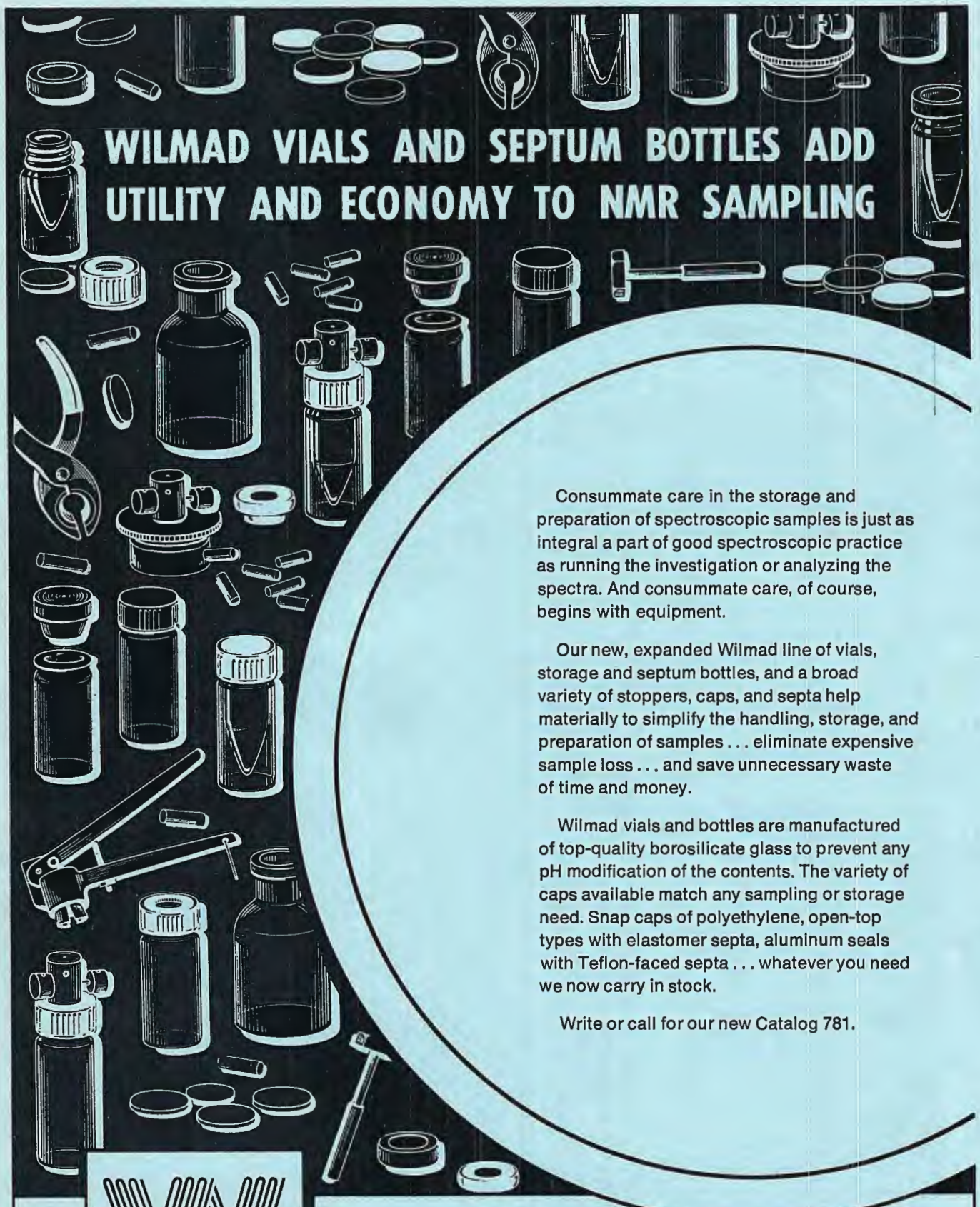
TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 281

February, 1982



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DEADLINE DATES: No. 282 1 March 1982
No. 283 5 April 1982

All Newsletter Correspondence, Etc., Should be Addressed To:

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

A U T H O R I N D E X - TAMU NMR NEWSLETTER NO. 281

PHYSICAL CHEMISTRY LABORATORY

OXFORD UNIVERSITY

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

January 6th 1982

Dear Barry,

"Revolution and counterrevolution"

One of the Founding Fathers' original intentions was that the Newsletter should report "partial or complete mysteries". Broadband decoupling theory is therefore a rich field of enquiry, and there have been many practical schemes suggested without any real theoretical basis. Now there are obvious dangers associated with the use of decoupling methods if the mechanism is not properly understood. There is one particular decoupling regime where we feel we are beginning to understand what is happening, using a theory developed by Malcolm Levitt (1). As yet it does not provide much insight into the earlier decoupling schemes, but at least it is a start.

This method of broadband decoupling inverts the proton spins repetitively (2) by means of a $90^{\circ}(X)\ 180^{\circ}(Y)\ 90^{\circ}(X)$ composite pulse, shown to be relatively insensitive to proton resonance offset. If this element is represented by R and its phase-inverted counterpart by $\bar{R}$, broadband decoupling is achieved by combining these elements into a suitable magic cycle, for example R R $\bar{R}$ $\bar{R}$ (but not R $\bar{R}$ R $\bar{R}$). This cycle is repeated at a rate fast compared with J(CH), which sets a practical lower limit on the level of B_2 such that $\gamma B_2/2\pi \gg J(CH)$. This limit appears to produce experimental problems unless $\gamma B_2/2\pi$ is at least 1 KHz, which is far less than most spectrometers use for conventional noise decoupling.

With higher levels of B_2 field, a proportionately wider band of proton resonances can be covered. For example with $\gamma B_2/2\pi$ = 5 KHz the effective bandwidth can be of the order of ± 5 KHz, which is what would be required if someone were to build a 1000 MHz spectrometer. The method thus performs better than noise-modulation. Malcolm's theory shows how to work out what constitutes a magic cycle, and how such cycles may be extended to improve the effectiveness of the decoupling. Some recent results will appear soon in a short note (3) and the detailed theory is in course of preparation (1).

There is an interesting common theme which seems to crop up in this and other decoupling techniques. One is the method of chirp-modulation (4). If we represent a chirp sweep through all proton resonances by C, and its phase-inverted counterpart by $\bar{C}$, it was found that the repeated sequence C C $\bar{C}$ $\bar{C}$ was much more effective than simple chirp modulation alone, although the rationale was not entirely clear.

Recently another dual-modulation scheme was described in this Newsletter 279, 31 (1981) by Robert Dykstra, showing a threefold improvement in carbon-13 sensitivity on a Varian XL-100 spectrometer. The proton transmitter was phase modulated by a 128 Hz square wave and then phase modulated by a 32 Hz square wave. If we suppose that one half cycle of the 128 Hz modulation imposes some kind of proton perturbation D and the second half cycle a phase-inverted perturbation $\bar{D}$, then the sequence may be written

$$\overline{D\,\bar{D}}\;\big|\;D\,\bar{D}\,D\,\bar{D}\;\big|\;\overline{D\,\bar{D}\,D\,\bar{D}}\;\big|\;D\,\bar{D}\,D\,\bar{D}\;\big|\;\overline{D\,\bar{D}}\;\ldots\;.$$

where the rectangular wave represents the 32 Hz modulation. Combining the two gives:

$$D\,\bar{D}\,\bar{D}\,D\quad\bar{D}\,D\,D\,\bar{D}\quad D\,\bar{D}\,\bar{D}\,D\quad\bar{D}\,D\,D\,\bar{D}\;\ldots\;.$$

which is $D\,\bar{D}\,\bar{D}\,D$ and $\bar{D}\,D\,D\,\bar{D}$ tacked together, sequences very similar to some of the magic cycles used for composite pulse decoupling or the phase-modulated chirp decoupling. Could there be a connection ? Clearly the gang-of-four is inextricably linked with the processes of revolution and counterrevolution.

Kindest regards,

Tom Frenkiel Malcolm Levitt Ray Freeman

Tom Frenkiel Malcolm Levitt Ray Freeman

(1) M. H. Levitt, R. Freeman and T. A. Frenkiel, Proc. Roy. Soc. (London) to be published.

(2) M. H. Levitt and R. Freeman, J. Magn. Reson. 43, 502 (1981).

(3) M. H. Levitt, R. Freeman and T. A. Frenkiel, J. Magn. Reson. (in press).

(4) V. J. Basus, P. D. Ellis, H. D. W. Hill and J. S. Waugh, J. Magn. Reson. 35, 19 (1979).

281-3

MINISTÈRE DE L'AGRICULTURE

INSTITUT NATIONAL DE LA RECHERCHE AGRONOMIQUE

STATION DE RECHERCHES SUR LA VIANDE

Références à rappeler :

Study of hydrated biological samples by NMR cross relaxation

Prof. B.L. SHAPIRO
Department of Chemistry
College of Sciences
Texas University

COLLEGE STATION TX 77843
(U.S.A.)

Theix, le 14th May 1981

Dear Dr. SHAPIRO,

It's well known that the study of magnetic relaxation can provide information on molecular motion. There have been numerous biological studies involving proton relaxation. Cross relaxation between protons in water W and protons in macromolecules M can have a large contribution to the proton relaxation rate of water in biological systems (1 - 5). Studies of cross-relaxation effects, have been studied extensively in the case of nonoverlapping resonances. In heterogeneous biological systems the two phases have overlapping proton resonances and conventional selective irradiation is not possible. Since, in most hydrated biological samples the spin spin relaxation rate in each phase are very different, it is possible to have the 180° pulse length τ_p in such a way that the water proton magnetization is completly inverted by the pulse whereas the macromolecular magnetization is only partially inverted (5).

We have used a method (7) to obtain a rate of cross relaxation. The free precession signal can be represented as the sum of exponential decays. At time t_o the first exponential decay is zero. We observe a cross relaxation between protons located on different sublatices, in experiments consisting of sequence of three $\pi/2$ pulses. The first pulse creates a situation with different longitudinal magnetization Wz, Mz. Starting from thermal equilibrium, the magnetizations rotate from the direction oz to the direction ox along which they undergo free decay. At time t_o the magnetization Mx goes through zero whereas the magnetization Wx has only partially decayed. The second $\pi/2$ pulse, in opposite phase with the first, is applied at that time t_o. The initial conditions thus prepared correspond to $Mz = 0$ $Wz \neq 0$. A third $\pi/2$ pulse applied at time τ variable after the second one allows the measure Mz and Wz from the shape and amplitude of the free decay signal. The amplitude h of the second exponential part of the decay varies, as a function of τ as the difference in two exponentials.

...

The decrease with a time constant Tm of a few hundred microseconds describes the cross relaxation between the two phases. The increase arises from spin lattice relaxation with a time constant T_1.

The T_1 and Tm values were obtained by fitting the exponential lines through the data points by a program of nonlinear regression (6).

We call h(o) the initial amplitude of the signal of the water and $h(\infty)$ the equilibrium value it would reach without spin lattice relaxation. The ratio $h(\infty) / (h(o) - h(\infty))$ is proportional to the ratio of number of protons in each phase.

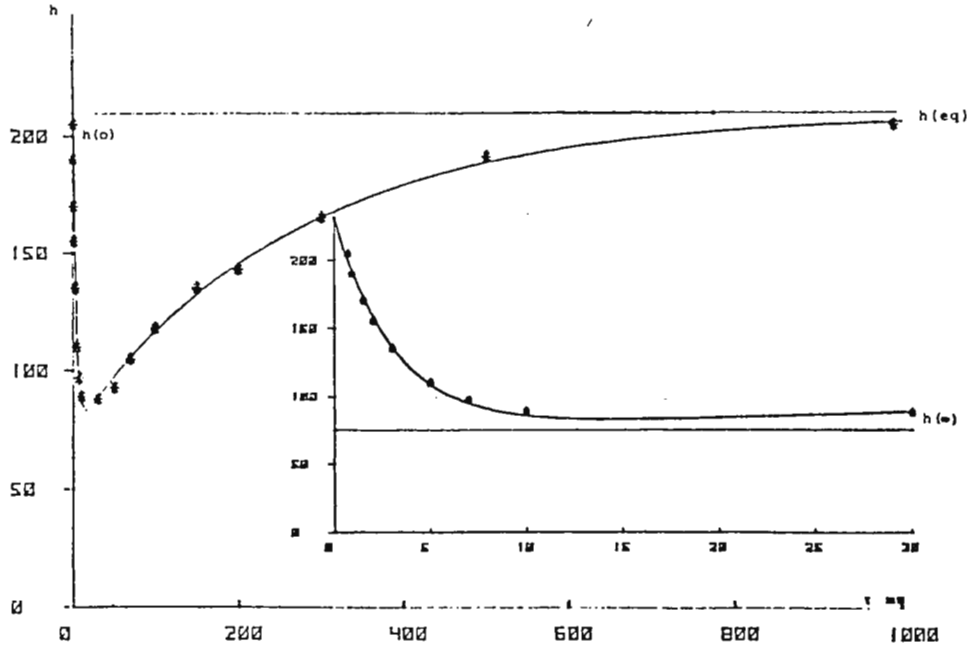
This sequence of pulse likely gives information from the values Tm and T_1 when we vary the biological sample but also allows to study the ratio $h(\infty) / h(o) - h(\infty))$ as a function of the temperature.

All data were very interesting for the caracterization of different biological samples at various relative humidity.

Sincerely yours,

J. ALIZON

J.-P. RENOU



VARIATION OF THE AMPLITUDE OF THE FREE DECAY OF WATER AS A FUNCTION OF THE TIME INTERVAL τ IN CROSS RELAXATION EXPERIMENT

(1) S.H. KOENIG, R.G. BRYANT, K. HALLENGA and G.J. JACOB - Biochem. 17.4348, 1978.

(2) M. EISENSTAOT and M.E. FABRY - J. Magn. Reson. 29.591, 1978.

(3) B.M. FUNG - Biophys. J. 18.235, 1977.

(4) H.T. EDZES and E.T. SAMULSKI - J. Magn. Reson. 31.207, 1978.

(5) H.T. EDZES and E.T. SAMULSKI - Nature London 265.521, 1977.

(6) J. KOPP - Communication personnelle.

(7) M. GOLDMAN and L. SHEN - Phys. Rev. 144.321, 1966.

281-5

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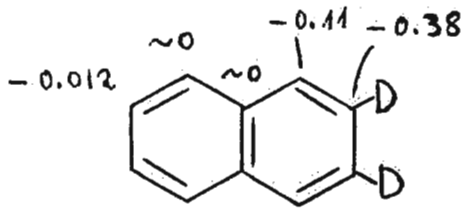
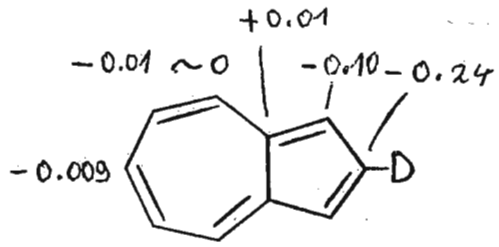
Dear Professor Shapiro,

Long Range Deuterium Isotope Effects in ^{13}C-NMR

Recently I have synthesized 2.3-dideuterionaphthalene 1 and 2-deuterioazulene 2. With our WH-400 nmr-spectrometer I was able to measure some interesting long range deuterium isotope effects which are given in the formula.



1



2

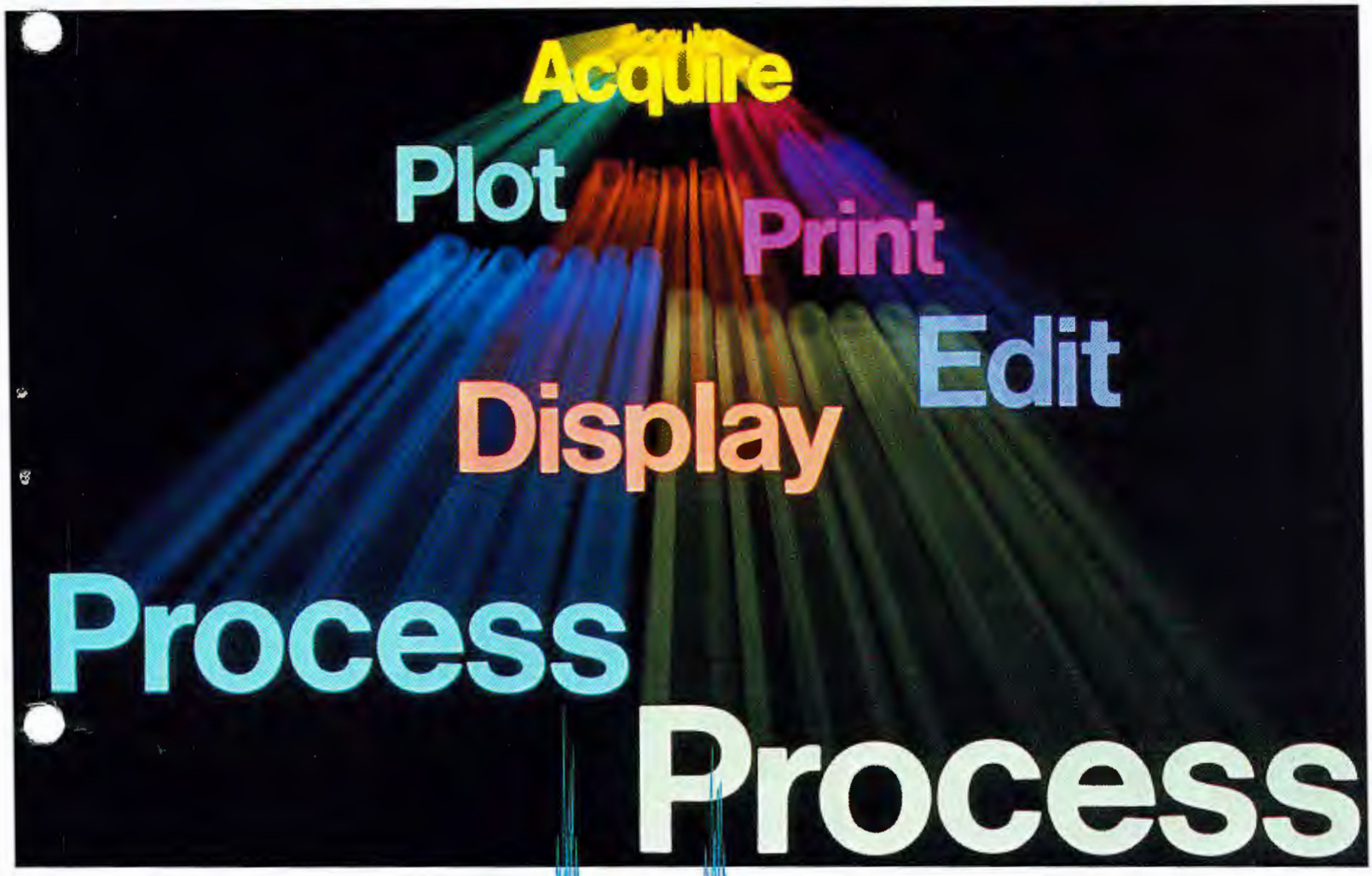
[ppm]

Note the sign change for the five membered ring in 2 and that both molecules contain carbon atoms which display no isotope effects.We are looking for a reasonable explanation of these data.

Sincerely yours,

Stefan Berger

Bruker NMR



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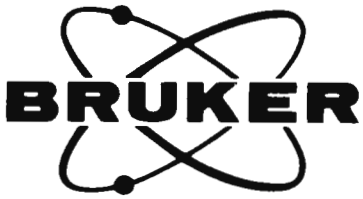

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Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000 Liège 1, Belgique

Professor B.L. SHAPIRO
Texas A&M University
College of Science
College Station, TX 77843

January 5, 1982

Complexation of Pr^{3+} By Two Different Ionophores Boosts Transport.

Dear Barry,

We measure the rate of transport of Pr^{3+} cations across phosphatidylcholine vesicles, by monitoring the ^{31}P resonances of the inner and outer phospholipid head groups. We have already shown[1] that Pr^{3+} ions are transported inside complexed with two molecules of the conjugate base of the etheromycin ionophore $\underline{\underline{1}}$. With such a stoichiometry, it became tempting to investigate the possibility of either positive or negative cooperativity in the presence of two different ionophores. Indeed, when lasalocid $\underline{\underline{2}}$ (which also transports Pr^{3+} with 2 : 1 stoichiometry) and etheromycin $\underline{\underline{1}}$ are incorporated together, in 1:1 ratio, into the lipidic phase, transport is faster than with each ionophore separately.

Assuming that a 1:1 mixture of $\underline{\underline{1}}$ and $\underline{\underline{2}}$ partitions itself statistically between $\underline{\underline{1}}.Pr^{3+}.\underline{\underline{1}}$ (one part), $\underline{\underline{2}}.Pr^{3+}.\underline{\underline{2}}$ (one part), and $\underline{\underline{1}}.Pr^{3+}.\underline{\underline{2}}$ (two parts), these complexes effect Pr^{3+} transport at intrinsic relative rates of 1,2, and 13.5, i.e. a remarkable synergism is set up.

With best regards,

Cordially yours,

Jean Grandjean

Pierre Laszlo

1. J. Donis, J. Grandjean, A. Grosjean, and P. Laszlo, BBRC, 102, 690-96 (1981).

THE ROCKEFELLER UNIVERSITY
1230 YORK AVENUE · NEW YORK, NEW YORK 10021

29 December 1981

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

Dear Professor Shapiro:

Since acquiring a NT-300 wide bore system last spring we have examined, among other things, some polystyrene samples by ^{13}C NMR. On the basis of results reported for lower field (1,2), it was assumed that the para aromatic carbon and methine backbone carbon were not sensitive to the stereochemical environment in atactic material. In fact the widths of these resonances were used in quantitative evaluation of T_2 (2). It is useful to note, as illustrated in Figure 1, that at 75 MHz significant structure presumably related to the stereochemistry can be observed. The widths of these lines provide at best a lower limit to the T_2 value.

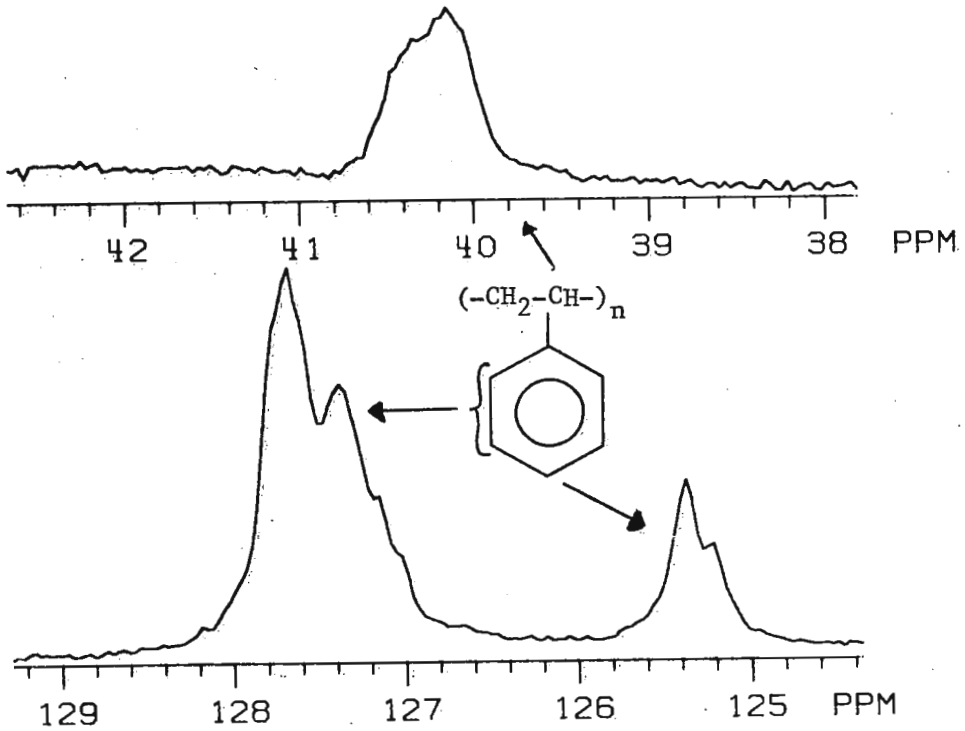


Figure 1. Proton decoupled ^{13}C NMR spectrum of 17,500 MW atactic polystyrene 20% w/v in chloroform. Chemical shifts are relative to TMS and peak assignments are indicated.

1. Inoue, Y.; Niishioka, A.; Chujo, R. Die Macromolecular Chemie, 1972, 156, 207.
2. Doscocilova, D.; Schneider, B.; Jakes, J. J. Mag. Res. 1978, 29, 79.

Sincerely yours,

David Live

DC:mmh

P.S. Please credit this contribution to David Cowburn's account.

Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74074

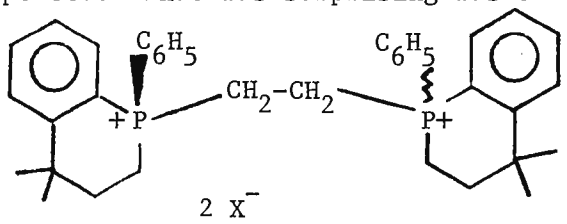
January 15, 1982

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

Title: Use of ^{31}P NMR Spectroscopy to Monitor the Resolution ofCertain 1-Phenylphosphinolinium Salts and the Observation of Non-equivalence of the P Atoms in the Presence of Chiral Hydrogen Dibenzoyltartrate

Dear Barry:

Although your reminder letter arrived, your office may recall that Dr. W. T. Ford of our Department and I both share sending in letters to meet our obligation so this letter is a little early but I trust it will keep our standing OK. We have recently completed the synthesis and resolution of stereoisomers of 1,1'-(1,2-ethanediyl)bis(1,2,3,4-tetrahydro-4,4-dimethyl-1-phenylphosphinolinium) salts I. We were able to use ^{31}P NMR analysis to monitor this resolution very nicely since the d,l-pair and the meso-isomers gave distinctly different ^{31}P signals as expected. What was surprising was that the meso-isomer, in the



presence of the anion L(+)-HDBT or D(-)-HDBT showed two signals for the P nucleus. When a drop of trifluoroacetic acid was added to the NMR tube, the two signals collapsed into one signal. The non-equivalence of the P atoms must arise, we feel, from interactions of the two P atoms with the optically active anion in a non-equivalent manner. We have not found another example in our search of the chemistry of phosphonium salts but suspect such might be found in other systems. We would welcome any comments on the observation by others.

Best regards for 1982.

Sincerely yours,

Darrell

K. D. Berlin
Regents Professor

281-11
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ADRESSE :
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Pr. B.L. SHAPIRO
TEXAS A.M. University
College of Science
COLLEGE STATION

TEXAS 77843
U. S. A.

VERT-LE-PETIT, le January 7, 1982

V/Référence

N/Référence

OBJET :

TITLE : Molecular interactions of dialkylphosphoric acid with a neutral phosphorus compound.

Dear Barry,

We have had recently to study the interaction of di 2 EHPA (di 2 Ethyl Hexylphosphoric acid). $\left[CH_3\ (CH_2)_3\ CH(CH_2CH_3) - CH_2O\right]_2\ P(O)\ OH$ with di n HOMPO (di n hexyl octyl methoxy phosphin oxid). $\left[(C_6H_{13})_2\ P(O)\ CH_2O\ C_8H_{17}\right]$ in kerosen (a mixture of saturated hydrocarbons).

Fig. 1 shows the change in chemical shift of the - OH proton peak for a 0.5^M di 2 EHPA solution in kerosen, versus the di n HOMPO molar concentration.

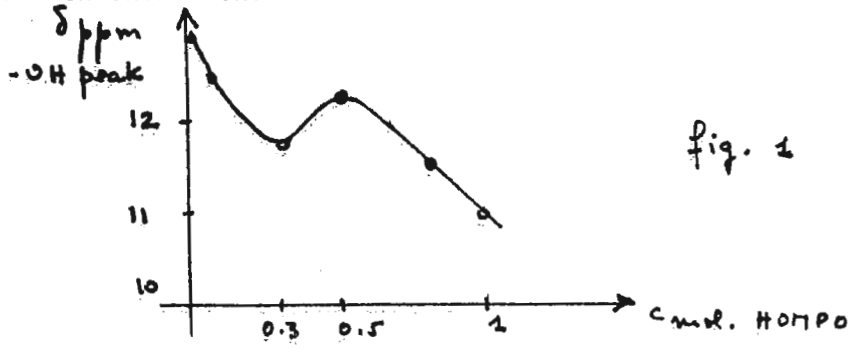


fig. 1

In pure state, di 2 EHPA is self-associated ($n \geqslant 2$) and its - OH peak uniformly shifts to higher fields, when diluted into cyclohexane (or another non complexing solvent).

In the mixtures we studied, the basic effect of the P (O) group from di n HOMPO must shift as well the - OH peak to higher fields if no complexation occurs. Conversely, if hydrogen bonding or complexation occurs it must shift to lower fields.

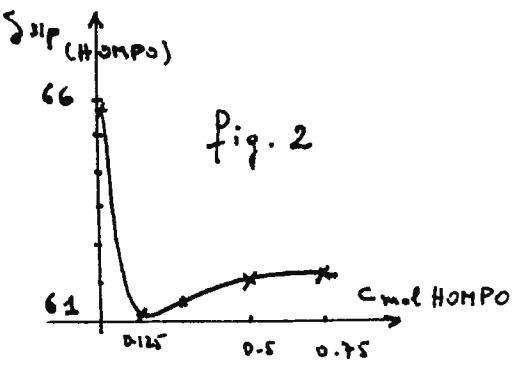
Fig. 1 clearly shows competiting mechanisms with a trend reversal in the 0.3 - 0.5^{M} range ; this can be taken as a proof of the existence of a 1/1 complex due to hydrogen bonding between the -OH of the acid and the P (O) group of di n HOMPO.

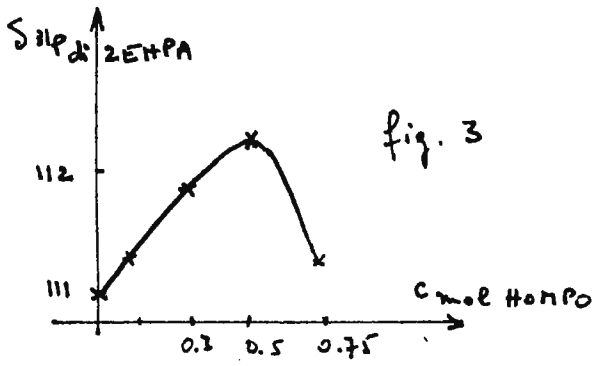
$$(RO)_2 \underset{\underset{O}{\|}}{P}\text{-OH} \;\cdots\; O = P\,(R_2)\,(CH_2O\,R')$$

On the other side, the constancy of the chemical shift of CH_2O protons of di n HOMPO shows that there is no significant interaction due to the oxygen of this group.

The ^{31}P N.M.R. study is in favor of the formation of a 1/1 complex with a donor effect of the P(O) of di n HOMPO (see Fig.2 and 3). On the di 2 EHPA side, one observes a maximum shift of 1 ppm to strong field of the peak for the 0.5^{M} concentration of di n HOMPO ; this effect is rather weak because the direct surrounding of the phosphorus (4 oxygen atoms) is disturbed only by hydrogen bonding two bonds away from phosphorus. On the di n HOMPO side, the effects on phosphorus chemical shift are more complex and show a very significant shift to lower field (ca. 5 ppm) for a concentration of 0.125^{M} of di n HOMPO. Some complexation involving one molecule of di n HOMPO and four molecules of di 2 EHPA could occur.

We are following this study.





G. MAVEL - M. PREVOST - R. MANKOWSKI-FAVELIER

Best regards and season's greetings

Gérard

Prof. Dr. F.H.Köhler
ANORGANISCH-CHEMISCHES INSTITUT
DER
TECHNISCHEN UNIVERSITÄT MÜNCHEN

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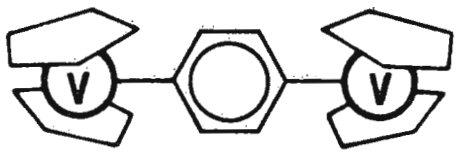
3109 Prof.Köhler

Prof. B.L. Shapiro
Department of Chemistry
Texas A a. M University
College Station, Texas 77 843
USA

Title: Magnetic exchange evidenced by nmr

Dear Professor Shapiro,

in response to your green letter addressed to Prof. H.P. Fritz I would like to touch a problem which we encountered when we linked two paramagnetic metallocenes together. First we did this by means of an intervening hydrocarbon residue which was designed to allow conjugation between the metallocene units as in 1.



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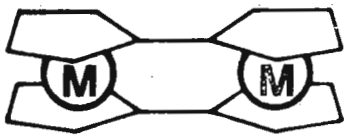

2

We expected some pairing of the two single electrons on each vanadium. However, the nmr spectra showed almost no change when compared with the results from the corresponding non-bridged compound. Since the hughe paramagnetic signal shifts should be a very sensitive probe for the individual magnetic properties of a molecule we conclude that in 1 the spin exchange is unimportant. The reason for this and further examples are given in a paper which just appeared[1]

Another possibility of linking two metallocenes is realized in 2. In the case of M = Cr we know that the ^1H signal of chromocene appears at about 324 ppm to low field. No signals are found in this range for dimeric chromocene; instead, the two expected resonances appear at only 42 and 49 ppm (same field side). This time considerable exchange seemed to be operating, and we confirmed this with variable temperature studies: the signal shifts increase with temperature (just opposite to the usual Curie-behavior) which indicates the thermal population of a low lying empty molecular orbital. In Angew. Chem. this will be further illustrated.

Yours very sincerely

Frank H. Köhler

1) F.H. Köhler, W. Prößdorf and U. Schubert, Inorg. Chem. 20 (1981) December issue.

MONASH UNIVERSITY

TELEGRAMS,
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DEPARTMENT OF CHEMISTRY

OUR REF.

YOUR REF.

19th January, 1982

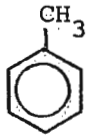
Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, Texas 77843,
United States of America.

Dear Barry,

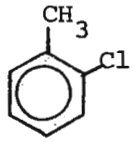
Methyl Group ^{1}H Relaxation

We thought that everyone else had lost interest in the relaxation of methyl hydrogens, so it was a (pleasant) surprise to see the contribution from Chazin and Colebrook (TAMU NMR 279 : 15).

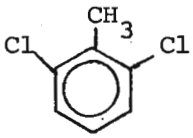
Our results are somewhat similar, and we also blame changing energy barriers for changing rotational rates and thus changing relaxation behaviour. For instance, our T_1 values (sec) for the methyl hydrogens of chlorotoluenes are shown below the formula.



12.5



7.5



12.8

We argue that, in the monochloro compound, the rotational energy maximum (H passing Cl) is raised, leading to slower rotation. In the dichloro compound, the minimum is also raised so the barrier (i.e. the difference between minimum and maximum) must remain about the same as that in toluene. At this stage we are assuming that overall tumbling for this part of the molecule is unaffected by chlorine substituents and/or that it's methyl rotation which really counts. Some experiments to check these points are in hand.

Please credit this contribution to Michael Heffernan's Monash subscription.

Kind regards,

Ian

Ian D. Rae.

JEOL GX REPORT #1

THE plexus DATA SYSTEM

PLEXUS: An interwoven network of parts or elements in a system.

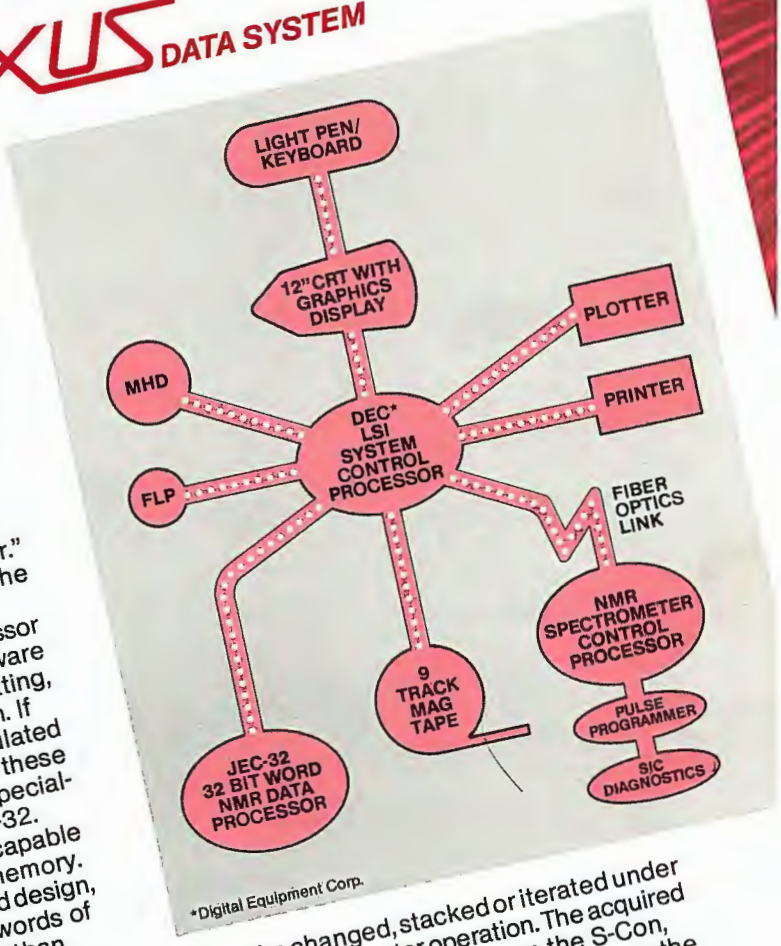
There is no better way to describe the data processing philosophy incorporated into the GX-400/500 FT-NMR spectrometers. To accommodate the increased demands placed on an FT-NMR data system, the PLEXUS data system deviates from the usual single computer approach. A multi-computer network using distributed processing software is employed to achieve trend setting levels of performance for speed, efficiency, and flexibility.

The center of the PLEXUS data system is the Digital LSI "system control processor." All interaction between the operator and the spectrometer pass through this hub. Job assignments are determined by this processor and distributed to the appropriate hardware for execution, for example; printing, plotting, disc storage or spectrometer operation. If actual data is to be acquired or manipulated (Fourier transformation, phasing, etc.) these jobs are assigned to a second, highly specialized "NMR data processor," the JEC-32.

The JEC-32 is a 32-bit computer, capable of accommodating 256K words of memory. Because of its unique and specialized design, fast Fourier transformations of 8K words of data (32 bit words) are done in less than 3 seconds! The real value of this amazingly fast FFT time can be appreciated more fully when considering large data sets, especially 2-dimensional FFT, where transform times are decreased dramatically, making 2-D NMR a much more practical and efficient experiment.

The spectrometer system is made complete by total computer control over all spectrometer functions by the PLEXUS data system. Through the "system control processor" and "spectrometer control processor," PLEXUS totally controls all spectrometer variables, including lock offset, lock phase, lock level, receiver gain and all irradiation and observation phases allowing any NMR parameter to be changed, stacked or iterated under unattended computer operation. The acquired experimental data is sent from the S-Con, over distortion-free fiber optics cables, to the JEC-32 where data treatment is carried out.

A further benefit of the PLEXUS concept is the SIC diagnostics (Status Integrity Check) which monitors all of the spectrometer hardware through status registers located on each board. Valuable service information concerning NMR hardware and computer components can then be extracted directly from the GX spectrometer or remotely.



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Department of
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Glenridge Campus
St. Catharines,
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Canada

January 21, 1982.

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

Dear Professor Shapiro:

DRASTIC ENEMA FOR A CONSTIPATED MAGNET

Our elderly A-60 (bought used 16 years ago!) still plods on, but is due to be replaced in April by a Bruker WP-80CW. In a final idiosyncratic gasp when the teaching and research load was at a maximum, and couldn't be handled by the multi-nuclear WP-60 alone, the magnet chose to become solidly plugged with corrosion and deposits which normal cleaning techniques couldn't budge. One cooling channel was plugged gas tight to nitrogen at 1000 psi! Attempts to free the plug with HCl admitted under vacuum and then pressurized with high pressure nitrogen failed, so drastic action was required. This consisted of attempting to force hydraulic oil through the coils with a pump rated at 10,000 psi. After some hours of such treatment, applied alternately from each end of the cooling coil, about 50 cm of a solid plug was forced out. The crackling noises coming from the magnet coil during this treatment did not bode well for its survival, but on reassembly of the magnet, other than requiring some coarse adjustments of the magnet power supply, the field homogeneity appeared better than ever.

I do not normally recommend such treatment for a "precision" piece of equipment, but when all else fails, bash it with the largest sledge hammer you have!

Yours sincerely,

Jack M. Miller,
Professor of Chemistry.

Timothy R. B. Jones,
Manager, Analytical Services.

281-19

FREIE UNIVERSITÄT BERLIN
Fachbereich Chemie (FB 21)
Institut für Organische Chemie (WE 02)

FU | BERLIN

Dr.Klaus Roth

Freie Universität Berlin,
FB 21, WE 02, Takustraße 3, 1000 Berlin 33

14.1.1982

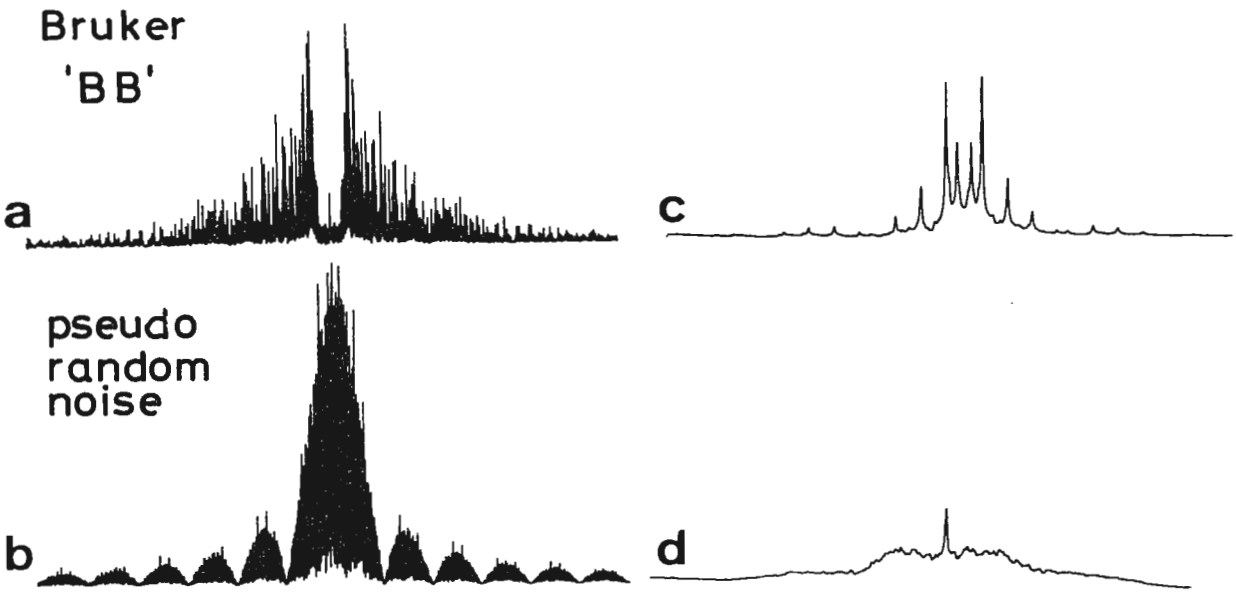
Dear Prof.Shapiro:

There's a hole in my decoupler

Within our double resonance studies we tried to measure a so-called low-power noise decoupled spectrum which should be equivalent to a noise off-resonance decoupled (NORD) spectrum (1,2). We measured the $^{13}C(^{1}H)$ spectrum of CH_3J in acetone-d_6 with our Bruker WH-270 and switched on the broadband modulated decoupler which was centered at the frequency of the CH_3-protons. After reducing the power to about 0.2 Watt the resulting spectra looked awful. Instead of the expected broad hump the signal was splitted into several sharp lines. After some sleepness nights we found out that this peculiar behaviour is due to the power distribution in Brukers 'BB'-field. Surprisingly there is a gap of frequency components around the center of about 380 Hz. Within a normal high power decoupling experiment this non-linear power distribution leads to a better decoupling of the carbon signals compared to other modulation techniques. In a low-power experiment the resulting spectrum is mainly determined by the power distribution around the center frequency of the decoupler field and therefore broad signals can only be obtained by using white noise. With a modification which allows the modulation with pseudo random noise we've obtained the second spectrum. Although there is a little residual sharp component in the center, the spectrum corresponds in principle to the $^{13}C(^{1}H)$ NORD spectrum of the same compound given in (2).
It seems that we've almost mended it.

Sincerely,

(Klaus Roth)



Distribution of frequency components of the 'BB' (a) and noise modulated (b) B_2-field
c) low-power 'BB' decoupled $^{13}C(^1H)$ spectrum of CH_3J
d) low-power noise decoupled $^{13}C(^1H)$ spectrum of CH_3J

Ref. 1) R.K.Harris et al, JCS Dalton Trans. 1980, 638
2) K.Roth, Org.Magn.Reson. 10,56 (1977).

281-21

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NS. RIF.

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

Title:"Quantitative analysis in the industrial laboratories"

Dear Prof. Shapiro,

apart from structural characterization NMR is not considered a technique of large application in the industrial analytical laboratory. However in the last years NMR has gained some rooom (thanks to FT development) in quantitative analysis. This happens mainly when standards are not available, identification of components is not complete or there is need of sample treatment (solvent extraction, chemical reactions, ...) with problems of reliability of final data.
One typical case is the following one. The reaction mixture from cumene hydroperoxide (CHP) acid decomposition (industrial process for production of phenol and acetone) is very complex[1]. Among the several byproducts it is of interest to quantify the presence of peroxides, particularly of dicumylperoxide (DCP) at low concentration (0.1-0.5%). Due to the complexity of the reaction mixture and to the reactivity of peroxides, the usual analytical methods (HPLC, polarographic analysis of the DCP fraction collected by HPLC, low resolution GLC) present difficulties.
Fig. 1 shows the high field portion of the ^{1}HNMR spectrum of a reaction mixtures sample. Using as internal standard the HMDS or one of the sample components it is possible to quantify the presence of DCP. The limit of detection can be safely estimated as 0.05%.

./.

Table I compares favorably NMR quantitative data and combined GLC + HPLC data for the remaining main components of the reaction mixture. We need about 2.5 hours for total components analysis mainly devoted to sample preparation and operating parameters optimization (0.5^h), to FID acquisition (1^h), to spectrum and accurate integral plotting (1^h, as it is impossible to have reliable area measurement by the present integration programs).
The combined GLC + HPLC analysis of the same sample takes about 1.5 hours (0.3^h, 1^h, 0.2^h for sample preparations, analysis and data elaboration respectively).
To be more competitive with other analytical techniques NMR needs more automation and accuracy of analytical procedures. It seems illogical that a technique so reliable as structural identification suffers so many limitations in practical applications[2].

Yours sincerely

E. Santoro

P.L. Cantini

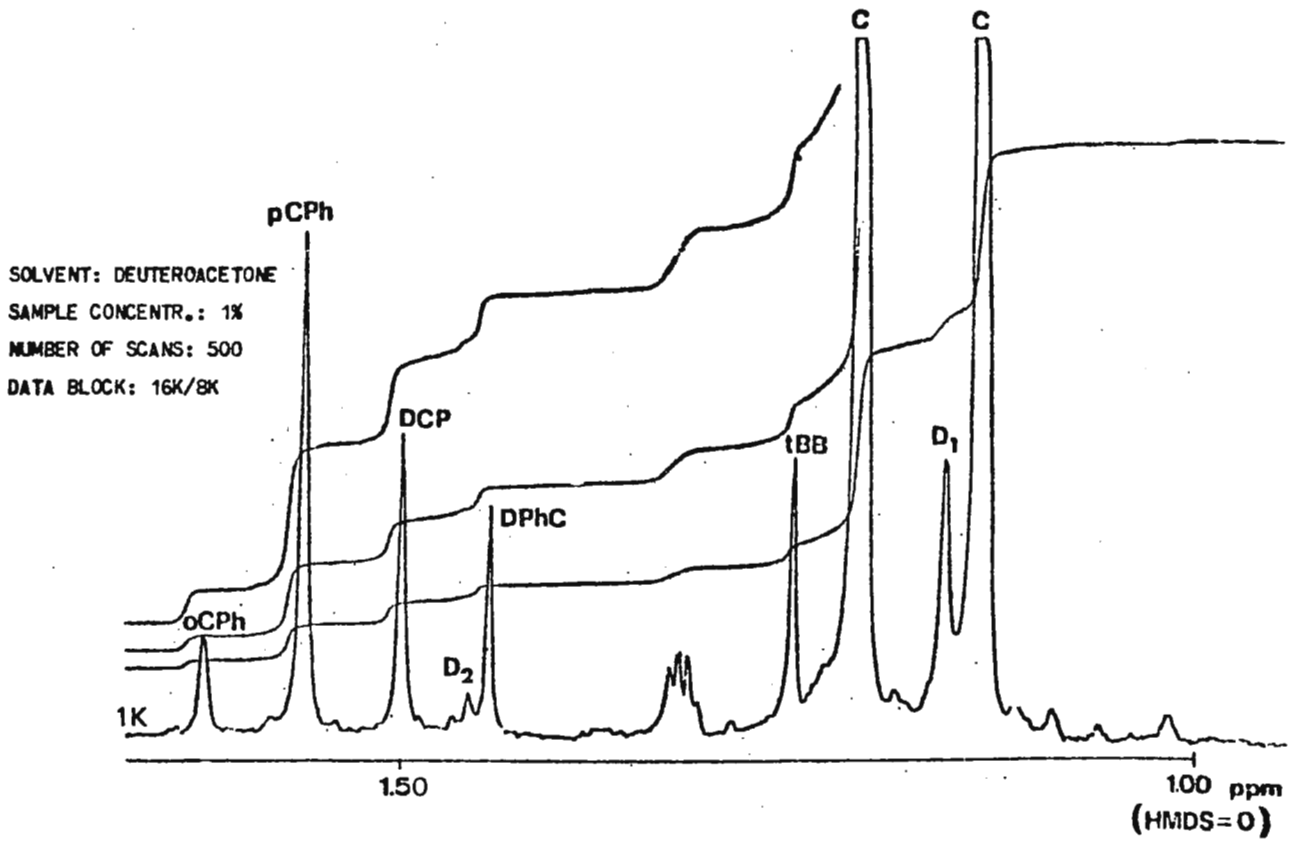

Fig. 1 - CHP acid decomposition. High field portion of the ^1H NMR spectrum (Sample A)

TABLE 1

Quantitative analysis of sample A from acid decomposition of CHP

Component	% by weight	
	^{1}HNMR	GLC + HPLC
Acetophenone (APh)	1.2	1.3
Acetone (Ac)	29.3	30.6
α-methylstyrene (MS)	2.4	2.8
Cumene (C)	10.5	10.3
t.butylbenzene (tBB)	0.3	0.3
α MS dimer I (D1)	1.0	0.9
α MS dimer II (D2)	0.1_1	0.1_5
o.cumylphenol (oCPh)	0.3_5	0.3_5
p.cumylphenol (pCPh)	1.7	2.0
dicumylperoxide (DCP)	0.3_5	-
dimethylphenylcarbinol (DPhC)	0.3_7	0.4_4
phenol (Ph)	50.6	47.4

REFERENCES

1) L. Motta, O. Mazzucchelli and V. Zamboni "Atti II Convegno Nazionale di Chimica Analitica", Padova (Italy) October 2-5, 1979

2) A.D.H. Clague "TAMU NMR Newsletter" 277, 45 (1981)

UNIVERSITY OF STOCKHOLM
Physical Chemistry

Dr. Bernard Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77840

January 19, 1982

Title: Dual Spin Probe Study of Solutions of $M(acac)_3$, M = Al, Ga, In.

Dear Professor Shapiro,

Thanks to the generosity of the Swedish Natural Science Research Council, I was able to invite Dr James Dechter from the University of Alabama to spend the summer of 1981 with my group in Stockholm. The main project on which we worked together was a dual spin probe study of a series of metal tris-acetylacetonate complexes, $M(acac)_3$, with M = Al, Ga, In.

By measuring ^{13}C T_1 for about 0.5M toluene-d_8 solutions of the complexes, we were able to determine the rotational correlation times as a function of temperature. The quadrupolar nuclei (^{27}Al, ^{69}Ga and ^{115}In) served as the second spin probes. The ^{27}Al lines were sufficiently narrow to allow a decent determination of the quadrupole coupling constant (qcc) on our XL 100; we found the qcc to be around 0.49 MHz, independently of temperature. The other isotopes of interest gave either too broad lines or were out of the frequency range of our instrument, but we were fortunate to get other people interested in the project. In cooperation with Dr Ulf Henriksson from the Royal Institute of Technology in Stockholm, we were able to run the ^{69}Ga and ^{71}Ga experiments on the CXP 100 and get the qcc's of around 11 and 7 MHz for the two isotopes, respectively. For the ^{115}In resonance, we have been forced to look for an even more powerful instrument and were finally able to obtain a 21 kHz wide line on the CXP 300 at the Bruker laboratory in Karlsruhe, due to the courtesy of Dr Müller there. When corrected for the differences in the nuclear quadrupole moments and the Sternheimer antishielding factors for the M^{3+} ions, the qcc's may tentatively be interpreted as indicating the $Al(acac)_3$ to be in solution a somewhat less distorded octahedron than both $Ga(acac)_3$ and $In(acac)_3$.

Yours sincerely,

Jozef Kowalewski

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DEPARTMENT OF CHEMISTRY

January 20, 1982

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

Efficient Rotations in the Computer Frame

Dear Barry:

We have on occasion found it convenient to rotate (i.e., shift back into one end what was shifted out of the other) spectral data by large fractions of the full spectral width. This function is useful for aligning spectra taken at different transmitter frequencies or for dealiasing (in quadrature detection) broad spectral features which have just edged past the spectral width. Rotation allows trial and error alignment without loss of data at the wings of the spectrum.

Rotate functions have been included in NMR software packages previously, but to the best of our knowledge these have been for a fixed number of positions (usually one), or have required temporary storage of part of the array. Given these constraints, if one wishes to rotate by, say, 1000 positions an array sufficiently large as to fill all available memory, one would have to resort to calling a single rotate routine 1000 times or else resort to using temporary disk storage.

A little quiet reflection on this annoying problem led us to the following in-place rotate algorithm. The algorithm is "efficient" in the sense that each data point is accessed only once, irrespective of the array length (LENGTH) or the number of positions rotated (NROT).

A pointer (TO) is set up to indicate the destination of the next datum to be shifted (FROM is its source). The first datum in the array is placed in a temporary location (TEMP), and the first transfer (FROM→TO) is carried out. The pointer is incremented by NROT, looping through the array modulo LENGTH, until FROM points to the original value of TO (=START). TO is then incremented to START+1, and the process is repeated until a total of LENGTH data points have been accessed. The execution time is a complicated function of LENGTH, LENGTH mod NROT, and the greatest common divisor of LENGTH and NROT. It will almost always compare favorably to the execution time of multiple calls to a single rotate routine, which is proportional to NROT * LENGTH.

Shown below are a segment of code excised from a test program, along with sample timings comparing the efficient and simple algorithms.

Sincerely,

Y.-Y. Lin
Yau-Yam Lin

Jerry Ackerman
Jerry Ackerman
Assistant Professor

dld

```
      IMPLICIT INTEGER (A-Z)
      DIMENSION DATA(10000)
C.....INITIALIZE WORD COUNT "I" AND LOOP START POINTER "START".
      I=0
      START=1
      GO TO 40
C.....INCREMENT POINTER MODULO "LENGTH".
   20 FROM=TO+NROT
      IF(FROM.GT.LENGTH)FROM=FROM-LENGTH
C.....IF NEW POINT HAS ALREADY BEEN ROTATED, SHIFT LOOP
C.....POINTERS BY ONE.
      IF(FROM.NE.START)GO TO 60
      DATA(TO)=TEMP
      START=START+1
C.....PICK UP FIRST WORD IN "TEMP" AND BEGIN LOOP.
   40 TEMP=DATA(START)
      TO=START
      GO TO 80
   60 DATA(TO)=DATA(FROM)
      TO=FROM
C.....INCREMENT TOTAL WORD COUNT AND CHECK IF ALL WORDS DONE.
   80 I=I+1
      IF(I.LE.LENGTH)GO TO 20
```

LENGTH	NROT	EFFICIENT SEC	SIMPLE SEC
10,000	1	0.50	0.23
	2	0.50	0.44
	3	0.50	0.67
	4	0.51	0.89
	5	0.51	1.11
	10	0.50	2.22
	100	0.51	22.15
	1,000	0.53	221.48
	4,999	0.53	
	5,000	0.60	
	5,001	0.53	
	5,002	0.53	
	5,500	0.54	
	6,000	0.57	
	7,000	0.55	
	9,999	0.56	

281-27

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

January 21, 1982

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

Dear Barry:

We are getting a nice collection of colored paper here, and we would like to try for the entire rainbow. But in the meantime, here are some Sn-119 spectra of tributyltin methacrylate (TBTM) and of various homopolymers and copolymers with methyl methacrylate (free radical initiated). The peak attributed to TBTM appears to a greater or lesser extent in all of the polymers spectra, indicating the difficulty of getting complete conversion of the monomer. Of greater interest is the observation that the Sn peak in the copolymers appears about 10 ppm downfield from the Sn peak in the homopolymer. Since the nearest neighbors to a TBTM fragment, in the homopolymer are necessarily other TBTM fragment, the failure to see a signal at 84 ppm in the copolymer suggests to us that the TBTM fragments in the copolymer are unlikely to have another TBTM as a nearest neighbor - this line of reasoning then leads to the idea that the 1:1 copolymer must have very nearly a regular alternating sequence of the 2 monomers. This is still very much of an open question with us and other interpretations are invited.

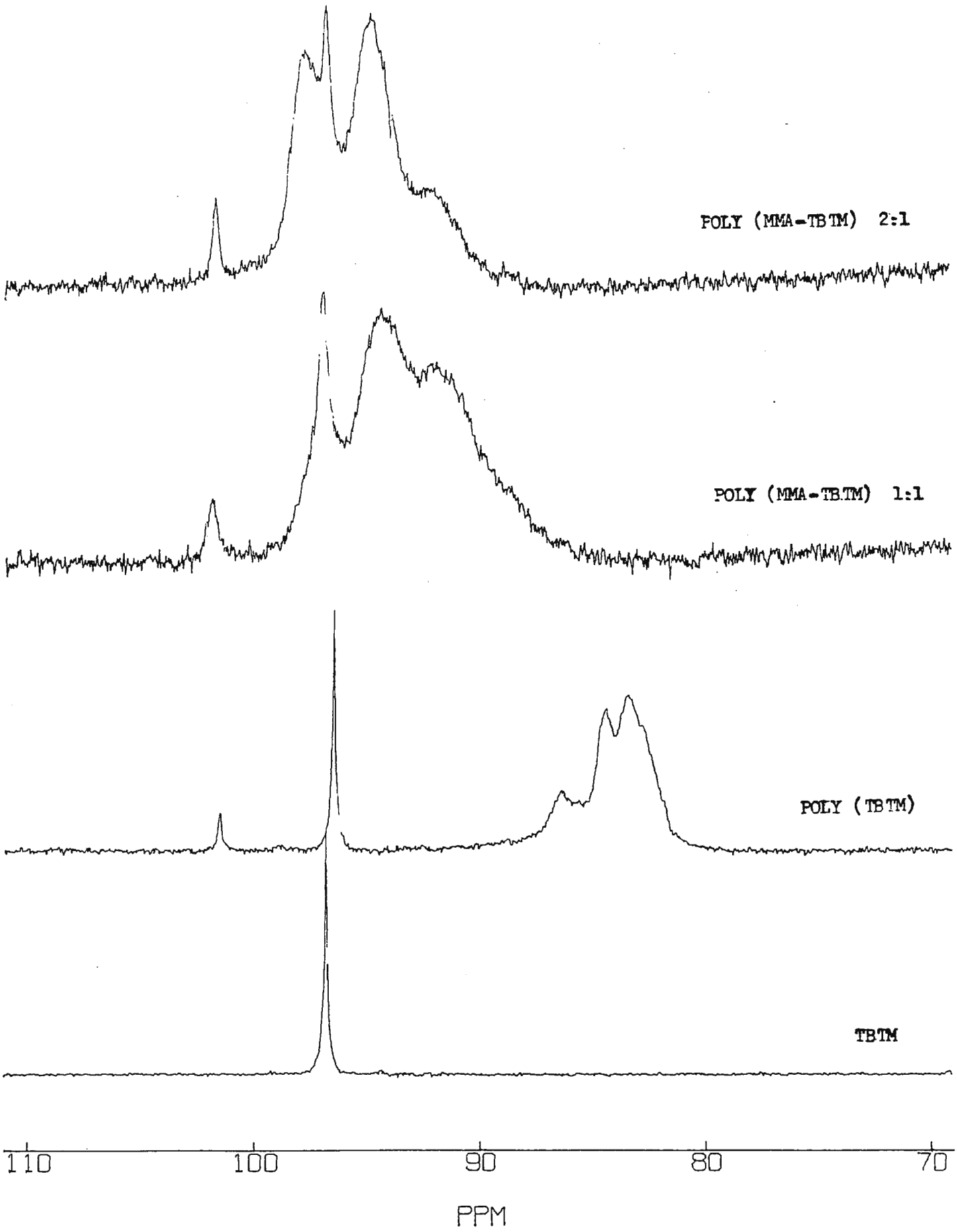
Please credit this contribution to Bruce Coxon.

Yours very truly,

Rolf

Rolf B. Johannesen
Chemical & Biodegradation Processes Group

Sn-119 NMR at 74.6 MHz



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January 7, 1982

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

^{13}C NMR Chemical Shift Assignments of Nonionic Surfactants

Dear Dr. Shapiro:

In the course of making ^{13}C NMR investigations of ethoxylated alcohols ($RO(CH_2CH_2O)_nH$), which are used as oil field chemicals, we found conflicting data on the chemical shift assignments of such species. In an initial study by Ribiero and Dennis[1], assignments were made for p-tert-octylphenyl-polyoxyethylene ether which they later corrected[2]. In our initial studies, the assignments for 2-phenoxyethanol, reported in reference 3, were used, ($-OCH_2-$ at 60.9 ppm, $-CH_2OH$ at 69.1 ppm). The alcohol value seemed to be much different than that of other alcohols as reported in reference 4. Thus, due to the limited and apparently conflicting nature of the reported ^{13}C NMR assignments, we undertook a detailed study of both ethoxylated phenols and ethoxylated linear alcohols.

Assignments were made using the lanthanide shift reagent $Eu(fod)_3$ and 0.10 M substrate in CCl_4 by varying the $[Eu(fod)_3]$ to [substrate] ratio. Both the degree of ethoxylation (n above) and the length of the alkyl group were changed. The assignments are given in Table I, along with those of Ribiero and Dennis. The carbons are identified according to the following scheme:

Dr. B. L. Shapiro January 7, 1982

$$R\,O - CH_2CH_2 \{EO\}_x CH_2CH_2OH$$

$$\alpha \quad \beta\cdots\cdots EO\cdots\omega\text{-}1 \quad \omega$$

Primed letters are used to identify carbon in the R group, and proceed from the point of ethoxylation.

The assignments are in agreement for the ethoxylate region of both types of surfactants. Due to the resolution of our instrument (JEOL FX-90Q), we were able to assign the shoulders in the ethoxylate region that Ribiero and Dennis could not. There is some disagreement on the assignments in the aliphatic region. From LSR work with alcohols with only one or two added ethylene oxide units and from literature data[4], we feel the assignments given are correct. Details of this work will be forthcoming.

Please credit this contribution to the account of Dr. R. M. Riddle.

Yours very truly,

Phillip E. Figdore

PHILLIP E. FIGDORE

PEF-CAS
Attach.
418001

REFERENCES

1. Ribiero, A. A. and Dennis, E. A.: J. Phys. Chem. (1976), 80, 1746.

2. Ribiero, A. A. and Dennis, E. A.: J. Phys. Chem. (1977), 81, 957.

3. Formacek, V., Desnoyer, L., Dellerhals, H. P., Keller, T., and Clerc, J. T.: "^{13}C Data Bank," Bruker Physik, W. Germany (1976), Vol. 1, 509.

4. Breitmaier, E. and Veelter, E.: "^{13}C NMR Spectroscopy," Verlag Chemie GmbH, Weinheim/Bergstr., Germany (1974).

TABLE I

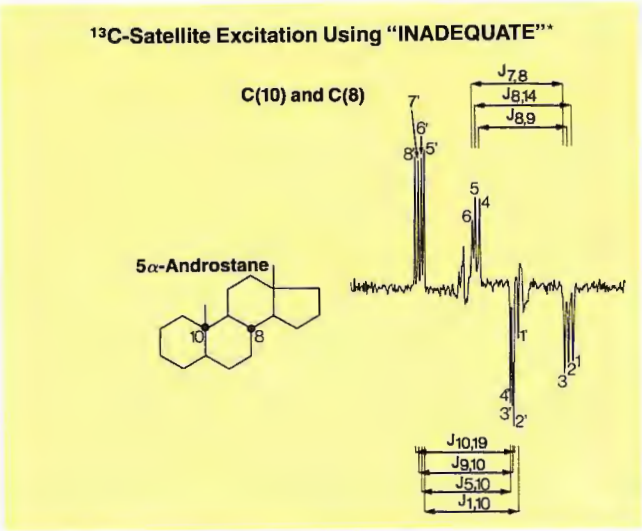
^{13}C CHEMICAL SHIFTS FOR $RO\langle EO\rangle_nH$ IN $CDCl_3$

TMS INTERNAL REFERENCE

Reference	R	γ´	β´	α´	α	β	γ	EO	ω-2	ω-1	ω
this work	phenyl				67.3	69.8	70.8	70.6	70.3	72.6	61.7
1,2	phenyl				67.1	69.6	70.2*	70.4	71.0*	72.6	61.3
this work	alkyl	26.1	29.5	71.6	70.1	←		70.6	70.3	72.6	61.6
1,2	alkyl	29.6	26.2	71.5	←			70.6	70.2	72.7	61.7

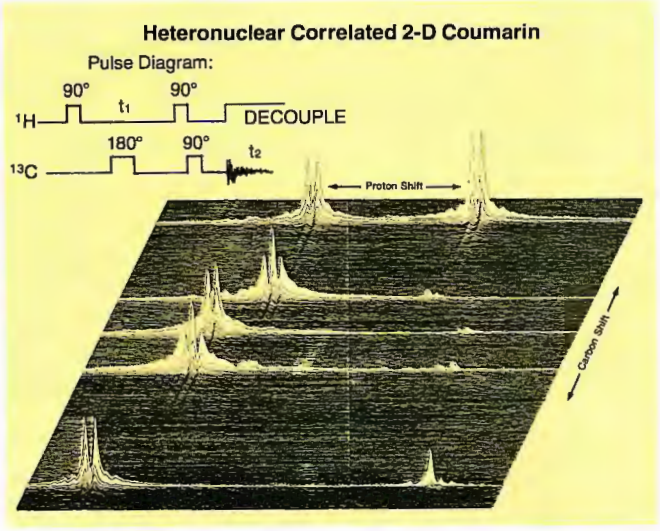
* could not always resolve these shoulders

We produced these spectra—



Expansion of the partial INADEQUATE spectrum of 5α-androstane, showing overlapping ^{13}C satellites of carbon 8 and 10. Note the efficiency of center-band cancellation resulting from the hardware stability and the software flexibility of the XL-200 pulse programmer. Assignments shown are the result of the "COSMIC" automatic analysis program on the XL-200.

*A. Bax, R. Freeman and S.P. Kempsell, *JACS*, 102, 4849 (1980).



Heteronuclear Correlated 2-D NMR on coumarin. Presence of a resonance indicates presence of a C-H bond. The sub-splittings along the proton direction are the homonuclear ^1H-^1H splittings, even though the experiment is ^{13}C observe. The phase cycling employed in the pulse sequence allows quadrature operation in both frequency domains.

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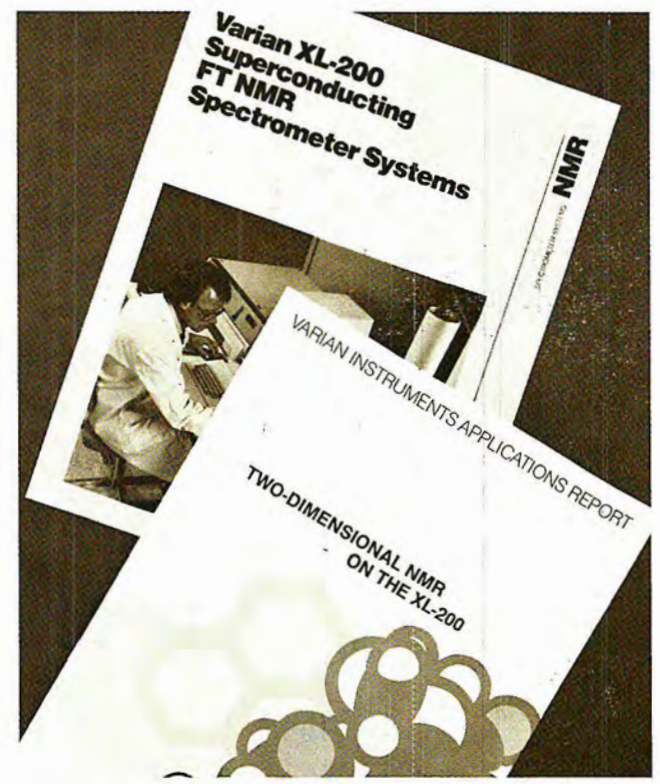

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JWE/HN

5th January, 1982.

Dr. B.L. Shapiro,
Department of Chemistry,
TEXAS A. and M. UNIVERSITY,
College Station,
Texas - 77843,
UNITED STATES OF AMERICA.

Dear Barry,

Meetings of the United Kingdom N.M.R. Discussion Group

Readers of the Newsletter who do not follow the affairs of the Royal Society of Chemistry may not know that there will be a symposium on "N.M.R. in Physical Chemistry" as part of the annual congress of the Society, this spring, at the University of Aston in Birmingham.

The symposium extends throughout the three days of the congress from March 30th to April 2nd, 1982 and covers the application of N.M.R. to studying simple fluids, solvation, liquid crystals (both thermotropic and amphiphilic) and macromolecules. Invited lectures will be given by A. Pines, J. Jonas, W.T. Raynes, J. Homer, M.C.R. Symons, P. Laszlo, W. Derbyshire, G.R. Luckhurst, Z. Luz, J.W. Emsley, J. Charvolin, N. Boden, B. Lindblom, D. Vander Hart, F. McBrierty, F. Heatley and R.K. Harris. Anyone wishing to attend the meeting should write for details to Dr. John Gibson, Royal Society of Chemistry, Burlington House, London, W1V OBN.

Looking further ahead, our next international meeting is to be held at the University of Edinburgh from 10th to 15th July, 1983. The first circular for this meeting will be sent out later this year and if you did not attend the Exeter meeting but would like to receive a copy, then again contact John Gibson.

Best wishes,

Jim

J. W. EMSLEY.

CHAIRMAN,
United Kingdom N.M.R. Discussion Group.

The University of Alabama in Birmingham
Comprehensive Cancer Center
205/934-5696
21 January 1982

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

In Vivo ^{31}P NMR of Solid Tumors

Dear Dr. Shapiro,

Within the past year this laboratory has been employing surface coil NMR, introduced by Ackerman et al (1), for the assessment of cancer therapy on subcutaneously implanted murine tumors. Among those examined are; Dunn osteosarcoma, MOPC 104E myeloma, mammary 16/C, ovarian M5, colon 26 and Lewis lung. The modalities under investigation include chemotherapy, radiation and hyperthermia. All treatments produce significant and distinct spectral changes not observed under normal tumor growth.

Recently, we have extended our studies to include human tumors. Figure 1 demonstrates the first high resolution ^{31}P NMR of a human mammary carcinoma in an athymic mouse.

All spectra are obtained with our Bruker CXP-200/300 operating at 80.96 MHz. Our homebuilt surface coil probe is a flat, 3-turn coil made from 16 gauge wire. Typical conditions for most spectra are 350 FID's obtained with a 25 μsec (65° flip) observe pulse and 3.2 sec recycle time. These parameters result in no detectable saturation of any signal.

The results obtained thus far indicate that in vivo ^{31}P NMR has potential clinical as well as cancer research applications.

Sincerely yours,

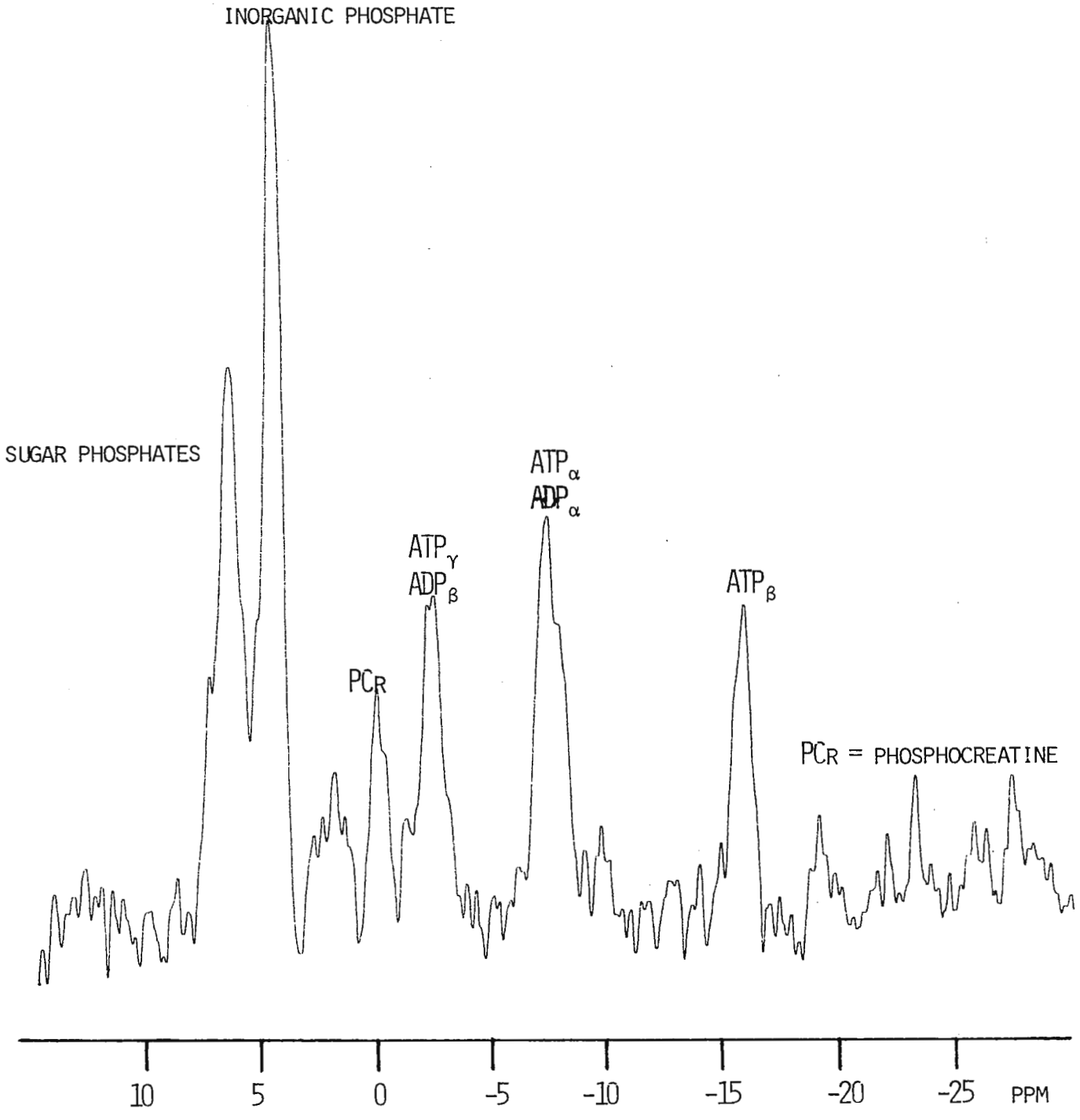
Jerry D. Glickson
Director, NMR Core Facility

W.T. Evanochko
Applications Manager

T.C. Ng
Operations Manager

(1) J.J.H. Ackerman, T.H. Grove, G.G. Wong, D.G. Gadian and G.K. Radda, Nature 283, 167(1980).

FIGURE 1. *IN VIVO* ^{31}P NMR OF A HUMAN MX-1 MAMMARY CARCINOMA IN A ATHYMIC MOUSE.



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82.01.22

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

Dear Barry,

Good examples of hindered rotation about sp^3-sp^3 barriers are fairly rare. An immediately obvious example is hexamethylethane. Unfortunately (from the viewpoint of workers interested in hindered rotation) the phase change and solid-state wide-line spectra of this compound eclipse any interest one might have in its internal rotation barriers. Also, it's too symmetric to be any real fun.

We here present a rather more interesting example of the above mentioned type of hindered rotation. As is our wont, clever use of $Eu(fod)_3$ is included. The molecule examined was the *tert*-butyl adamantanone derivative shown with the attached spectra. Spectra were taken at 90 MHz in $CDCl_3$ with the LSR and substrate concentrations 0.4 M and 0.2 M, respectively.

Spectra were taken in the range -40°C to +70°C; only a few are shown here. Each sweep goes from 21.00δ to 4.00δ. The *tert*-butyl is clearly resolved into two resonances at -20°, as indicated by the solid arrows. At +10° the *tert*-butyl is broadened almost to the point of vanishing. The +30° spectrum shows considerable broadening; at +60° narrowing is almost totally accomplished. The relevant peak is indicated by the fat, open, arrow in the latter three spectra.

The bridgehead proton adjacent to the carbonyl shows broadening as the temperature is lowered, as would be expected. This resonance is indicated by the double-dashed arrows. At low temperatures, a relatively sharp peak appears out of nowhere and moves rapidly *upfield* with decreasing temperature. All substrate resonances are accounted for; if anyone can tell us what this peak might be (indicated by the obnoxious arrow at -20°), we'd like to know!

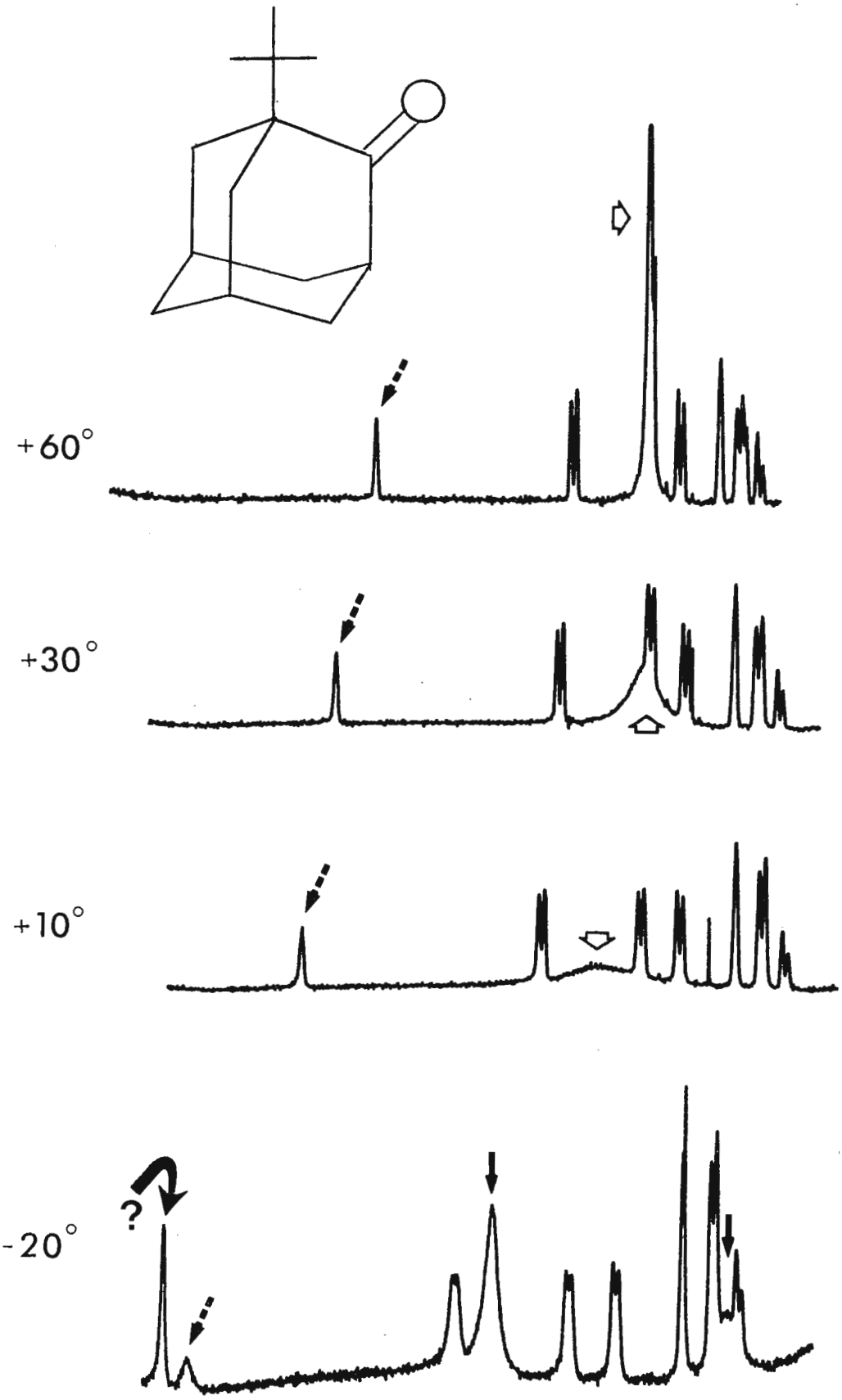
Best regards,

Milt

Milton D. Johnston, Jr.

Doug

Douglas J. Raber


+60°
+30°
+10°
-20°
?

281-39

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22nd January, 1982

Dr. B.L. Shapiro
Department of Chemistry

Please include this letter in the next issue of TAMUNMR newsletter as an advertisement.

RESEARCH FELLOW POSITION IN MULTIPULSE/MULTINUCLEAR NMR

Salary has been granted by the Australian National Energy Research Development and Demonstration Council for a Research Fellow to help develop and demonstrate new Multipulse/Multinuclear NMR methods for the study and quantitation of coal, oil shale, coal liquification products, shale oil and petroleum products. In general, methods to simplify complex spectra to give unambiguous information. As the new methods are shown to be viable they will be transferred to other Australian groups, so routine work is not envisaged. The nature of the methods will be such that they will be more generally useful than in just the fossil fuels area. The research will build on work that other groups and ourselves (JACS, 1980, 102 6388: JACS, 1981, 103, 934: JACS, 1981, 103, 4603: J. Mag. Res., 1981, 42, 298: J. Mag. Res., 1981, 44, 32: J. Mag. Res., 1981, 44, 238: J. Mag. Res., 1981, 45, 8) have already published, and new and more accurate pulse sequences yet to be published (for example we have been recently able to routinely obtain separate quaternary, methine, methylene and methyl 13C spectra in which other resonances are cancelled to better that 5%).

We envisage doing some solid-state work but we want someone with a liquid state multipulse background. We don't wish to spend a protracted period training someone in heteronuclear multipulse NMR as well as in the operation of Bruker Instruments - A CXP-300 and an HX-90 is available. The latter will be upgraded with a very wide-bore 200 MHz magnet in middle-to-late 1982. Both instruments have four phases on two nuclei simultaneously. The work won't be concerned with the minute details of the content of fossil fuels and no prior knowledge of fossil fuels is required.

The position will be for a minimum of nine months with the liklihood of an additional year's funding. The salary is midway up the lecturer salary scale, 22,843 Australian dollars per annum, and it will be supplemented for cost-of-living increases. (25,500 US dollars). Assistance with Air Fares may be given depending on the applicant. We would prefer someone to start by April, 1982 but others should apply because we are not likely to find someone for the early start. The salary could be added to an overseas salary for someone on study leave. Interested parties should reply immediately with relevant particulars to:

Dr. M.R. Bendall, Griffith University,
Nathan, Queensland, 4111 Australia.

Yours sincerely,

Dr. M.R. Bendall.

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THE ROCKEFELLER UNIVERSITY
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OFFICE OF THE SUPERINTENDENT OF PURCHASING

January 26, 1982

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

Dear Dr. Shapiro:

Available Equipment

In a previous note (TAMU 266-30) we had advertised for sale, two old NMR spectrometers. Several items have been sold or used in other equipment, but there still remains a Bruker 2.1 T 12" electromagnet, a Bruker HX console, some old Bruker probes, and some parts of a Varian HR-220 console. Before we summon the scrap dealer, we should like to offer this equipment to the NMR community, at no cost other than moving expenses. Anyone interested should telephone me at (212) 570-8200. First come, first served!

Sincerely,

James J. Stewart
Superintendent of Purchases

JJS:ad

281-41

National Research Council Canada
Conseil national de recherches Canada

Division of Biological Sciences
Division des sciences biologiques

File Reference

11 January 1982

Professor B.L. Shapiro
Texas A and M NMR Newsletter
College Station, Texas 77843
U. S. A.

Dear Barry,

GORDON CONFERENCE ON MAGNETIC RESONANCE IN BIOLOGY AND MEDICINE,
Tilton School, New Hampshire, August 9-13, 1982

The above conference has now been finalized and I enclosed a copy of the programme. Final details regarding registration will be announced in the March 5 issue of Science. We expect the conference to be oversubscribed, so those wishing to attend are encouraged to apply early.

Chairman: Ian C.P. Smith, Division of Biological Sciences, National Research Council of Canada K1A OR6
Telephone: (613) 995-7852

Vice-Chairman: Philip Aisen, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, New York 10461, U.S.A.
Telephone: (212) 430-2248

1.	ESR Studies of Membranes and Lipids	B.J. Gaffney, discussion leader; D. Marsh, L.H. Piette, D.D. Thomas
2.	Radicals and Spin Traps	E.G. Janzen, discussion leader; R.A. Floyd, R.P. Mason, H. Rosen
3.	NMR of Membranes	K.R. Jeffrey, discussion leader; R.A. Byrd, R.G. Griffin
4.	Lipid-Protein Interaction	M. Bloom, discussion leader; J.H. Davis, F.W. Dahlquist
5.	Metabolic Mapping	B. Chance, discussion leader; D. Shaw, S.M. Cohen
6.	NMR Imaging	P.C. Lauterbur, discussion leader; M.H. Mendonca-Dias, W. Hinshaw, L.F. Crooks
7.	NMR Techniques	P.D. Ellis, discussion leader; G.A. Morris, S.J. Opella, O. Jardetzky, T.J. Schaafsma, G.C. Levy
8.	Bioinorganic Applications	W.E. Blumberg, discussion leader; B. Hoffman, J.S. Hyde, B.C. Antanaitis

9. Contributed posters to be displayed throughout the conference.

Yours sincerely,

Ian

Ian C.P. Smith

Ottawa, Canada
K1A 0R6

PURDUE UNIVERSITY BIOCHEMICAL MAGNETIC RESONANCE LABORATORY

January 15, 1982

PRACTICAL NMR INSTRUMENTATION
A Shortcourse, 10-13 May 1982

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

Dear Barry:

For several years Purdue has offered a shortcourse, "Practical NMR," that has been popular with industrial and academic research spectroscopists. Prof. John Grutzner, the prime mover behind this course, is spending a leave of absence with the NSF this year. We have decided in John's absence to slant the shortcourse toward instrumentation, novel experiments, and management of an NMR laboratory. The four-day course will contain an equal mixture of lectures and hands-on laboratory experience in intimate groups. It should appeal to laboratory managers, research personnel who already have some background in interpretation of NMR spectra but who would like to learn more about instrumentation, and technical and field service personnel. Topics will include spectrometer design, purchasing a spectrometer, laboratory layout, the use of test equipment, maintenance, troubleshoooting, probe design, acquisition and processing of NMR data, decoupling and newer experiments such as 2D FT, INEPT, photo CIDNP, and in vivo NMR.

Anyone interested should contact one of the undersigned or the Purdue Continuing Education Office.

Greeting and best wishes.

Sincerely,

John L. Markley

William M. Westler

Robert E. Santini

Chemistry Building
West Lafayette, Indiana 47907
(317) 749-2438
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281-43

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January 20, 1982

Professor B. L. Shapiro
Texas A & M NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77483

Re: Position available

Dear Barry:

We have a position available for an NMR spectroscopist in the Analytical Section at the Western Research Center. A solid background in organic chemistry is required. In-depth knowledge and experience in NMR, preferably high field NMR is also essential. The successful candidate will work closely with chemists to elucidate new chemical structures and reaction pathways. The ideal candidate will be a pHD* or equivalent in physical organic chemistry with a specialization in NMR spectrometry.

Stauffer offers outstanding career opportunities, a competitive salary, and membership in a highly motivated and successful team effort. Our recently constructed laboratories offer excellent facilities in San Francisco Bay Area. We are an equal opportunity employer. Interested applicants should send resumes in confidence to me.

Sincerely yours,

CKTseng

C. K. Tseng, Supervisor
Analytical Section

CKT/mn

* *Ken: Would you settle for a Ph.D.? Or do you really need an acid or basic person?*

Barry

SYRACUSE UNIVERSITY

N.I.H. RESOURCE FOR MULTI-NUCLEI NMR AND DATA PROCESSING
DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, NY 13210

21 January, 1982

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

A NEW JOURNAL - "COMPUTER ENHANCED SPECTROSCOPY"

Dear Barry,

I am presently contacting colleagues both to present details of this new journal and to seek papers for early issues.

The scope is outlined below, but I would stress the essentially practical nature which we envisage for this periodical. I hope we may look forward to your use of our pages for your forthcoming research reports, comments, reviews, technical notes and correspondence. There are no page charges, we provide 50 free reprints of your paper and speed of publication **is assured.** Please do not hesitate to contact me for any other comments and information.

Should you desire to submit a manuscript to **Computer Enhanced Spectroscopy,** please send 3 copies to me. I promise that all manuscripts will receive **prompt** and fair reviews.

With best wishes,

Sincerely,

George C. Levy
North American Editor, **CES**

Computer Enhanced Spectroscopy (Published by Heyden and Son, Ltd) **- Aims and Scope**

This timely journal will be essentially practical in nature and is designed as a communications medium for the laboratory scientist. This content will center on minicomputers and microcomputers, their applications in the control and operation of spectrometers and the acquisition and evaluation of data, the relevant software and user-developed programs, the associated hardware and the man-machine interface. Papers on more sophisticated computers and spectrometers will also be welcome, especially where the implications will be beneficial across a broader range. Letters to the Editor are also invited, so that a worthwhile interchange of ideas and results will be established. A strict refereeing system is applied to all submitted material. Selected reviews on topics of special interest will be included.

281-45

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January 27, 1982

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

Title: Data Transfer with JEOL FX Systems and Job Opening

Dear Barry,

We have had our JEOL FX 900* and FX-200 for about eight months now and we have been very pleased with their dependability. As part of our systems set-up we had the two computers hooked together such that data can be transferred between them. Upgrading of the FX-90Q to 48K words is helpful in this respect since it allows efficient transfer of 16K data tables in either direction. This takes less than one minute total time for such transfer. We have found that data transfer is quite convenient using the JEOL software and is very useful when a laboratory has the role of high throughput as well as the need for multinuclear operation. Thus when the order of the day is ^{15}N for the FX-200; accumulation in the background allows foreground processing of FX-900 data. I hope that this "operational" contribution will postpone the consequences of the glowing yellow slip I am looking at.

NMR SPECTROSCOPIST: Person to work in Laboratory with JEOL FX-90Q and FX-200 and permanent magnet spectrometer systems. Job applicant should have BS/MS degree or equivalent with 2-5 years experience and should have working knowledge of structural organic chemistry, high resolution nmr techniques including interpretation of ^{1}H and ^{13}C nmr spectra. Experience with biochemical systems would be helpful.

Sincerely,

Michael

Michael Shapiro
Unit Head
NMR Laboratory

MS;rck

PS: For Sale: 1.7 mm ^{13}C } XL-100 inserts
1.0 mm ^{1}H }

* *Wow! Michael: you wouldn't exaggerate by a factor of 10, would you?*

Barry

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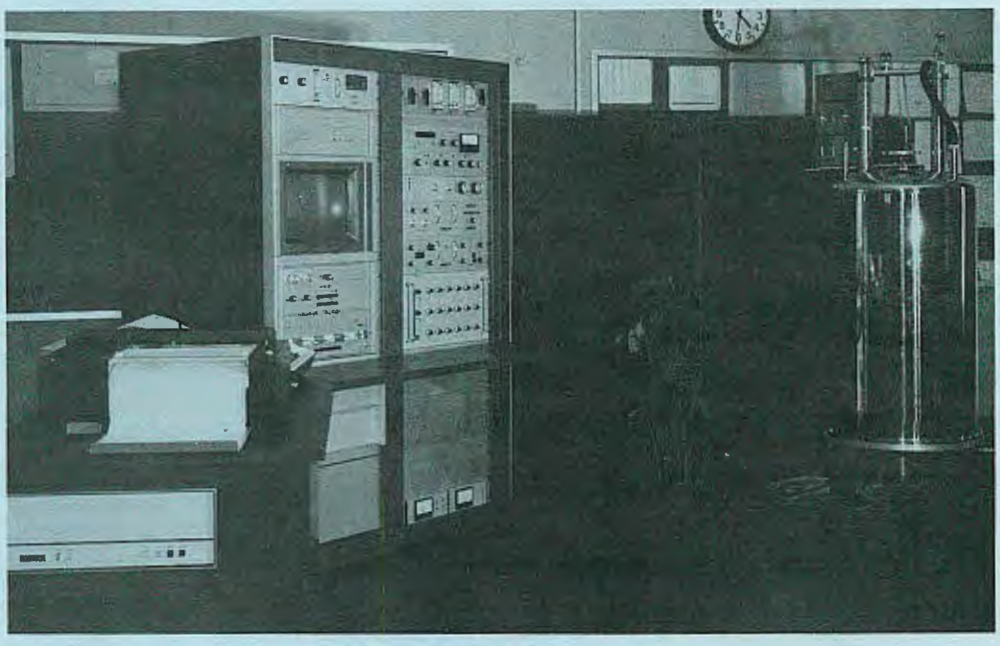

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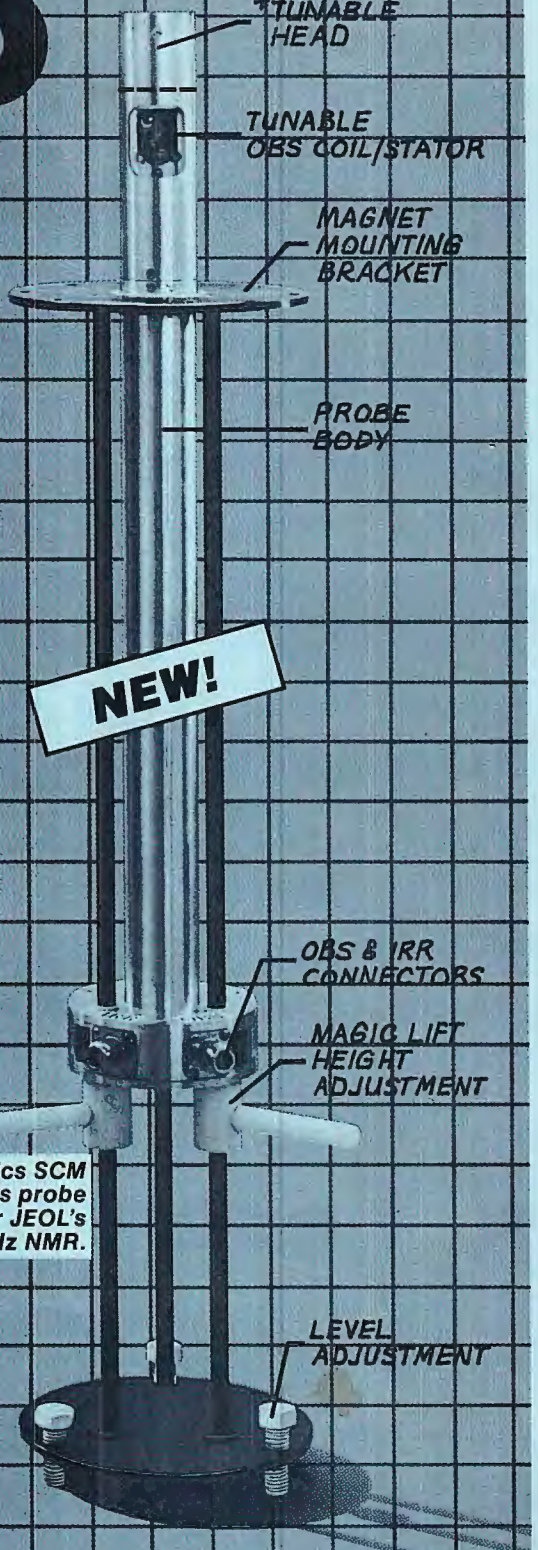

Chemagnetics SCM Solids probe for JEOL's 200 MHz NMR.

SOLIDS UPDATE – NOW AVAILABLE

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- WIDE BORE MAGNET WITH VARIABLE TEMPERATURE SOLIDS FOR THE FX 200

JEOL

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