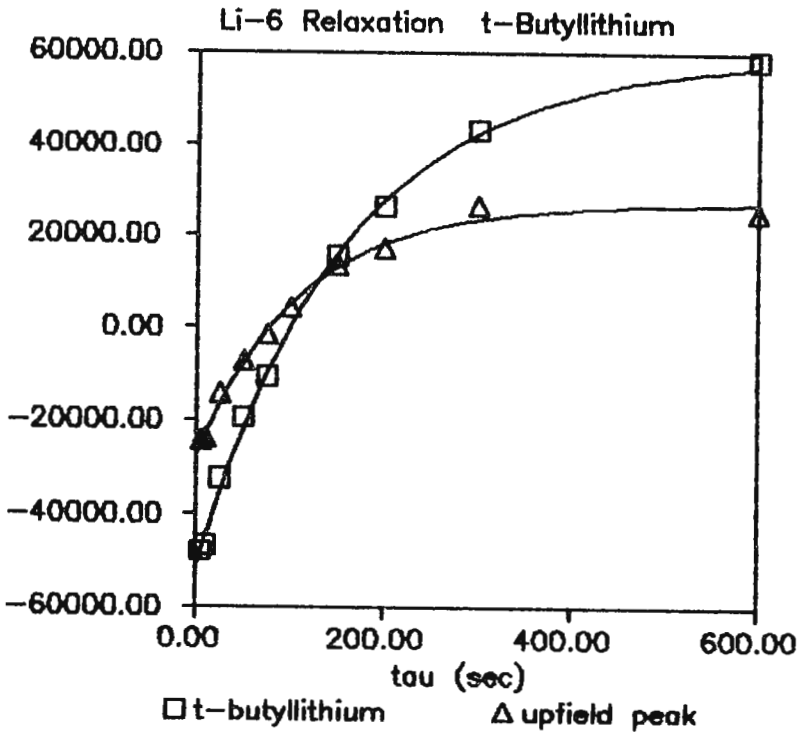
Please credit this contribution to Alan Marchand's account.

Sincerely,

Ruthanne D. Thomas

Ruthanne D. Thomas
Assistant Professor of Chemistry





WASHINGTON UNIVERSITY

ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

February 21, 1986

Professor Bernard L. Shapiro
Editor and Publisher
TAMU NMR Newsletter
Texas A&M University
Department of Chemistry
College Station, TX 77843

PROTON DECOUPLED FLUORINE NMR OF 2-FLUORO-2-DEOXY-D-GLUCOSE IN SITU

Dear Barry,

As your readers are aware, we have been studying the metabolic fate of 2-fluoro-2-deoxy-D-glucose (2FDG) in intact rat cerebral tissue in situ by ^{19}F NMR (TAMU NMR Newsletter no. 318, pg. 22, March (1985)). A complicating factor in these studies is that the fluorine nuclide can experience significant scalar couplings (J_{FH}) to neighboring protons which are on the order of the tissue resonance linewidths (0.2-0.4 ppm). This can result in a significant reduction of the achievable spectral resolution. In this case, removal of the (J_{FH}) interaction, by proton decoupling of the fluorine nuclide, will result in a greater apparent frequency resolution, and hence a greater signal-to-noise ratio, in the ^{19}F NMR spectrum of 2FDG and its metabolites.

Proton decoupling of fluorine is a technologically difficult problem in regard to achieving sufficient rf isolation between two frequencies which are only seperated in frequency by 6%. However, a geometrically orthogonal cross coil configuration will provide adequate isolation (i.e., 40 dB at 2 watts proton power with an animal in place) between the observation and decouple channels. In addition, this type of coil arrangement will allow independent optimization of the efficiency of both decoupling and observation antennas.

Sequentially obtained ^{19}F NMR spectra, Figure 1, of functioning cerebral tissue in situ (male Sprague-Dawley rats, ca. 250 g) were taken ca. 2 hours post intravenous injection of 2FDG (200 mg/Kg) under either proton coupled or decoupled conditions. The top spectrum, obtained under proton coupled conditions, reveals that only two fluorine resonances can be observed. In contrast, the observation of five peaks, seen in the bottom spectrum, illustrates the dramatic improvement in frequency resolution obtained upon proton decoupling.

Sincerely,

Bruce A. Berkowitz

Joseph J.H. Ackerman
Associate Professor

JJHA/kk

Proton Coupled vs. Decoupled ^{19}F NMR Spectra of Rat Brain *In Situ*

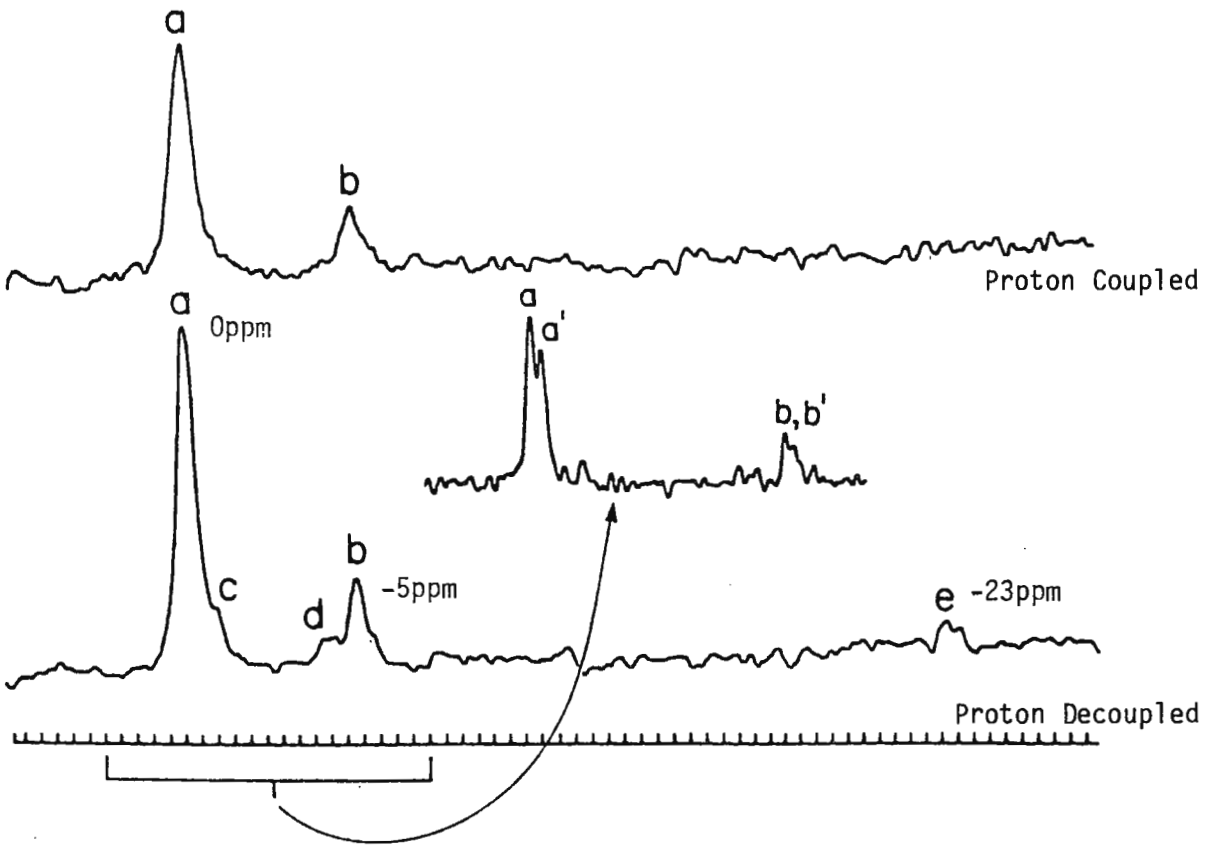


Figure 1 [Berkowitz and Ackerman]

The top spectrum represents a 10 minute proton coupled ^{19}F acquisition employing a two turn, 2 cm OD surface coil tuned for ^{19}F at 188.2 MHz and placed on the dorsal aspect of the rat's head. For decoupling, a two turn, 3 cm OD decoupling coil arranged in a Helmholtz fashion was positioned on either lateral aspect of the rats head; the decoupling antenna is independent of the observation antenna. The bottom spectrum represents a 10 minute proton decoupled ^{19}F acquisition taken immediately before obtaining the coupled spectrum by gating the decoupler on, in a broad band fashion, at 3 watts during the acquisition and off for a set delay to achieve an average power of 1.8 watts. The resolution enhanced insert in the bottom spectrum illustrates the fine structure obtainable upon proton decoupling. The animal was under a non-fluorinated anesthetic at all times during this procedure and was sacrified at the conclusion of the experiment.

330-50

Department of Physical & Inorganic Chemistry
THE UNIVERSITY OF ADELAIDE
GPO Box 498, Adelaide
SOUTH AUSTRALIA 5001

Telephone (08) ~~228-5333~~ 228-5365
Telex UNIVAD AA 89141

28 January 1986

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

Dear Professor Shapiro,

As I mentioned in our letter of 19 November 1985, Evan Williams has left for Palo Alto. We thought some of your readers might be interested in applying for the vacancy the details of which are as follows.

RESEARCH OFFICER IV IN NMR SPECTROSCOPY

A Research Officer IV is required to manage and control the research support programs on the FT NMR spectrometers operated jointly by the Chemistry Departments.

Three instruments, a Bruker CXP300, a Bruker HX90E, and a Bruker WP80 are utilised primarily for research undertaken by academic staff in the Chemistry Departments, but the incumbent would also be expected to act as a consultant to other users both within and outside the University as required, and to collaborate in the undertaking of research projects and the development of the facility.

It is anticipated that the successful applicant would have had several years research experience in the field of nuclear magnetic resonance. Some experience in the field of solid state NMR (PE/MAS) techniques would be an advantage.

Qualifications: An appropriate degree from an Australian University or qualifications recognised by the University as equivalent thereto.
Salary: $(Aus)36728.

Applications, together with the names and addresses of three referees, should be sent to Chairman, Department of Physical and Inorganic Chemistry, The University of Adelaide, G.P.O. Box 498, Adelaide, South Australia 5001, by 31 March 1986.

The position is also offered as an RO III at $(Aus)31866 in which case "undertaking of research projects and the development of the facility" would not be part of the job specification.

Yours sincerely,

Peter Allen

P.E.M. Allen

THE UNIVERSITY OF UTAH

27 January 1986

DEPARTMENT OF CHEMISTRY
HENRY EYRING BUILDING
SALT LAKE CITY, UTAH 84112

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

An Efficient Double-Tuned $^{13}C/^{1}H$ Probe Circuit For High Field CPMAS NMR

Dear Professor Shapiro:

Recently we have developed an efficient double tuned $^{13}C/^{1}H$ probe circuit for high field CPMAS NMR, to replace the probe circuit used in the Bruker CXP-200.

The features of this new probe circuit are as follows:

(1) The tuning and matching can be adjusted separately in each channel and made exactly equal to 50 ohms.

(2) An efficient isolation of the observation (^{13}C) from the decoupling channel (^{1}H) (about -40 db).

(3) When the sample coil diameter is 0.38 inch, the 90 degrees pulse is 3.5 US, and it decreases to 2.3 US when the diameter is 0.24 inch.

(4) The sensitivity (S/N) of observation channel (^{13}C) for 90 mg of adamantane from a CPMAS experiment of ten scans is close to 70.

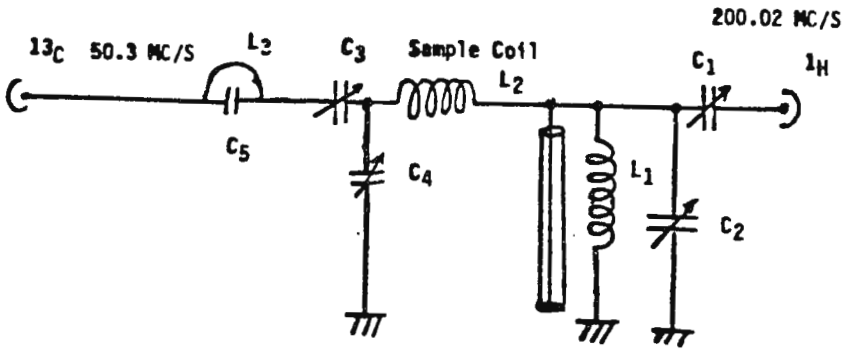


Figure 1. Schematic diagram of the CPMAS probe circuit.

Sincerely,

Yi Jin Jiang Ronald J. Pugmire David M. Grant

Yi-jin Jiang Ronald J. Pugmire David M. Grant

330-52

The University of Texas Medical Branch at Galveston

Medical School
Graduate School of Biomedical Sciences
School of Allied Health Sciences
School of Nursing

Marine Biomedical Institute
Institute for the Medical Humanities
UTMB Hospitals at Galveston

January 31, 1986

STAFF POSITION - NMR OPERATOR

The University of Texas Medical Branch seeks to hire an operator for its newly installed JEOL GX270WB NMR spectrometer. The operator will be responsible for maintenance, trouble shooting, and operation of the instrument in a multi-user arrangement. Interactions with staff involved with our newly installed GE CSI (Chemical Shift Imaging, 4.7 Tesla) and Technicare human patient imaging NMR instruments will also be expected. A strong background in chemistry and/or electronics is required; experience with Fourier transform, super-conducting magnets, and computer-controlled spectrometry is desirable, also an intent to grow with advances in NMR operations. Salary is in the range $25-30K. Contact: Dr. Leland L. Smith, University of Texas Medical Branch, Galveston, TX 77550; (409)-761-2811.

The Magnetic Resonance Laboratory of Wright State University School of Medicine and the Charles F. Kettering Memorial Hospital are seeking an MR SPECTROSCOPIST to join its staff. A Ph.D., postdoctoral training in chemistry of an appropriately related field, and evidence or research productivity with in vivo or in vitro MR are required. The successful applicant will be expected to establish a vigorous independent research program and be able to collaborate with Magnetic Resonance Laboratory users on the design and interpretation of MR experiments. The successful candidate will be recommended for appointment to the faculty of the Wright State University School of Medicine as an assistant professor in a suitable department or program.

The Magnetic Resonance Laboratory currently has a whole animal spectrometer-imager with a 40-cm bore 2.3T magnet, a 9-cm bore 360 MHz spectrometer equipped for solution and solid-state spectroscopy, and a human-body imager with a 1.5T magnet.

Applicants should send curriculum vitae and the names and addresses of three references to:

Dr. Gerald Alter, Chair
Magnetic Resonance Center Search Committee
Biological Chemistry
Wright State University
School of Medicine
Dayton, OH 45435

To be considered, applications must be postmarked prior to 1 May 1986. Wright State University is an Equal Opportunity/ Affirmative Action Employer.

DEPARTMENT OF HEALTH & HUMAN SERVICES

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National Institutes of Health

National Institute of Arthritis,
Diabetes, and Digestive and
Kidney Diseases
Bethesda, Maryland 20205
Building: 2
Room : B2-02
(301) 496- 2692

February 18, 1986

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

Dear Dr.Shapiro

Manual VT

To improve the regulation and make the sample temperature control independent of computer operations, we added the circuit shown in Fig. 1 to our two NT spectrometers. The modes of operation are as follows:

MODE:	COMPUTER:	FRONT PANEL, S2:
OFF	VT OFF	Comp
Computer Control	VT on, set Temp.	Comp
Manual Control	VT OFF	MAN, set Temp. on R1

On manual, the circuit uses the amplified analog output of the pyrometer, compares it with a reference derived from + or - 15V, and feeds the output to the power controller.

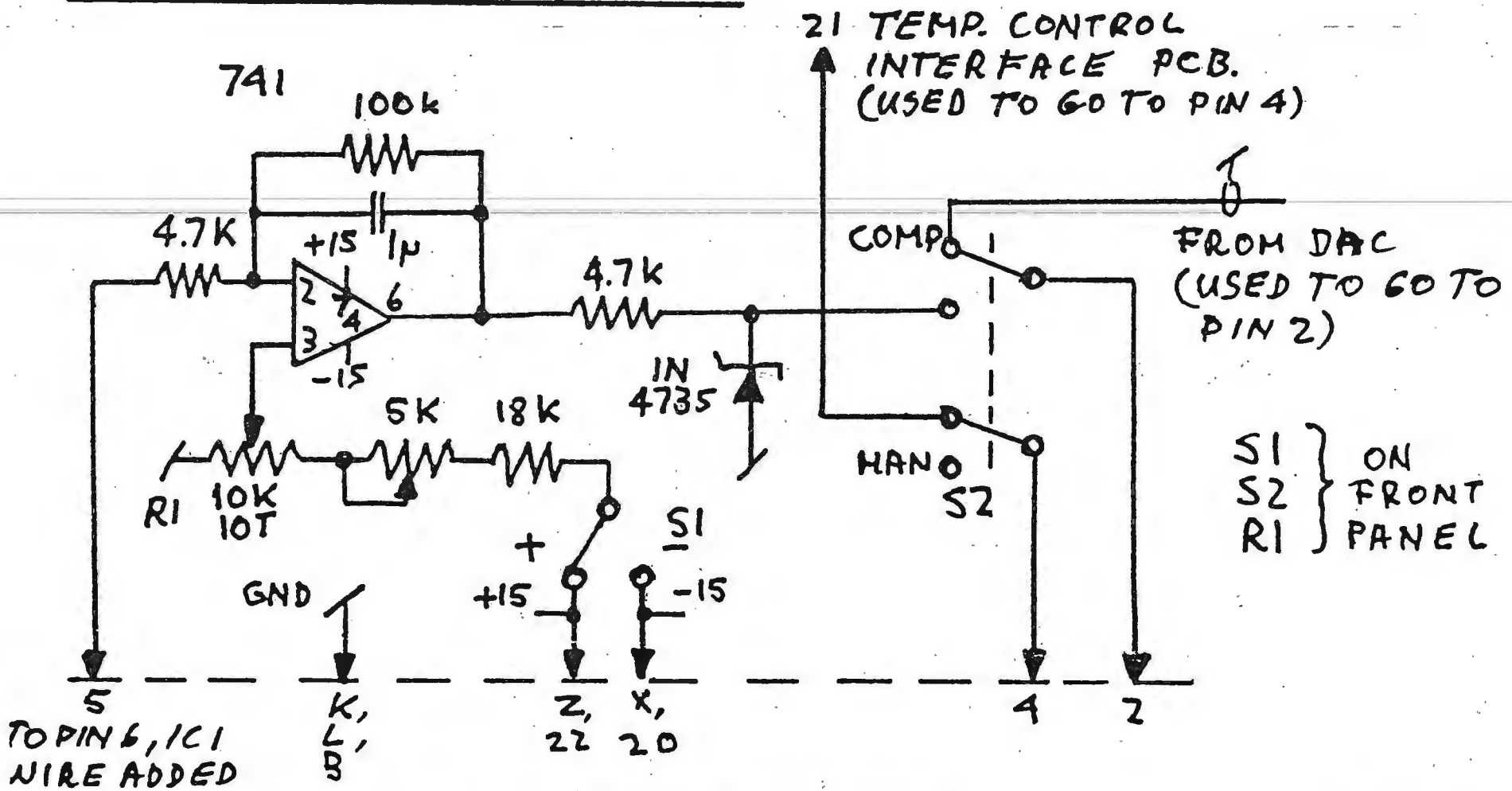
The circuit works for both standard units and units modified for 0.1°C operation. Manual adjustment is limited to $\mp$ 100°C as shown, but can easily be changed for different ranges by changing R1 et al. Stability and settling time appear to be equal or better than under computer control.

Sincerely,

R. Tschudin

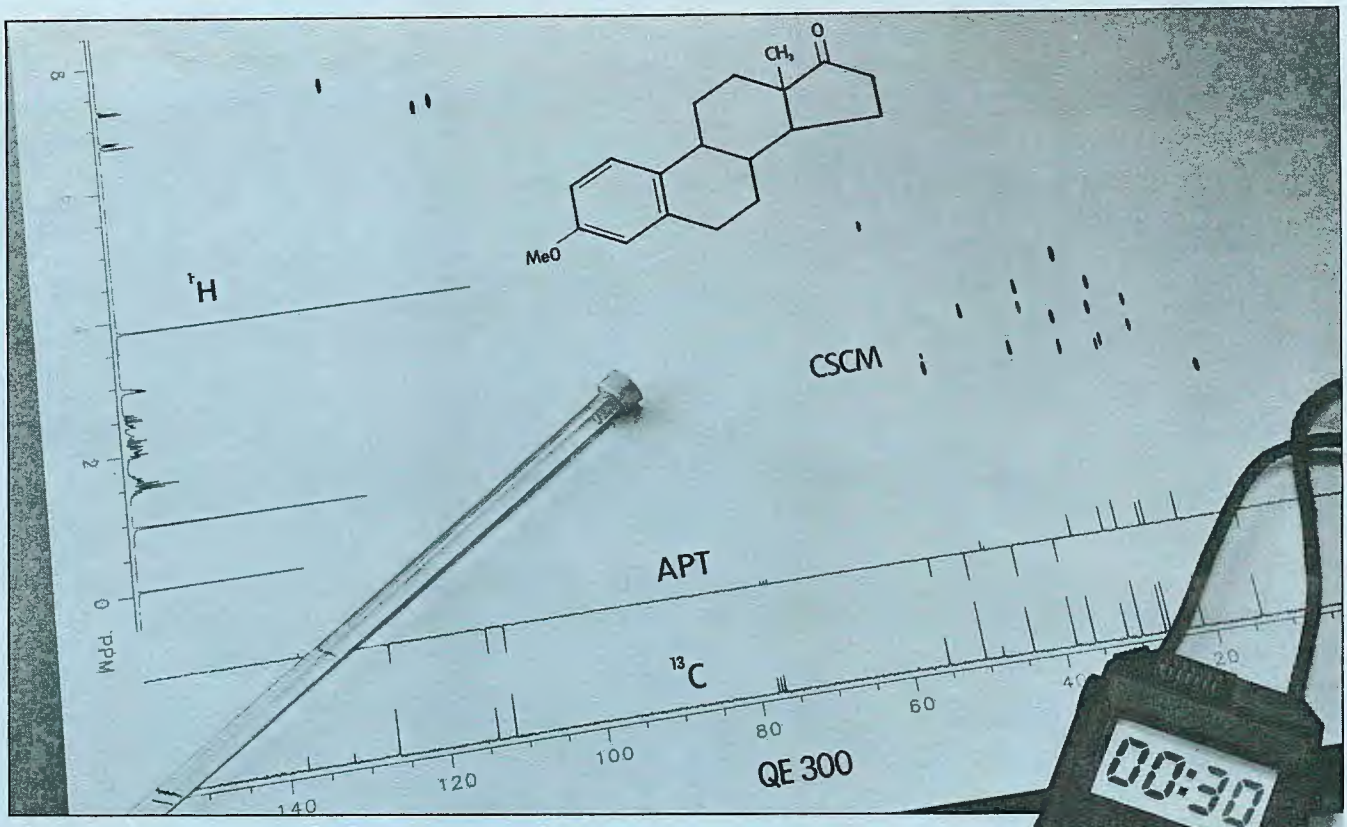
Rolf Tschudin
Laboratory of Chemical Physics

NT. TEMP. CONTROL (107237C)



J4, TEMP. CONTROL REGULATOR PCB.

FIG. 1



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The GE QE-300 does it all – faster than any other NMR spectrometer.

A ^{1}H spectrum, ^{13}C spectrum, an attached proton test (APT), and a ^{1}H-^{13}C chemical shift correlation map (CSCM). All these analyses can be performed in as little as ½ hour, on as little as 50 mg. of sample, for most organic compounds. And the QE-300 does them all – automatically.

With the NMR industry's most advanced automation.

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Set-up starts with *Autolock*. Lock on as little as 10% $CDCl_3$ in a 5 mm tube.

Use *Compushim* for touching-up spinning shims or complete shimming with both spinning and non-spinning gradients using the lock signal or observe FID.

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After data acquisition, *Autophase* accurately phases ^{1}H and ^{13}C spectra.

And finally, the analysis is completed with *Autointegrate*.

All these routines can be called up from QE-300 MACROs. In fact, any QE-300 operation, including pulse programs, can be implemented via MACROs for automatic, unattended sample analysis.

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The QE-300 is available with the industry's most reliable, highest capacity (100 positions!) *Automatic Sample Changer*. Plus, you can add an array processor, a variety of hard disks, and switchable probes for even higher sample throughput and performance.

Structural elucidation simplified.

For many organic molecules, the four experiments presented above will be all you need to determine or confirm molecular structure. For more complex applications, GE/NMR offers an extensive ^{13}C library with outstanding search capability. This library contains data from over 10,000 compounds and is currently being expanded using a QE-300 in operation at the Aldrich Chemical Company.

High throughput and performance demonstrated.

Get all the facts on the GE/NMR QE-300. Better yet, arrange for a demonstration. Call the GE/NMR group at (415) 490-8310. Or write General Electric Company, NMR Instruments, 255 Fourier Avenue, Fremont, CA 94539.

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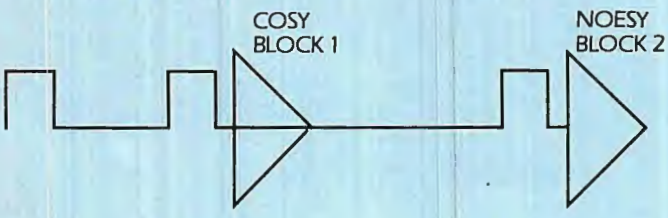
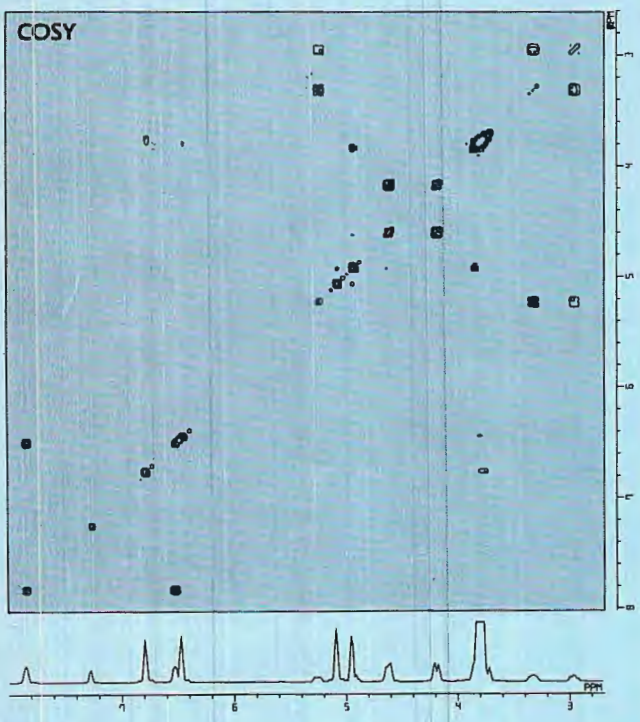
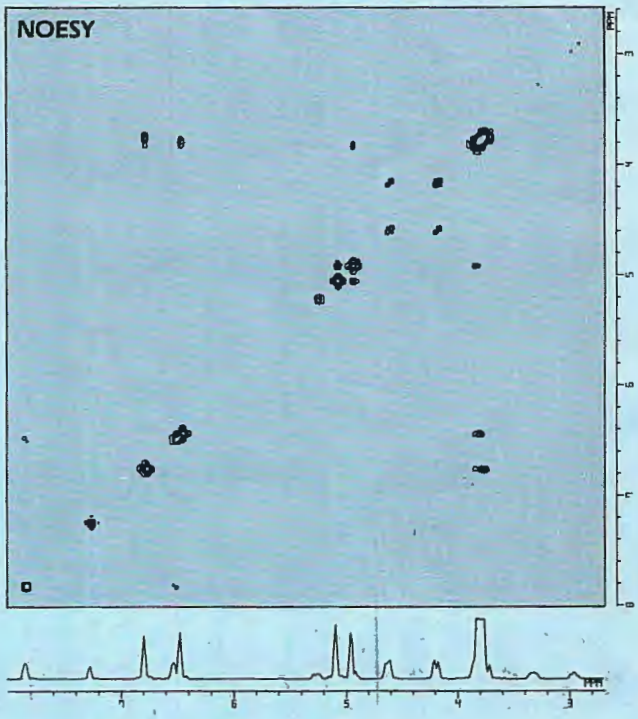


- Simultaneous acquisition of COSY and NOESY





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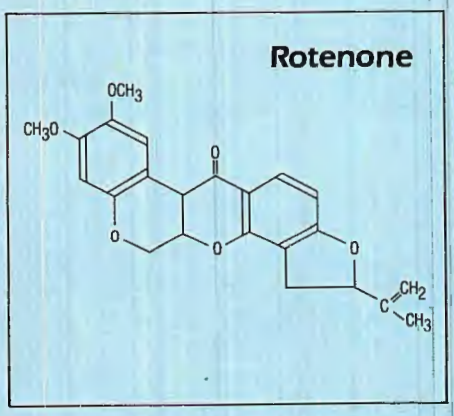
*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])



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