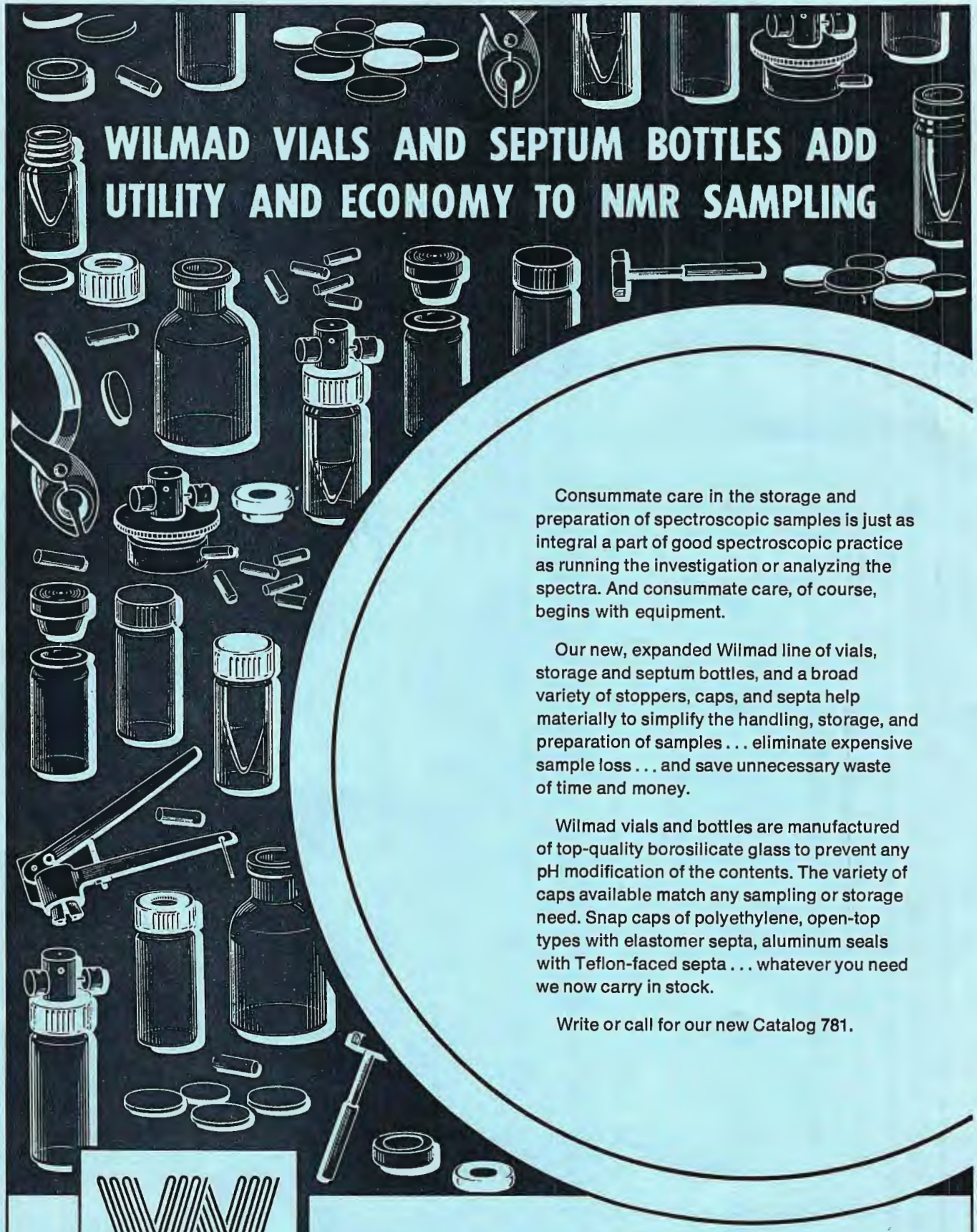
Texas A&M University N-M-R Newsletter

No. 278

November, 1981



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DEADLINE DATES: No. 279 7 December 1981
No. 280 4 January 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.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 278

The
Guelph-Waterloo Centre
for Graduate Work in Chemistry

Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1 519/824-4120

5 October 1981

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

High-Resolution MAS Spectra on a Bruker WH-400 Spectrometer

Dear Barry:

While on sabbatical leave from Brock University in 1980-81, I have been working with Colin Fyfe at the University of Guelph, and learning about high-resolution solid-state nmr. In particular, we are excited about application to inorganic solids, using a wide variety of nuclei. Resolution and sensitivity can be enhanced greatly by the use of very high magnetic fields, in our case the 9.4 T field of the Bruker WH-400 spectrometer of the Southwestern Ontario High-Field NMR Centre, located at the University of Guelph.

Our initial work on ^{29}Si MAS nmr of zeolites, carried out on a Bruker CXP-100 spectrometer (2.1 T), gave adequate spectra allowing peaks to be resolved from $Si(OAl)_n(OSi)_{4-n}$ (n = 0 - 4) atoms in the aluminosilicate framework, i.e., allowing determination of the ordering (or lack of it) of Al and Si atoms in the framework: of great interest to zeolite chemists (1). Because there are no protons in the aluminosilicate framework, we could dispense with high-power proton decoupling and ^{1}H-^{29}Si cross-polarization. In other words, although we were using a high-power CXP instrument, we were doing a conventional low-power high-resolution experiment, but on a solid undergoing magic-angle spinning. Such an experiment can be done on any high-resolution instrument if a MAS probe is available (2). We therefore built a MAS probe for the Bruker WH-400, which has worked so well for ^{29}Si that we have extended the work to other nuclei (^{27}Al, ^{9}Be, ^{11}B, ^{207}Pb, ...).

Comparison of ^{29}Si spectra obtained at 2.1 T and 9.4 T shows that resolution has increased somewhat. However, sensitivity has increased greatly, so that really good S/N can be obtained in a relatively short time. The silicate work

(done in collaboration with Prof. J.M. Thomas and colleagues at Cambridge) is the farthest along (3), but the potential of very high-field MAS nmr is much wider than this. Magnetically-dilute I = ½ nuclei (^{29}Si, ^{207}Pb) are best, but it appears thay nucleus with I = ½ or with half-integral I > ½ can provide useful information. In particular, quadrupolar nuclei with non-integral spins will best be investigated at the highest possible fields where the second-order quadrupolar effects are minimized. The experiments should be applicable to a wide range of problems in inorganic chemistry.

Please credit this overdue contribution to the Brock University subscription.

Yours sincerely,

J.S. Hartman, Professor
Brock University

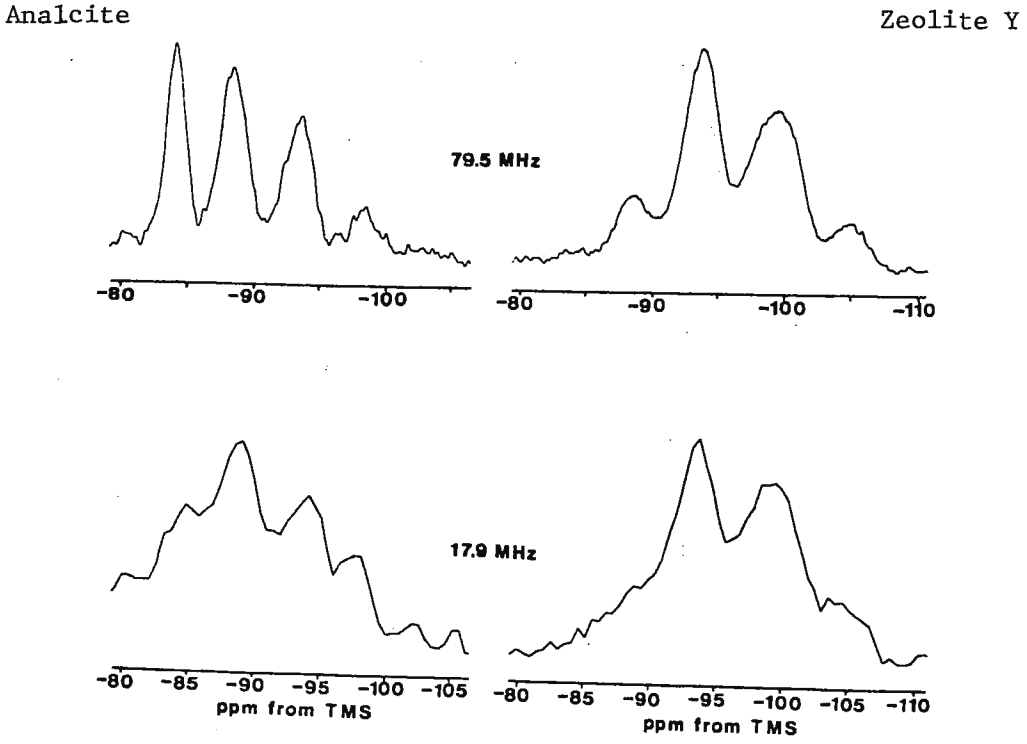
C.A. Fyfe, Professor
University of Guelph

G.C. Gobbi, Graduate Student
University of Guelph

R.E. Lenkinski, Manager
SW Ontario NMR Centre

References

1. J. C. S. Chem. Comm., 570, 678 (1981).
2. D.J. Burton, R.K. Harris and L.H. Merwin, J. Mag. Res., 39, 159 (1980).
3. S. Ramdas, J.M. Thomas, J. Klinowski, C.A. Fyfe and J.S. Hartman, Nature, 292, 228 (1981).



278-3

Laboratory of the Government Chemist
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Professor B.L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843.

Your reference

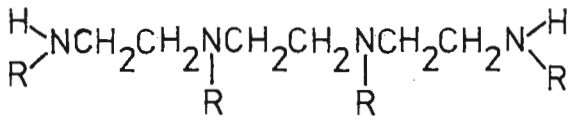
Our reference

Date 5 October 1981

Dear Professor Shapiro,

HINDERED ROTATION IN THE m-TOLUOYL DERIVATIVE OF TRIETHYLENETETRAMINE

During an investigation of the HPLC analysis of amines using m-toluoyl derivatives (1) it was necessary to establish the number and positions of m-toluoyl groups added to triethylenetetramine (TETA). The pure product of the reaction between TETA and excess m-toluoyl chloride was obtained by preparative HPLC. The 60 MHz ^{1}H spectrum indicated four toluoyl groups per TETA and a failure to observe any proton exchange with D_2O suggested that one toluoyl group was attached to each nitrogen to give secondary and tertiary amide functions:-



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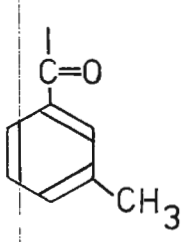


This was confirmed by the ^{13}C spectrum which, at ambient temperature in $CDCl_3$ (Fig 1), gave aromatic chemical shifts consistent with a mixture of mono- and di- alkyl N-substituted m-toluamides. However, the ethylenic carbons appeared as five signals instead of the three expected.

Spectra recorded at higher temperatures in $CDCl_3$ or o-dichlorobenzene (Fig 2) confirmed that this was the result of hindered C-N bond rotation of the tertiary amide moieties; coalescence of the four high frequency CH_2 peaks at 55° being followed at higher temperatures by resolution into two sharp signals.

M.L. Trimble E.S. Zai E. O'Kane

(1) E.C.M. Chen and R.A. Farquharson; J. Chromatog., 1979, 178, 358.

Please credit this account to Dr. C.P. Richards' subscription.

Fig 1

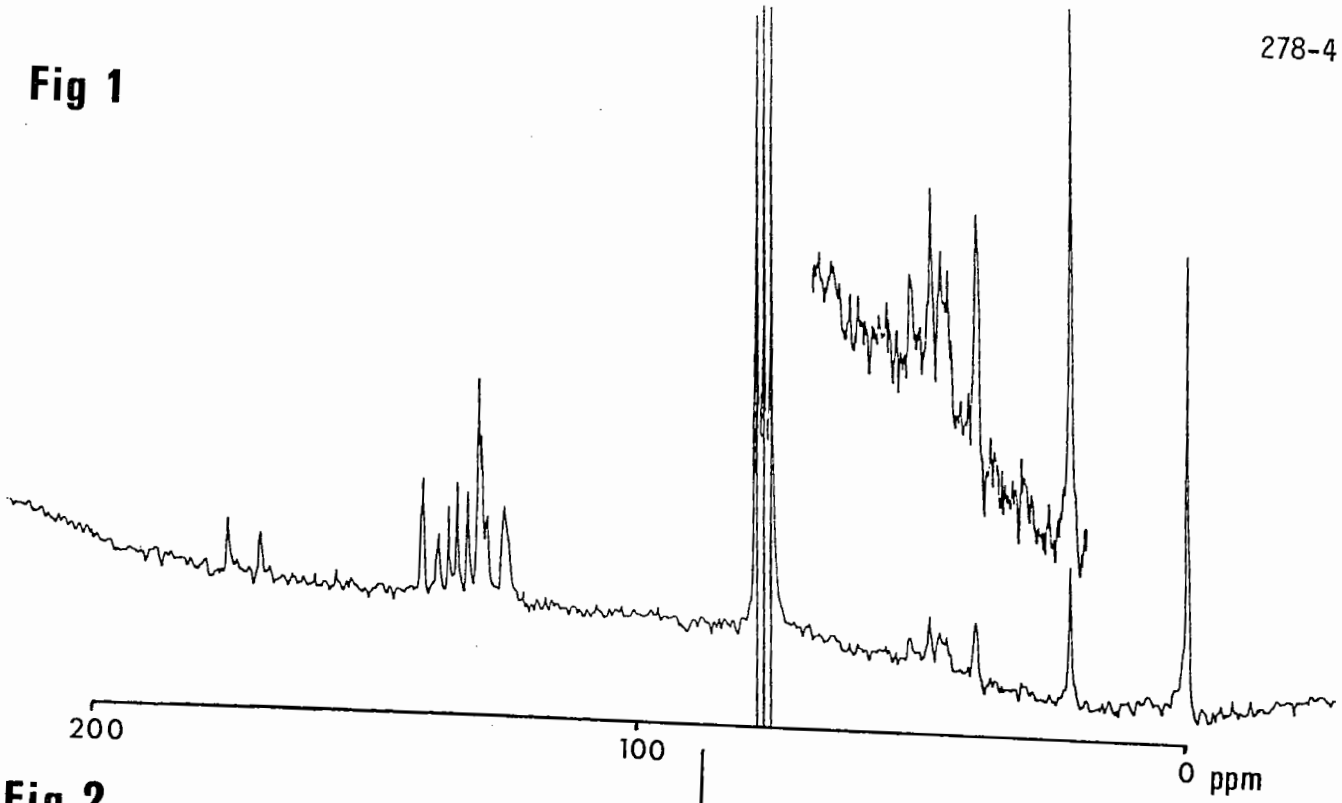
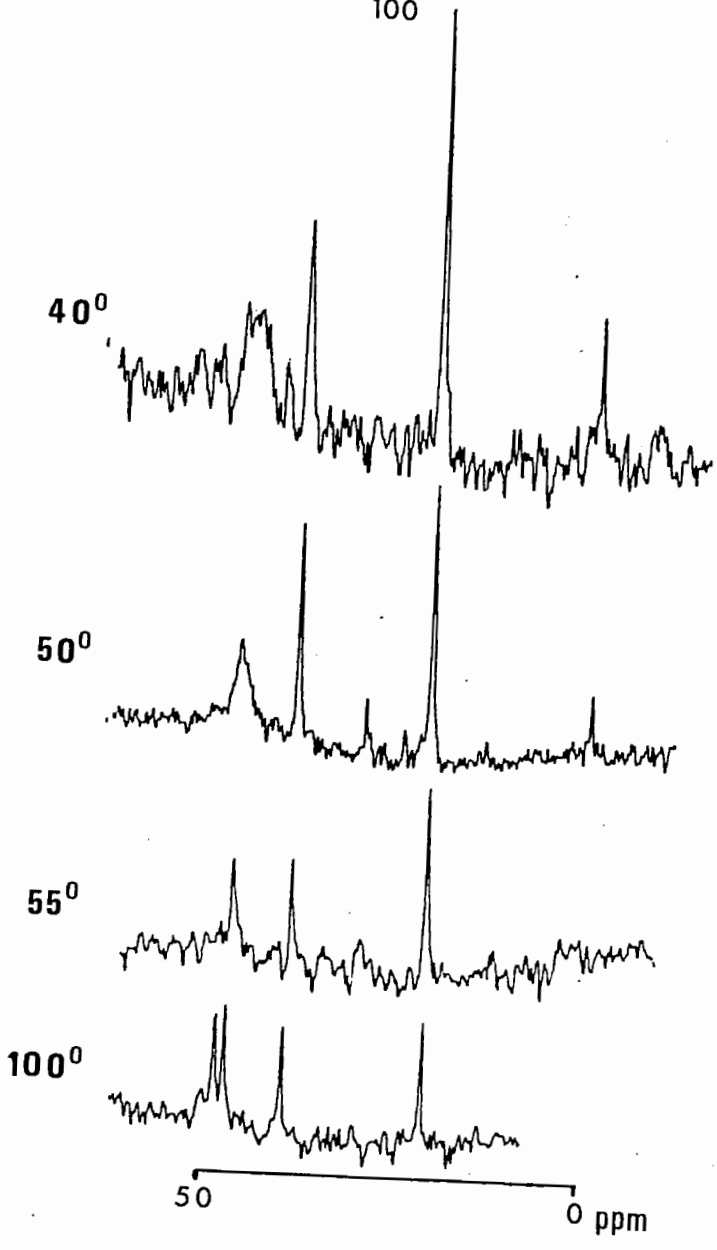


Fig 2



278-5

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September 24, 1981

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

Dear Dr. Shapiro:

Proton NMR of Whole Cell Extracts Reveal Over Thirty Compounds of Intermediary Metabolism.

Non-invasive study of whole cell biochemistry has been pioneered through investigations of energy metabolism by ^{31}P-NMR spectrometry of ATP (1,2). Addition of carbon-13 enriched metabolites to cell suspensions has demonstrated the potential of ^{13}C-NMR monitoring of metabolic processes involving these compounds (2,3). However, ^{1}H-NMR can detect a wider range of compounds simultaneously and at higher sensitivity than ^{31}P-NMR (4,5). ^{1}H-NMR also has the advantage that isotopic substitution of ^{1}H for ^{2}H is readily observed (6). We have found that many compounds of a cell's intermediary metabolism can be rapidly monitored by ^{1}H-NMR which requires small enough numbers of cells (10^{8})for the technique to be applicable, in general, to mammalian cells grown in culture. Over 70 signals are seen by alternating phase, spin echo (90-ζ-180) at 300 and 470 MHZ without the need for H_2O replacement by D_2O. Some 64 signals have now been assigned to 12 amino acids (phe, tyr, thr, pro, asp, ala, glu, leu, val, gly, met and ile) and 18 other compounds of intermediary metabolism (adenine, cytosine, guanine, uracil, glucose, fumarate, lactate, choline, betaine, glycerol, carnitine, phosphorylcholine, phosphocreatine, citrate, succinate, pyruvate, acetate and beta-hydroxybutrate). Changes in the intensity of many of these signals can be detected during the in vitro differentiation of an erythroid cell line.

Sincerely yours,

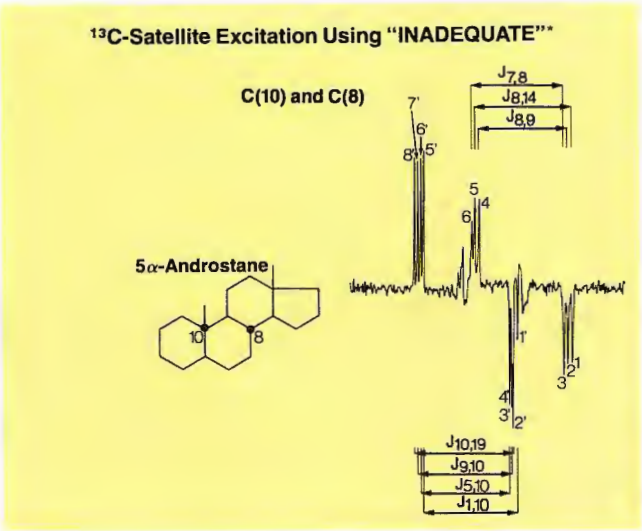
Paul F. Agris
Assoc. Professor

PFA:ga

Please credit this contribution to
Tuck C. Wong's account.

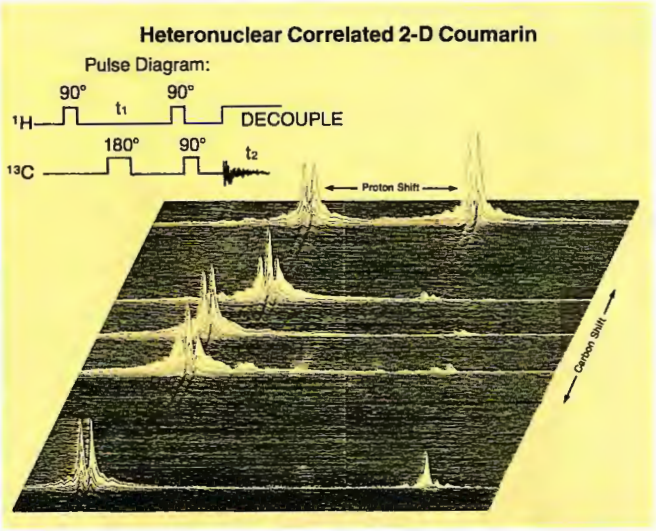
1. R.B. Moon, J.H. Richards, J. Biol. Chem. 248, 7276 (1972).
2. R.G. Schulman, T.R. Brown, S. Ogawa, S.M. Cohen, J.A. der Hollanders, Science 205, 160 (1979
3. S.M. Cohen, R. Rognstad, R.G. Schulman, J. Katz, J. Biol. Chem. 256,3428 (1981).
4. F.F. Brown, I.D. Campbell, P.W. Kuchel, D.L. Rabenstein, FEBS Lett. 82, 12 (1977).
5. C. Nicolau, H.D. Klink, A. Rieman, K. Hildebrand, H. Bauer, Biochem. Biophys. Act 511, 83 (1978).
6. K.M. Brindle, F.F. Brown, I.D. Campbell, D.L. Foxall, F. J. Simpson, Biochem. Soc. Trans. 8, 645 (1980).

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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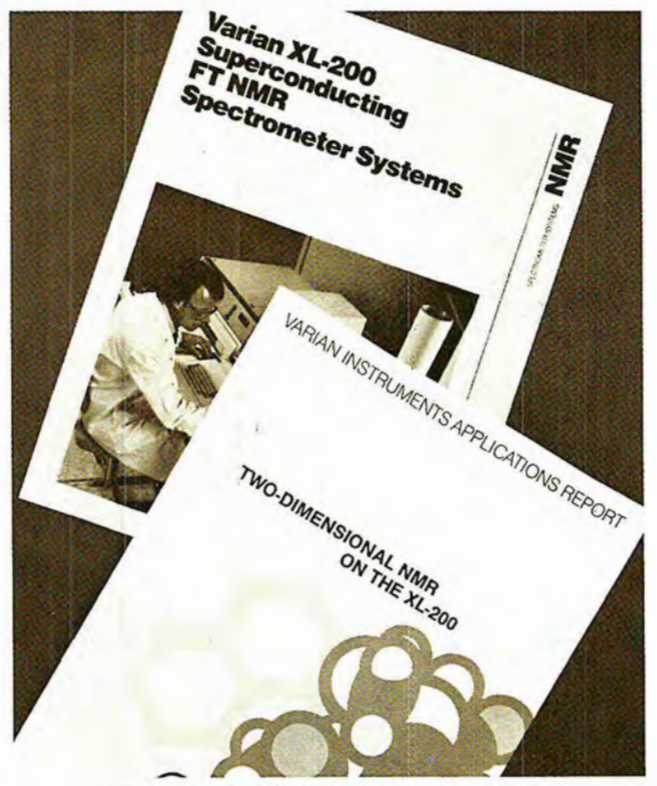

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Prof. B. L. Shapiro
Texas A&M University
Department of Chemistry
College Station, Texas 77843
U S A

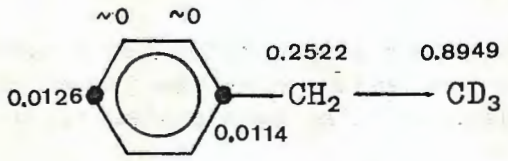
5900 Siegen 21, October 23, 1981
Adolf-Reichwein-Straße
Postfach 210209
Telefon (0271) 7401
Durchwahl 740–4390/4400

More on $^{2}H/^{1}H$ Isotope Effects $^{n}\Delta$ on ^{13}C Chemical Shifts

Dear Barry,

as it turns out, we are only second with our finding $^{2}\Delta > {}^{1}\Delta$ in phenylacetylene (cf. our Newsletter contribution of August 21, 1981). Prof. H. Fritz of Ciba-Geigy called our attention to a paper by Doddrell and Burfitt (Aust. J. Chem. 25, 2239 [1972]), where a similar observation is described for 1-deuteriohept-1-yne ($^{1}\Delta$ 0.22, $^{2}\Delta$ 0.50 ppm).

As a substitute we therefore offer an intrinsic isotope effect over six bonds recently resolved in ethylbenzene-β-d_3:



High field (9.4 T) and triple substitution made it possible to detect $^{6}\Delta$ which amounts to 0.0042 ppm per deuterium. It is interesting that $^{4}\Delta$ and $^{5}\Delta$ are zero within experimental error. All shifts are to high field. Comparison with the results for ethylbenzene-β-d_1 shows that additivity is strictly observed. Note, however, that $^{6}\Delta > {}^{3}\Delta$!

Sincerely yours,

H. Günther J. Wesener

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

October 12, 1981

DIPOLAR COUPLING CONCERTINA IN LIQUID CRYSTALS

Dear Professor Shapiro,

The most severe limitation encountered in chemical applications of liquid crystals as solvent in NMR is due to the size of the dipolar couplings which invariably give rise to second order spectra difficult to analyse.

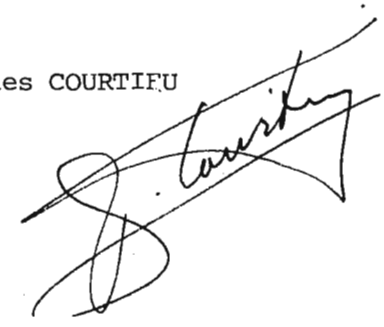
We have been able to reduce the dipolar couplings by a factor up to 100. Such reduction is accomplished by making the angle α between the nematic director and the magnetic field any value between 0° and the magic angle. This is accomplished by spinning the sample at moderate speed ($\simeq$ 75 Hz) about an axis which makes an angle less than the magic angle with the magnetic field. In this condition, the director of the nematic aligns on the spinning axis.

This method allowed us to turn a second order ABC spectrum into an AMX spectrum when spun close to the magic angle. The joined spectra show the reduction of the dipolar coupling in an A_2 spin system using this technique.

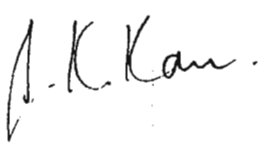
This work has been done in collaboration with the NMR group of the University of UTAH, namely with D.W. Alderman and David M. Grant. The analysis of the director dynamic and the NMR applications will soon be published.

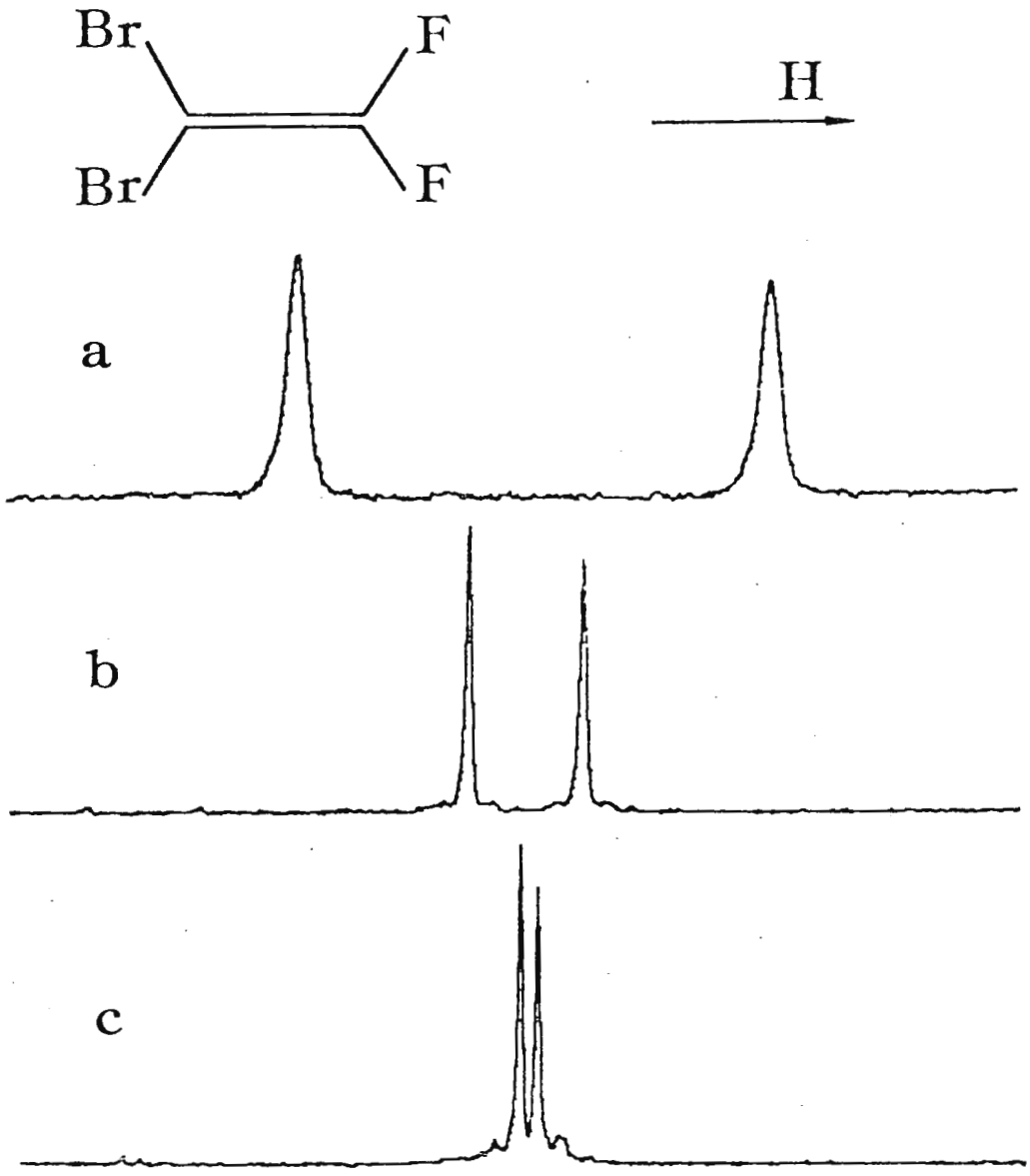
Yours Sincerely,

Jacques COURTIEU



S.K. KAN





a - Static spectrum ($3D_{FF}$ = 1845 Hz)

b - Spectrum obtained when rotated at $\alpha = 45°$

c - Spectrum obtained when rotated at $\alpha = 52°$

TEMPLE UNIVERSITY
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DEPARTMENT OF CHEMISTRY

13 October 1981

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

Gas Phase NMR Spectra

Dear Barry,

After a short lag, we have again undertaken study of gas phase kinetics of alkene reactions with hydrogen chloride by the NMR method.[1]

Some alkenes apparently cannot be co-frozen with HCl since they are reported[2] to react very rapidly. Thus, sealing the NMR tube becomes a real problem. After much experimentation with unsuitable valves, we have developed and had made (by Lab Glass, Inc., Vineland, N.J.) a modified ST 10/30 joint set as indicated on the enclosed sketch. This is just right for sealing onto standard 12 mm tubes. The other end of the inner joint has a second ST10/30 joint for attachment to the vacuum rack. Once the tube is filled with gas (below 760 torr) rotation of the grooved tube away from the 4 mm hole seals the tube - which can then be removed at the upper joint away from the vacuum rack.

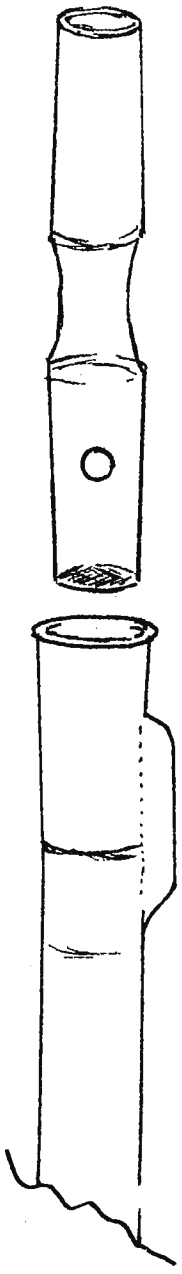
A typical ^{1}H CW scan of 640 torr of 2-methylpropene is also shown. The XL-100 is locked externally and SW = 1000 Hz. The spinning side bands, while not a problem to us, can probably be removed by more careful balancing of the tube with a small piece of glass cemented opposite to the groove but, with all of the additional weight of the joint along the main lengthwise axis of the tube, spinning is not a problem and spinning rate changes are easy.

Clearly the tube which is, of course, reusable, is also ideal for degassing, etc. of more routine samples.

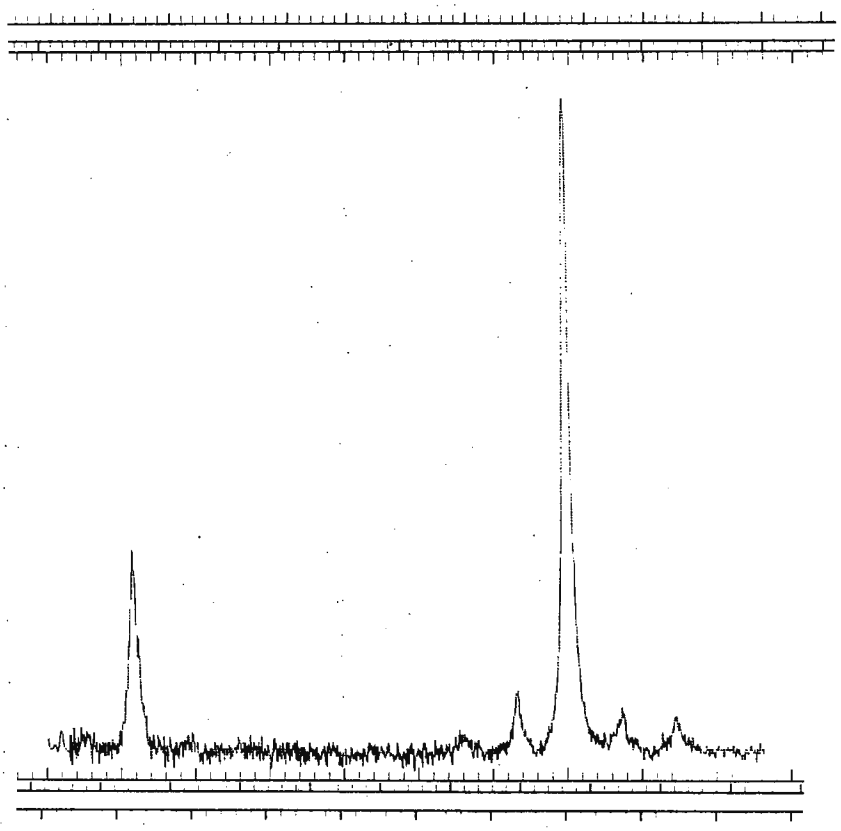
Warmest personal regards,

David R. Dalton
Professor of Chemistry

(1) M.J. Haugh and D. R. Dalton, J. Am. Chem. Soc., 97, 5674 (1975).
(2) D. Cook, Y. Lupien and W. G. Schneider, Can. J. Chem., 34, 957 (1956).



T 10/30 set attached to 12 mm NMR tube for gas samples.



^{1}H CW spectrum (XL-100-15) of 640 torr of 2-methylpropene. Spectrometer externally locked to H_2O. SW = 1000 Hz.

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, october 23, 1981.

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

Title: A New Triple Resonance Experiment.

Dear Prof. Shapiro:

Within the framework of this laboratory,where we are looking,experimentally as well as theoretically,for relations between molecular structure and J-Coupling Constants,the problem arose about the determination of the sign of a lone,long range coupling constant. That is, to determine in an ABC...X case the sign of, say, J_{AX} when $J_{BX} = J_{CX} = \text{etc.} = 0$.

Years ago a method was devised for this purpose by Cohen *et al.* (Mol Phys. 7 ,45 , (1963)), a method which could be called "double tickling" and succesfully applied to an AMX case. Ours being an ABCX case we tried a slightly different approach which could eventually benefit from the advantages of both, "tickling" and INDOR techniques.

A systematic survey was made about the feasibility of a triple resonance experiment, a "tickled INDOR" or TINDOR, as we used to call it.

Experience shows that the experiment is feasible,that is, that "doublets due to tickling behave properly under an INDOR experiment" or, in other words, that "lines in an INDOR experiment can be split by tickling" , provided that the following condition is fulfilled: That al the transitions involved shall be "chain" connected. The experiment fails if they are "branch" connected.

This work was part of the local requirements for the Ph.D. of Miss Marta Etcheverry de Milou and is due to appear shortly in the J. of Magn. Res.

Yours, sincerily

V. Kowalewski

Dr. V.J.Kowalewski.
Professor.

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28th October, 1981

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

Dear Professor Shapiro,

^{1}H and ^{195}Pt-NMR studies on species formed in the reaction of 5'-AMP with cis-$[Pt(NH_3)_2Cl_2]$

We have recently examined the kinetics of the reaction of 5'-AMP with excess cis-$[Pt(NH_3)_2Cl_2]$ in the presence of KCl by ^{1}H-NMR, and further characterised the species formed by ^{195}Pt-NMR (1). The reaction involves a branching pathway: 5'-AMP reacts with cis-$[Pt(NH_3)_2Cl_2]$ to form either species IA or IIA; species IA and IIA then react with cis-$[Pt(NH_3)_2Cl_2]$ to form species IIIA, the final product of the reaction. Species IA is characterised by signals at 8.30 ppm (H2) and 9.16 ppm (H8), species IIA with signals at 8.64 ppm (H2) and 8.53 ppm (H8), and species IIIA with signals at 8.79 ppm (H2) and 9.17 ppm (H8). The shifts of the H2 proton for species IA, IIA and IIIA are almost identical to those for complexes between adenosine and $[Pt(dien)Cl]^{+}$ with binding of a Pt-atom in a monodentate mode to N1 (8.60 ppm), N7 (8.31 ppm), and both N1 and N7 (8.79 ppm) respectively (2). Such assignments for species IA, IIA and IIIA are further supported by the results from ^{195}Pt-NMR studies which show that only two ^{195}Pt resonances arise from these three species: species IA gives rise to a resonance at -2359 ppm, species IIA to a resonance at -2398 ppm, and species IIIA exhibits two resonances of equal intensity at positions identical to those for species IA and IIA.

Please credit this contribution to the account of Dr. G.C.K. Roberts.

Yours sincerely,

G.M. Clore. A.M. Gronenborn.

(1) G.M. Clore and A.M. Gronenborn (1982) J. Am. Chem. Soc., in press.

(2) P.C. Kong and T. Theophanides (1975) Inorg. Chem., 13, 1981.

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DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

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AREA CODE 301

October 21, 1981

NOE Studies of Enzyme-Bound ATP

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

Dear Barry:

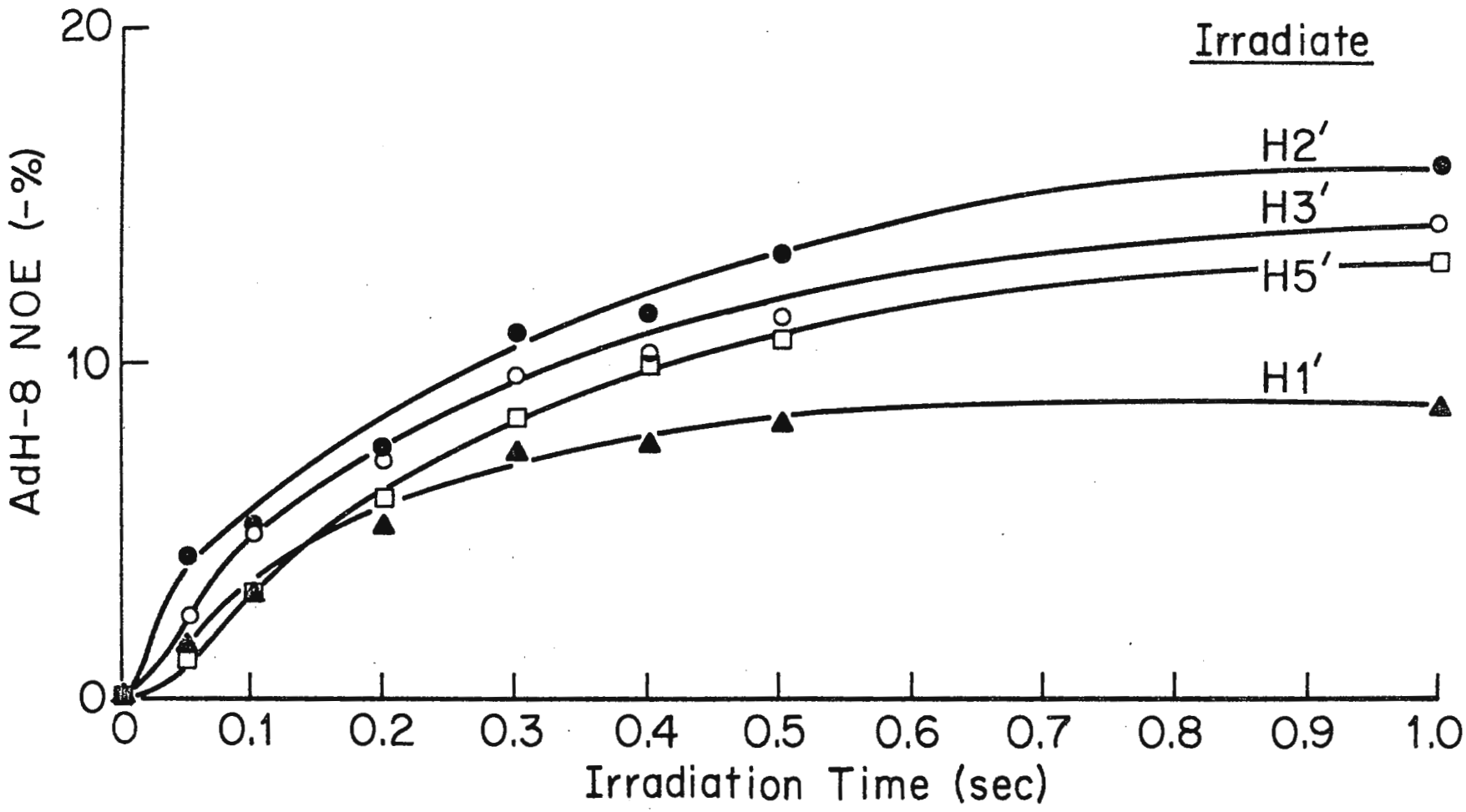
A problem in the determination of the conformation of flexible enzyme-bound substrates such as ATP, by distance measurements from a paramagnetic reference point, is that an average conformation is detected. Moreover, since the sixth power of the distance is measured, a root-mean-sixth average conformation is obtained. From the average conformation alone, it is not possible to determine the number and nature of the individual conformations that give rise to this average. In the pyruvate kinase-metal-ATP complex we have approached this problem by the use of an independent method, interproton nuclear Overhouser effects of enzyme-bound ATP at 250 MHz. Our preliminary results are as follows. Intramolecular negative NOE's were observed on the adenine H-8 proton of enzyme-bound MgATP upon pre-irradiation of certain of the ribose protons of the bound nucleotide. The magnitudes of these NOE's were studied as a function of pre-irradiation time to distinguish primary NOE's from higher-order ones. The magnitudes of the primary NOE's decreased in the order $H_2' = H_3' \geq H_5' > H_1' > H_4'$ from a value of 16% to <4% (see figure) indicating correspondingly increasing distances between the adenine H-8 and these ribose protons.

These effects are qualitatively and quantitatively consistent with a previous determination of the glycosidic torsional angle of 30 ± 10° for pyruvate kinase-bound ATP from the paramagnetic effects of enzyme-bound Mn^{2+} on the T_1 of the protons of ATP (Sloan and Mildvan, J.B.C. 251, 2412), provided a slightly 3'-endo ribose conformation is assumed. This agreement in the nucleotide conformations determined by the diamagnetic NOE, and the paramagnetic probe-T_1 methods, which differ by 10^3 in the time over which the conformation is averaged, and in the location of the reference points, can be explained by the existence of a unique average conformation about the glycosidic bond of ATP on pyruvate kinase. Such studies are being extended to the differing conformations of ATP on creatine kinase, protein kinase, and adenylate kinase.

With best wishes,

Al Mildvan

Paul Rosevear



Time dependent NOE's of Ribose Protons of ATP (10.2 mM) in the presence of pyruvate kinase (1.04 mM), $MgCl_2$ (14 mM), KCl (85 mM), KPIPES (1.4 mM), pH 7.1; T=25°, 128 transients, acquisition time 1.4 sec, delay 2.3 sec. 250 MHz.

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October 23, 1981

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

Dear Dr. Shapiro:

^{13}C NMR SPECTRAL INTERPRETATION

A major task in the interpretation of ^{13}C NMR spectra is to estimate the ^{13}C chemical shifts of actual or suspected compounds. Two approaches are generally used: (1) Look up the chemical shifts of similar compounds in spectral libraries; (2) Calculate the ^{13}C shifts by using empirical substituent chemical shift rules. For the first approach the spectral collections of Sadtler (1), Bremser (2), Breitmaier (3), and Stothers (4) among others, are very useful. The CNMR program of Chemical Information Systems (5), and other computer-assisted structure determination methods (6) can also be very helpful.

In the second approach, there exist empirical rules such as those devised by Grant and Paul (7), Lindeman and Adams (8), and Carman, et al. (9) for hydrocarbons, Sarneski, et al. for amines (10), and numerous others observed for specific functional groups. Clerc and Pretsch have devised general additive rules for 28 functional groups (11). Although these rules have varying accuracy they serve as good starting points for spectral interpretation, especially when no simple analogs can be located in the spectral libraries.

I have recently computerized (with the assistance S. J. Ellingsen) the Clerc-Pretsch rules on the company INTERDATA computer. The program CSHIFT was written in FORTRAN IV and can handle aliphatic carbons carrying the 28 functional groups as listed by Clerc and Pretsch. It can also take care of alicyclic compounds, although the accuracy tends to be poorer. Interested readers should inquire for details. Please credit this letter to Dr. Freeman's subscription.

Yours sincerely,

H. N. Cheng
Analytical Division

HNC/cmp

References:

1. Sadtler Research Laboratories, Inc., 3316 Spring Garden St., Philadelphia, PA 19104.

2. W. Bremser, et al., "Carbon-13 NMR Spectral Data," Verlag Chemie, Weinheim, 1981.

3. E. Breitmaier, G. Haas, and W. Voelter, "Atlas of Carbon-13 NMR Data," Heyden, London, 1979.

4. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, 1972.

5. Chemical Information Systems, Inc., 7215 York Road, Baltimore, MD 21212.

6. For Example, (a) W. Bremser, H. Wagner, and B. Franke, Org. Magn. Resonance, 15, 178 (1981), (b) G. Szalontai, et al., Anal. Chim. Acta, 133, 31 (1981), (c) N.A.B. Gray et al., J. Org Chem., 46, 703 and 3399 (1981).

7. E. G. Paul and D. M. Grant, J. Amer. Chem. Soc., 86, 2984 (1964).

8. L. P. Lindeman and J. Q. Adams, Anal. Chem., 43, 1245 (1971).

9. C. J. Carman, A. R. Tarpley and J. H. Goldstein, Macromolecules, 6, 719 (1973).

10. J. E. Sarneski, et al., Anal. Chem., 47, 2116 (1975).

11. J. T. Clerc and E. Pretsch, TAMU Newsletter, May 4, 1973.

Examples:

n-Butylamine

C * C * C * C * N

13.700PPM
20.200PPM
36.600PPM
42.000PPM

2-Methoxypropane

C * O * C * C
C

51.100PPM
70.600PPM
22.700PPM
22.700PPM

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SADIS BRUKER SPECTROSPIN, Boîte Postale N 67160 WISSEMBOURG

Professor B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station

TX 77843

USA

N./Réf.
V./Réf.

Wissembourg, le 6 octobre 1981

^{31}P INEPT and Spin 1/2 Transition Metal NMR

Observing (or trying to observe) low γ, spin 1/2, transition metals resonances is generally a real headache for the spectroscopist (very long T1, low sensitivity, large chemical shift scale, etc... etc...), although a wealth of informations can be gained from transition metal NMR concerning the electronic structure of the complexing metal site (1), (2).

We have recently shown the applicability of the ^{1}H INEPT sequence to ^{109}Ag and ^{103}Rh observation (3) together with the huge sensitivity enhancement one can obtain (ca. 400/900 in time !) compared to normal observation. On the other hand, a vast family of transition metal complexes are stabilized by phosphine ligands and then, well characterized $J_M - ^{31}P$ coupling exist, ranging from 50 to 400 Hz, an ideal situation for ^{31}P INEPT experiments which we consequently started.

They work very well and the sensitivity gain is still high enough $\left(\frac{\gamma 31P}{\gamma M}\right)$ to get, for example, a very good spectrum of an 0.02 M solution of $Rh(CO)Cl(P\emptyset_3)_2$ (10 mm tube) in 3 hours ! (Fig. 1)

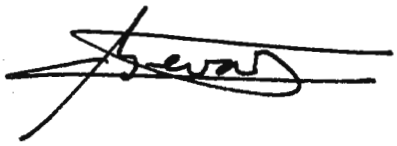
Figure 2 examplifies what one can expect for ^{57}Fe. The same kind of results have also been obtained with ^{183}W.

It is clear, now that the INEPT method will not only serve the organic chemist as a ^{13}C spectrum editing sequence but will also find a broad spectrum of applications in Inorganic chemistry.

A full paper about these results (experimental set-up, influence of ^{31}P T1, pulse misadjustment, offset effects, ...) is being written up.

Sincerely,

C. BREVARD



(1) W. Von Philipsborn et Al. : J. Organometal. Chem. 205 211 (1981)

(2) R.G. KIDD : Nuclear Shielding of the Transition metals
Annual Report on NMR Spectroscopy 10A 2 (1980)

(3) C. Brevard, G. Van Koten, G. Van Stein : J.A.C.S (in press)
A.F.M.J Van der Ploeg, G. Van Koten, C. Brevard : Inorg. Chem. (submitted)
G. Van Stein, G. Van Koten, C. Brevard : Chem. Comm. submitted)

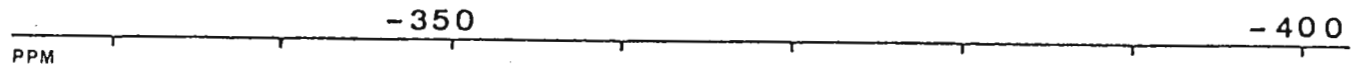
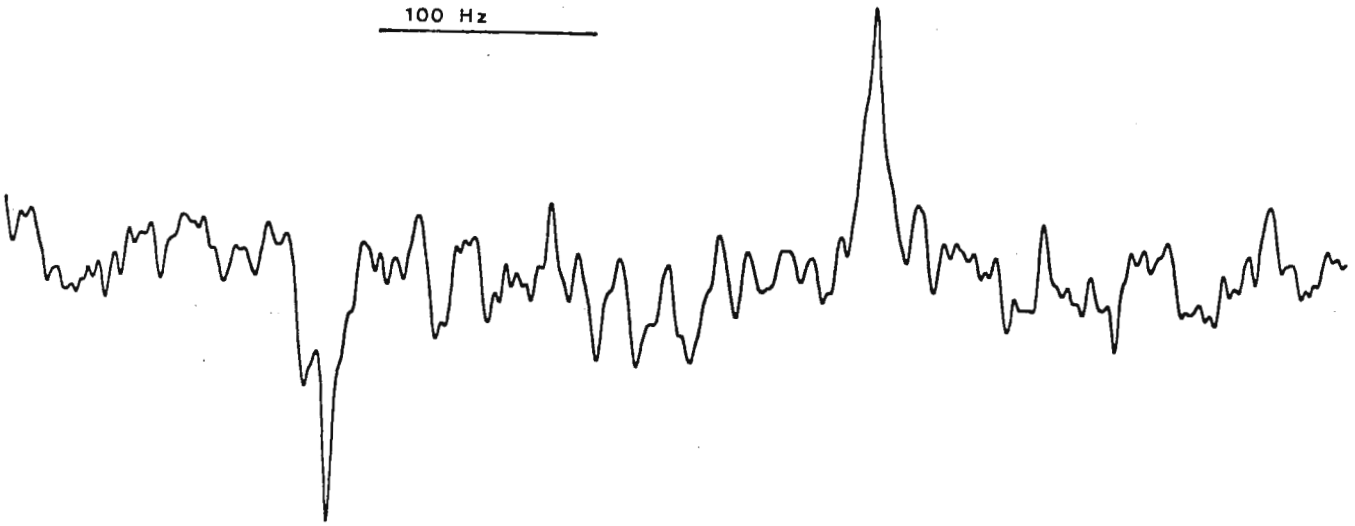


Fig. 1 $\{^{31}P\}$- ^{103}Rh INEPT spectrum of $Rh(CO)Cl(P\phi_3)_2$, 0.02 M in CD_2Cl_2, 9.000 scans (5 hours), 10 mm tube. Reference : Ξ = 3 . 16 MHz



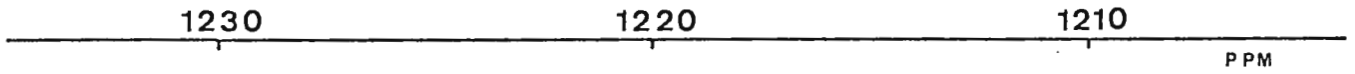
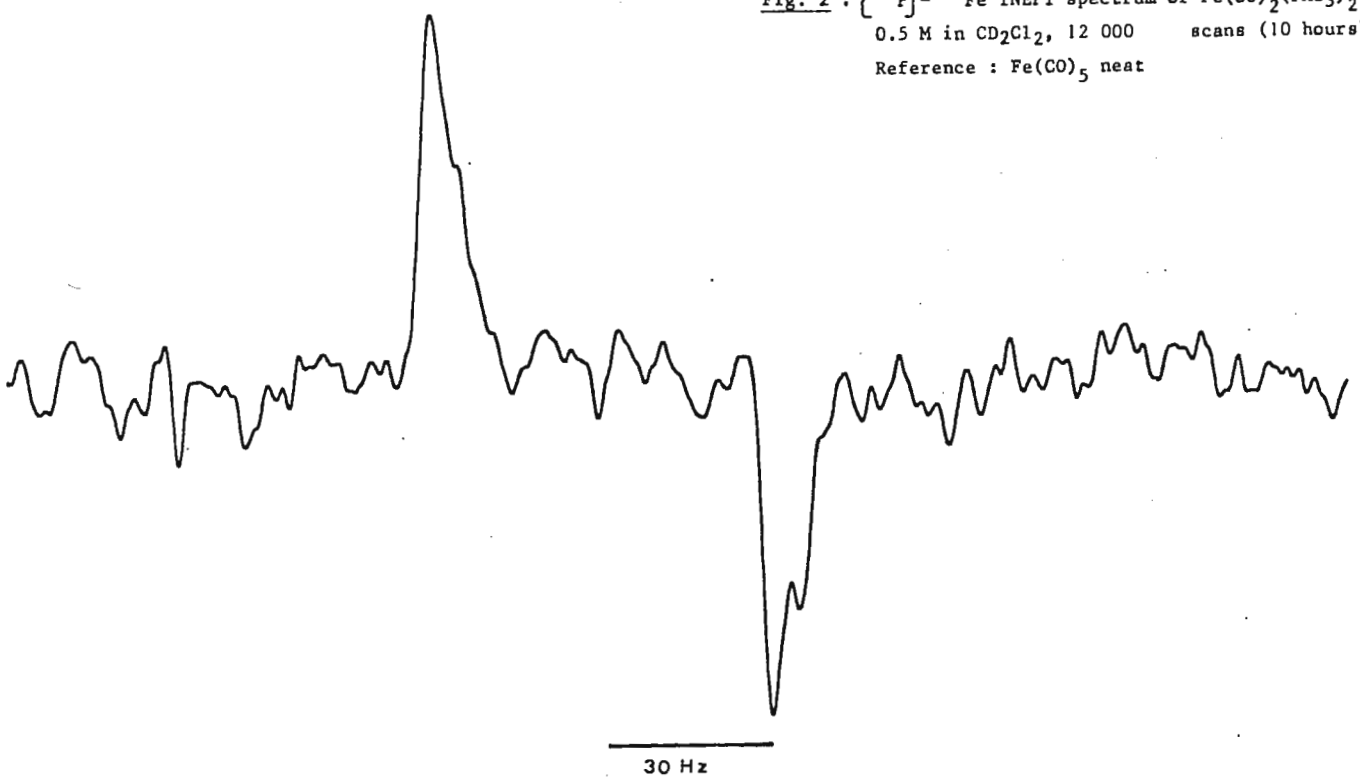


Fig. 2 : $\{^{31}P\}$- ^{57}Fe INEPT spectrum of $Fe(CO)_2(PMe_3)_2\ CS_2$, 0.5 M in CD_2Cl_2, 12 000 scans (10 hours), 10 mm tube
Reference : $Fe(CO)_5$ neat



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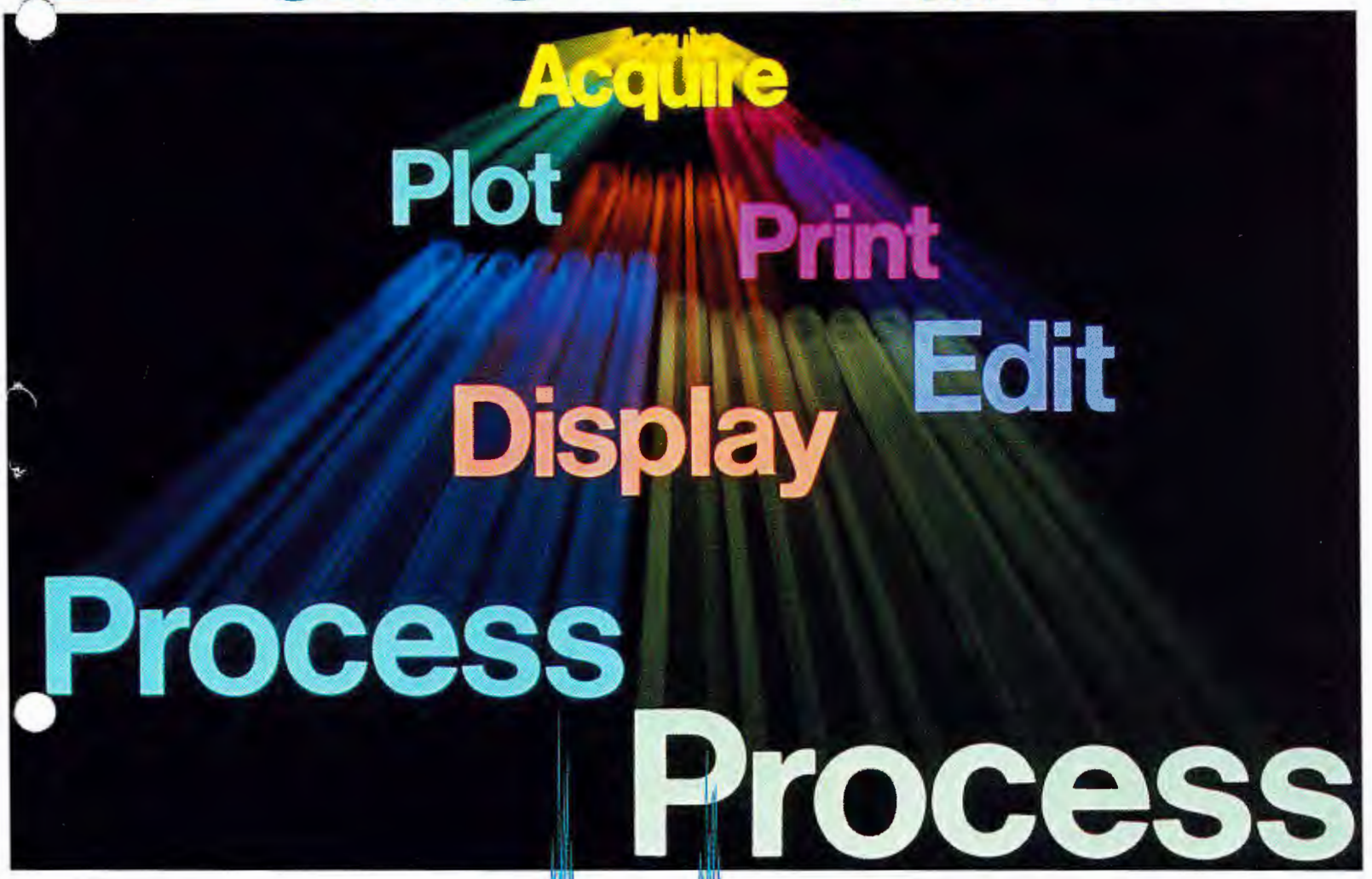

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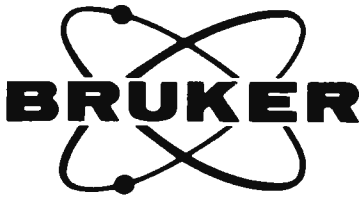

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PROFESSEUR B. P. ROQUES

PARIS, LE October, 10th, 1981

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

Triple irradiation on Brüker WH 270.

Dear Professor Shapiro,

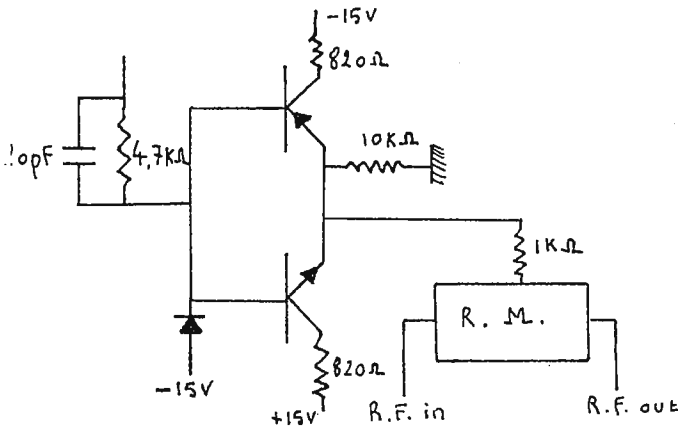
Structural determination and/or conformational analysis of peptides using ^1H NMR or more sophisticated methods (NOE for distance) is complicated by the occurrence of the overlapping signals. This difficulty can often be overcomed using triple irradiation. For such a purpose simple modification of Bruker WH 270 was performed. When two sinusoidal signals with frequencies F_1 and F_2 are mixed on a ring modulator, two different out signals are obtained with respective frequencies $F_1 + F_2$ and $F_1 - F_2$. Therefore, it will be possible to performe triple irradiation if the decoupling frequency is modulated (as described). Let F_1 be the decoupling frequency and F_2 be a low frequency sinusoidal signal. As shown scheme 1, the NMR spectrum will not be decoupled at frequency F_1 but simultaneously at frequencies $F_1 + F_2$ and $F_1 - F_2$.

Scheme 1.

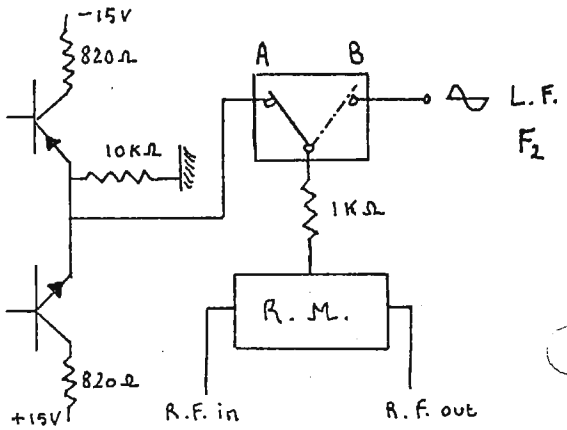
Consequently, two NMR signals can be decoupled using for the modulating signal a frequency equal to half the frequency difference $\Delta\nu$ between these two signals.

The modifications of the decoupler is made at the level of the "Broad Band Modulation" print. In the Bruker WH 270 decoupler, the high frequency signal is modulated at the level of the ring modulator (Scheme 2) either by a pulse generated

by the computer (selective decoupling) or by a noise modulation (broad band decoupling) arising from the broad band generator. This modification is obtained by insertion of a relay just before the 1 KΩ resistance as shown on scheme 3. When positioned on A, the normal mode of irradiation is performed. When it is in the B position, the frequency sinusoidal signal F_2 can be mixed with the high frequency decoupling signal F_1. Therefore, triple irradiation is obtained at $F_1 + F_2$ and $F_1 - F_2$. The intensity of the modulating signal F_2 is optimized following the shape of the high frequency signal at the decoupler RF output ; modulation of F_1 must be carefully selected in order to avoid overmodulation leading to several spikes in the ^1H NMR spectrum.



Scheme 2.



Scheme 3.

Figure 1 shows the ^1H NMR spectrum of t.Boc D-alanine performed in Me_2SO at 20°C with a Bruker WH 270 operating in the Fourier transform mode, and the expansions of the αCH proton :

A. with irradiation out of range,

B. with irradiation of the NH proton,

C. with irradiation of the CH_3 group,

D. with irradiations of both the NH and the CH_3 group, showing the efficiency of the triple irradiation performed with the modified decoupler.

Sincerely yours.

J. BELLENEY B. GAUGAIN B.P. ROQUES.

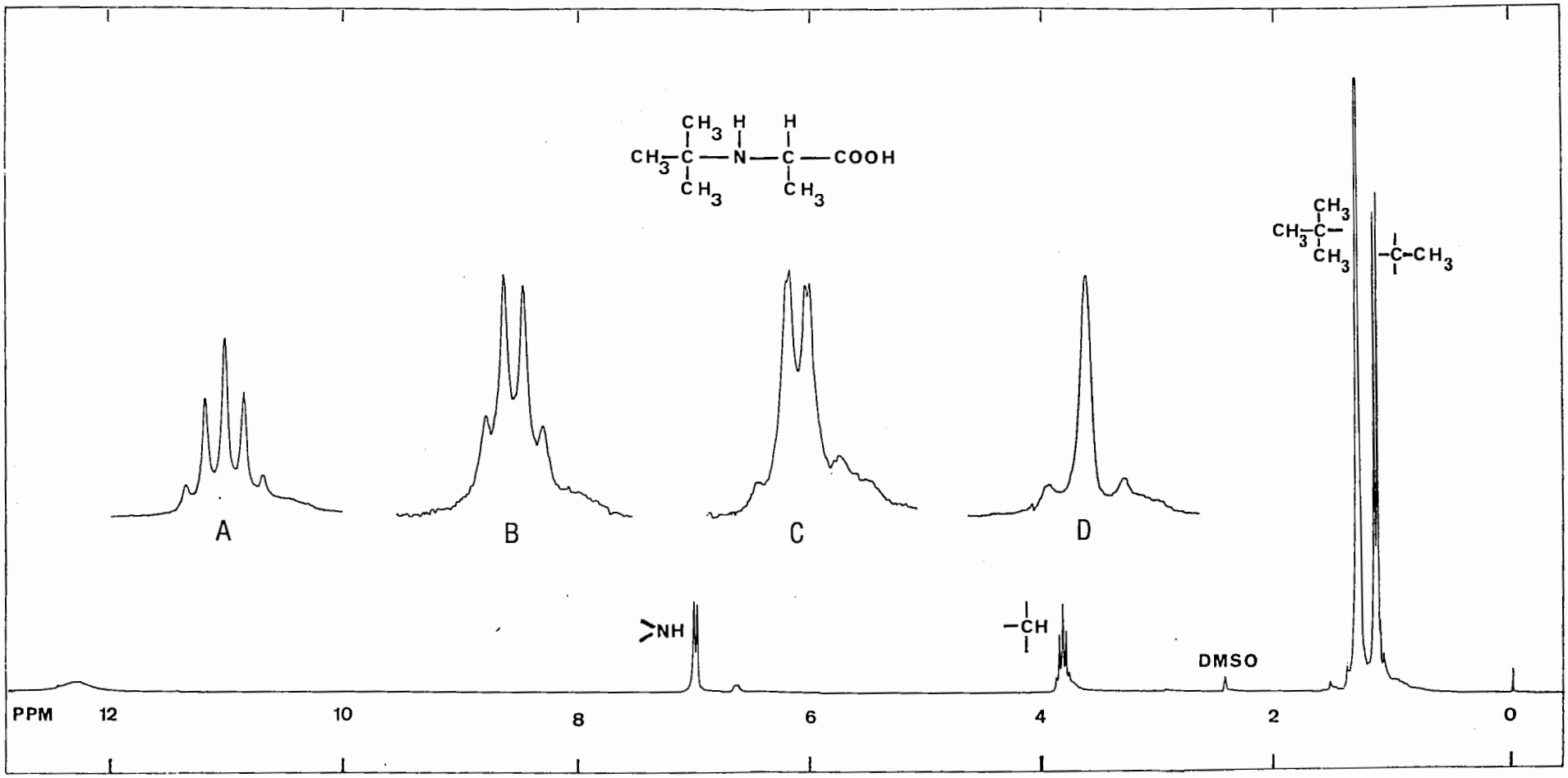


Figure 1.

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P.O. Box 9502, 2300 RA Leiden Phone: 71-148333, extension: .....

Your letter:
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Our reference:

LEIDEN, October 26, 1981.

Subject: 9-Demethyl-9-deutero-retinal

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

Dear Professor Shapiro,

Last September our Bruker WM 300 NMR-apparatus was installed. We are very happy with this addition to our NMR capabilities. In connection with our work on visual pigments we prepared all-trans-9-demethyl--9-deutero-retinal (fig 1), with a deuterium incorporation of 99% and we measured the 300 MHz ^{1}H-NMR, 75 MHz ^{13}C-NMR, and 46 MHz ^{2}H-NMR spectra. In tables I and II the results are reported. Fig 2 shows the ^{1}H-NMR spectrum with the expanded vinylic region in the insert. Assignments were checked by double resonance techniques. In the case of the ^{13}C-NMR the peaks of C_7, C_{10} and C_{12} were assigned on comparison with published data of retinoids[1]. The signal of C_9 is a low intensity triplet due to the coupling with deuterium. The ^{2}H-NMR in CCl_4 at 46 MHz shows one signal at 6,48 ppm for the 9-D.

Table I. ^{1}H-NMR of all-trans-9-demethyl-9-D-retinal in $CDCl_3$ relative to TMS at 300 MHz.

Proton	δ_H	Proton	δ_H		
1,1'-CH_3	1.04	7-H	6.35	J(7,8)	15.6 Hz
2,2'-H	1.46	8-H	6.19	J(10,11)	11.0 Hz
3,3'-H	1.61	10-H	6.30	J(11,12)	15.2 Hz
4,4'-H	2.03	11-H	6.82	J(14,15)	8.2 Hz
5-CH_3	1.74	12-H	6.34		
13-CH_3	2.29	14-H	5.96		
		15-H	10.10		

Table II. ^{13}C-NMR of all-trans-9-demethyl-9-D-retinal in $CDCl_3$ relative to TMS at 75,5 MHz.

Carbon	δ_C	Carbon	δ_C	Carbon	δ_C
1	34.15	8	132.61	15	191.00
2	39.74	9	138.73	16	28.89
3	19.09	10	130.01	17	28.89
4	33.35	11	136.60	18	21.75
5	131.83	12	134.02	20	12.96
6	137.34	13	154.47		
7	135.16	14	129.04		

1. G. Englert, Helv. Chim. Acta, 58, 2367-2390 (1975).

Sincerely yours,

J.A. Pardoen G.K. 't Lam C. Erkelens J. Lugtenburg

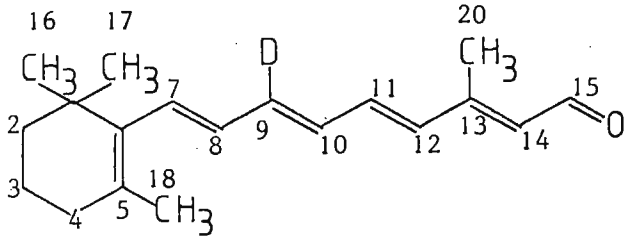


Fig 1. All-trans-9-demethyl-9-D-retinal.

(intensity reduced by Editor)

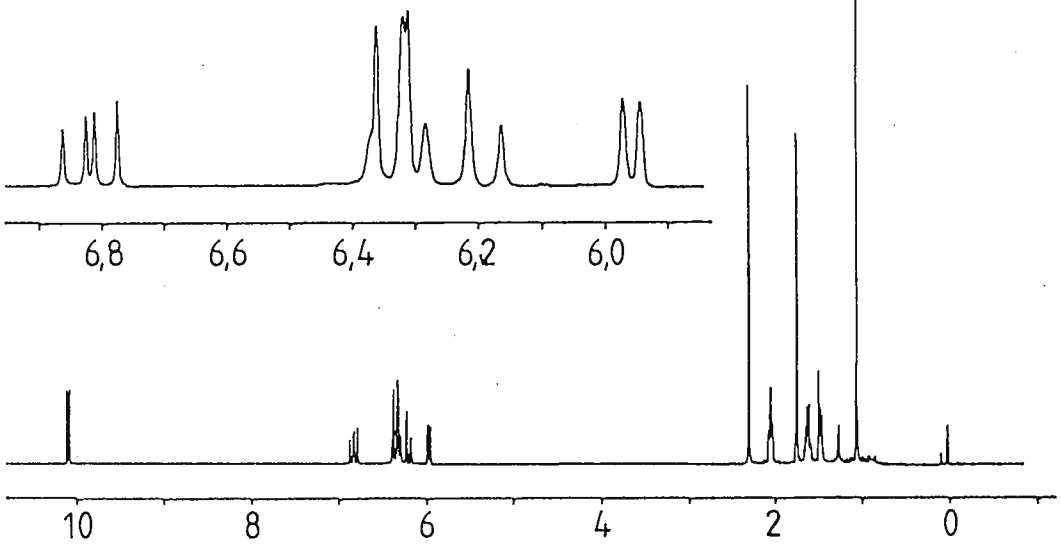


fig 2. ^{1}H-NMR (300 MHz) spectrum of all-trans-9-demethyl-9-D-retinal in $CDCl_3$ relative to TMS.

United States Department of Agriculture
Science and Education Administration
Agricultural Research Northeastern Region Eastern Regional Research Center
600 East Mermaid Lane Philadelphia Pennsylvania 19118

October 27, 1981

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

Subject: Structural alteration during ^{13}C CP-MAS NMR spectroscopy

Dear Professor Shapiro:

In recent studies of crystalline carbohydrates by CP-MAS ^{13}C NMR spectroscopy, we have examined α-D-glucose in its anhydrous[1] (orthorhombic) and monohydrate[2] (monoclinic) states. During the course of these experiments we observed that after long periods of signal averaging which were necessary to obtain spectra of glucose (T_{1_H} α-D-glucose·H_2O 77 sec, T_{1_H} α-D-glucose anhydrous = 40 sec), the α-D-glucose·H_2O was partially transformed into the anhydrous form. This phenomenon appears to depend on the duration of sample ^1H irradiation and spinning. The accompanying figure shows the progress of the α-D-glucose·H_2O transformation with a 256 msec acquisition time and a magic angle spinning rate of 2.1 KHz. The resonances at δ61.77 and 64.51 represent the C-6 carbons of the monohydrate and anhydrous forms (established independently with pure compounds). An increase in the acquisition time to 0.5 sec resulted in an increase (approximately 50%), in the rate of conversion of the monohydrate. Neither ^1H irradiation (11 Gauss at 15 MHz) nor magic angle spinning (2.1 KHz) alone, for comparable periods of time, produced this structural modification. It appears that a combination of centrifugation (12-15 G of force acting on some portion of the sample) and low energy microwave irradiation (11 Gauss at 15 MHz) has a synergistic effect on the liberation of water from the crystalline state. Ultimately this water must diffuse to the walls of the rotor whereby it may escape through the vapor permeable threads of the rotor cap. Conversion seems to be limited to approximately 40% which is probably a consequence of the pressure drop across the cross section of the sample within the rotor.

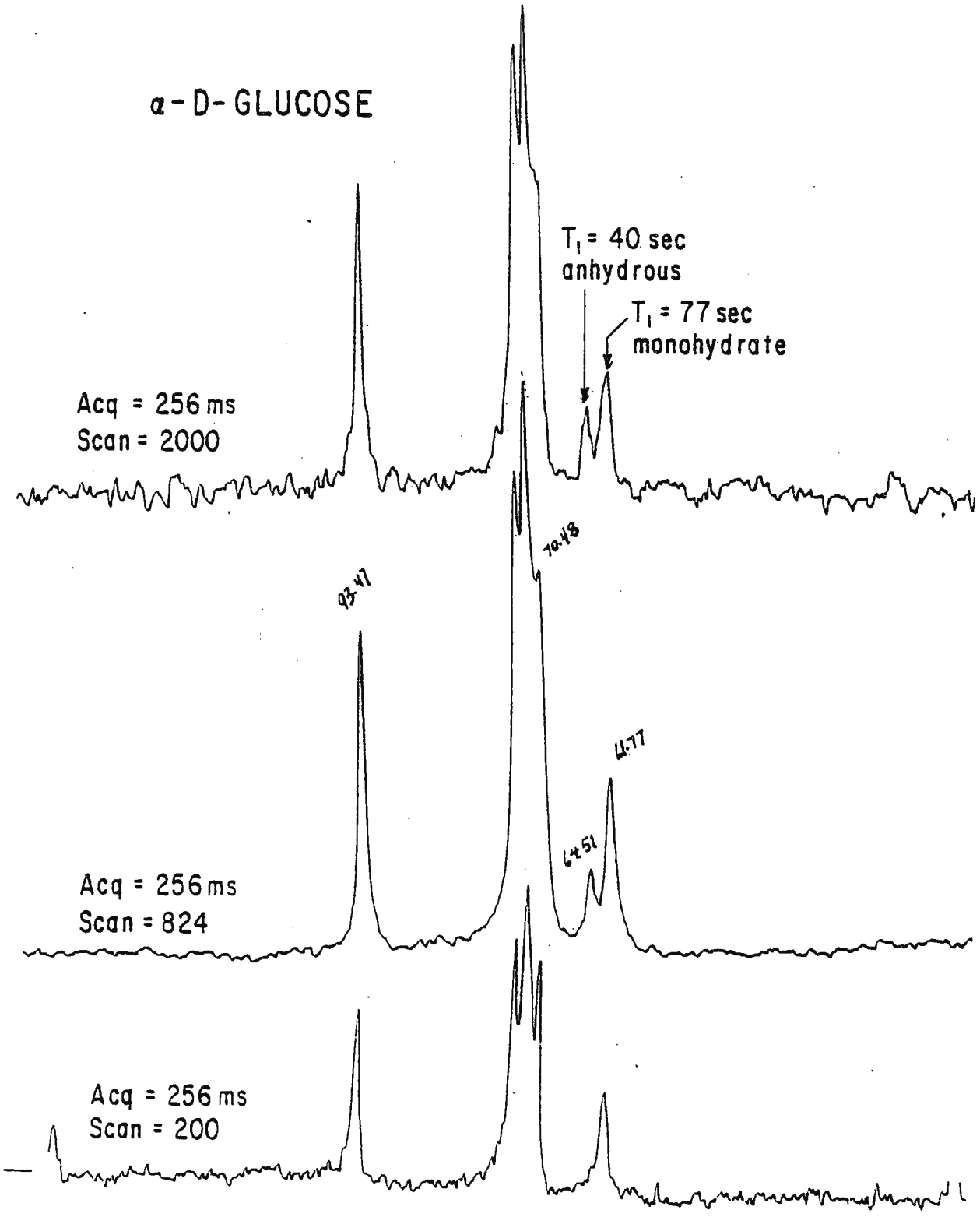
So far we have only observed this effect with the monohydrate of α-D-glucose, presumably because water is known to be loosely bound to the glucose molecule[3]. In any event, care should be taken when examining hydrated crystals by CP-MAS NMR not to irradiate and spin the samples for unnecessarily long periods of time.

Sincerely,

Philip E. Pfeffer

Kevin B. Hicks

1. G. M. Brown, H. A. Levi, Science (1965) 1038.
2. R. C. G. Killean, W. G. Ferrier, and D. W. Young, Acta Cryst., 15 (1962) 911.
3. T. Hatakeyama, H. Yoshida, C. Nagasaki, and H. Hatakeyama, Polymer 17 (1976) 559.



15 MHz ^{13}C CP-MAS spectrum of α-D-glucose · H_2. Conditions: spectral width = 2 KHz, contact time = 1 msec, repetition rate = 280 sec.

278-33

Wesleyan UNIVERSITY

HALL-ATWATER LABORATORIES
MIDDLETOWN, CONNECTICUT 06457
TEL.: (203) 347-9411

Dr. Philip Bolton
DEPARTMENT OF CHEMISTRY

October 27, 1981

Proton Observe INEPT

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

Dear Barry:

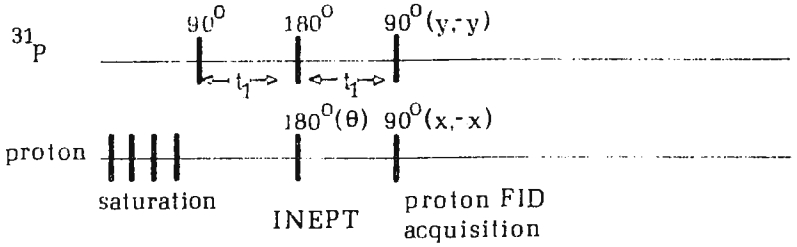
Sometime ago there was an effort here to see how well proton observe INEPT could actually be. For many samples the proton observe INEPT might be a viable alternative to the two-dimensional experiments I have been doing in collaboration with Geoffrey Bodenhausen. The proton observe INEPT could also be used, in principle, to detect the carbon-13, nitrogen-15, etc. proton satellite peaks. However, the suppression of the background signals was never quite good enough as discussed below. Gareth Morris and Ray Freeman published the basic idea a few months ago but the level of suppresion of unwanted signals they obtained was even worse than that obtained here.

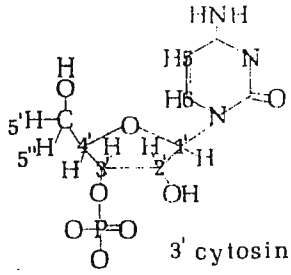
The basic idea for the experiment is quite simple. The proton magnetization is saturated for two reasons: to build up the population differences between energy levels connected by phosphorus-31 transitions via the NOE and to eliminate all of the normal proton magnetization. A straightforward INEPT procedure is then used to transfer the phosphorus-31 population differences to protons with subsequent observation of the proton signals. The real trick in this experiment is to effectively suppress all signals not arising from population transfer.

The method used here hits a level of suppression of about 50,000 fold compared to Morris and Freeman's 800 fold. An elaborate phase cycling, 64 different combinations, is needed to reach this level of suppression. The example shown in the figure shows the signals from 3' CMP in water. In the normal proton spectrum the intensity of the HOD signal is about 1,250 times that of the H_5 and H_1, signals of the nucleotide each of which is about 8 times as high as the H_3, signal. In the proton observe INEPT spectrum the H_3, signal is about 6 times that of the HOD signal. Thus, the H_3, signal is enhanced relative to the HOD signal by about 50,000 fold. Nevertheless, this is not good enough for most demanding experiments compared to the perfect suppresion obtained in two dimensional experiments. Also, the proton observe INEPT experiment is relatively worthless when inequivalent protons are coupled to the phosphorus-31. Thus, the approach was abandoned.

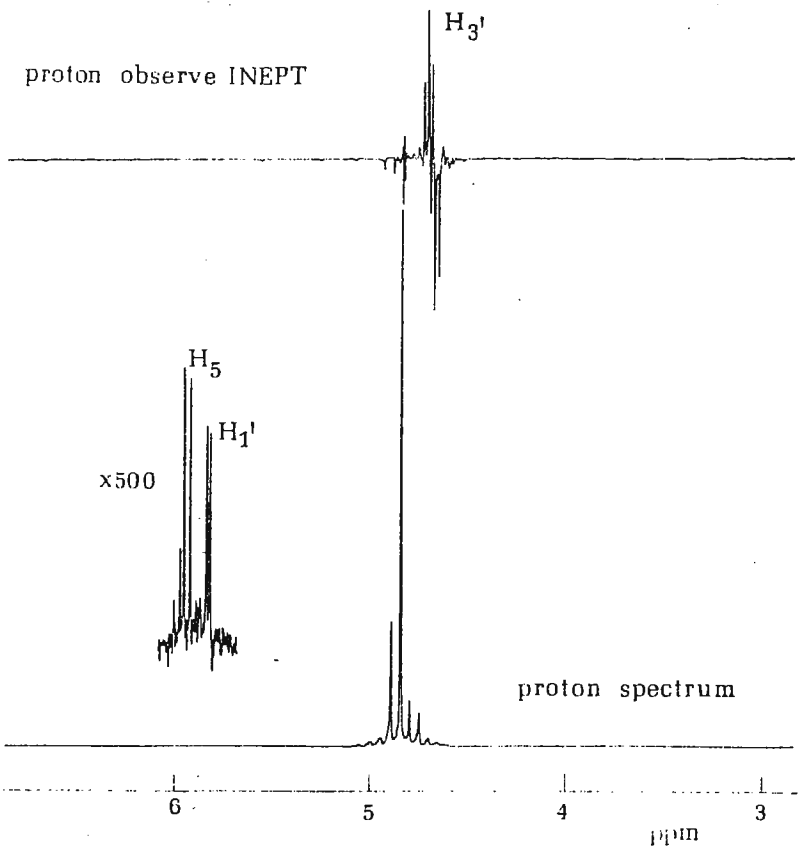
Sincerely, Philip Bolton

proton observe INEPT





3' cytosine monophosphate



phase cycling:

θ (X, X, Y, Y, -Y, -Y, -X, -X)

for each θ saturation phase (X, Y, -Y, X)

for each saturation phase ^{31}P 180° (X, -X)

Varian / 611 Hansen Way / Palo Alto / California 94303 / U.S.A.

varian

Dear Barry

October 15, 1981

I'd like to take this opportunity to announce our new series of NMR Workshops for 1981-82. We have expanded our format to cover advanced topics as well as basic, and have split the course into two parts. The Advanced Workshop may be of interest to experienced NMR spectroscopists, since it covers many of the new techniques which have appeared on the scene only within the last two years. Although the cost for each workshop is $200, those who take both the Advanced and Basic get both for a total of $300. The agendas are given below. For details of registration, call a local Varian Sales office or me at (415) 493-4000.

Sincerely yours,

George A. Gray
NMR Applications Laboratory
Varian Instrument Division

Workshop I

Basic ^{13}C NMR and FT Spectroscopy

Basic Pulsed NMR
Fourier Transform Techniques
^{13}C NMR Techniques and Applications

Since Varian's ^{13}C NMR Workshops began in 1974, more than 1,000 chemists, biochemists and spectroscopists have participated. Conducted by a faculty of knowledgeable NMR scientists, this two-day, non-commercial course is open to all interested persons at a nominal charge of $200 to cover the costs of tuition and printed materials.

Dates and Locations

Dec. 8, 9	G.D. Searle Research Laboratories Chicago, Illinois
Jan. 26, 27	University of Houston Houston, Texas
May 18, 19	NASA Lewis Cleveland, Ohio

FIRST DAY

8:00-9:00	Registration
9:00-10:00	**General Overview of ^{13}C NMR** Properties of ^{13}C nucleus, methods of detection, spectral characteristics, chemical shift range, spin-spin coupling measurements, relaxation, proton decoupling, structure-solving techniques, off-resonance decoupling.
10:00-11:00	**The Chemical Shift** Empirical chemical shift correlations, model compounds, additivity of ^{13}C shifts, solvent effects, conformational effects, functional groups.
11:00-12:00	**Problem Session #1** A session devoted to applying basic chemical shift data and off-resonance spectra for determination of chemical structure. Direct class participation with staff-student interaction on one-to-one level.
12:00-1:00	Lunch
1:00-2:00	**Problem Session #2** Continued problem-solving.
2:00-3:00	**Coupling Constants and Decoupling Experiments** Off-resonance, gated and suppressed Overhauser decoupling, selective decoupling, graphical methods. The use of direct and long-range coupling data for structure determination and assignments.
3:00-3:30	Break
3:30-5:00	**The Pulsed Fourier Transform Experiment: Basics** Pulsed excitation, NMR detection, pulse width and repetition rate effects, the rotating frame model, hardware requirements, digital requirements, signal processing, the Fourier transform.

SECOND DAY

8:30-9:30	**The Pulsed Fourier Experiment: Optimization and Quantitation** Sensitivity and resolution enhancement, use of T_1 criteria, Overhauser effect variability, gated decoupling requirements, digitization and data point considerations, chemical methods, sample preparation, sample size and optimization, operational opportunities and pitfalls.
9:30-10:00	Break
10:00-11:00	**Problem Session #3** Further spectral interpretation involving coupling data and off-resonance spectra. Structure determination. Exercises in proper choice of instrumental parameters for different types of samples.
11:00-12:00	**Applications of ^{13}C NMR: An Overview** Several examples of the use of ^{1}H and ^{13}C NMR data in solving structural problems, particularly with respect to the strategy involved and the use of different experiments for special purposes. Applications in the areas of homopolymers, copolymers, biomolecules and natural products.
12:00-1:00	Lunch
1:00-2:00	**Problem Session #4** Further practical problem-solving.
2:00-3:30	**Special Experiments: T_1, T_2, NOE and APT** Introduction to the mechanisms and measurements of spin-lattice and spin-spin relaxation. Illustration of typical considerations involving estimate of T_1 and T_2. Use of T_1 and T_2 as assignment criteria. Description of the nuclear Overhauser effect, its measurement and value in quantitation and detailing of molecular motion. Determination of numbers of protons per carbon using APT.
3:30-4:00	Break
4:00-5:00	**Problem Session #5 and Wrap-up** Further spectral interpretation and relaxation experiment interpretation. Questions and answers.

Workshop II
Advanced Techniques in NMR

Advanced Pulsed NMR
Two-Dimensional NMR
High-Resolution in Solids

The objective of this new Varian NMR Workshop is to familiarize users with some of the new concepts in NMR and to encourage their use as practical techniques for problem-solving.

These new concepts include *2-D NMR*, which, in conjunction with more powerful magnet systems, has stimulated the study of increasingly intricate structural, conformational, and dynamic problems.

Advanced Pulsed NMR techniques allow spectroscopists to overcome the former limitations of selectivity and sensitivity in order to explore applications that have been, until now, inaccessible.

Another new, promising analytical tool, *High-Resolution NMR in Solids*, which is now emerging from the research laboratories for practical use, will also be studied.

Dates and Locations

Dec. 10, 11	G.D. Searle Research Laboratories Chicago, Illinois
Jan. 28, 29	University of Houston Houston, Texas
May 20, 21	NASA Lewis Cleveland, Ohio

FIRST DAY

8:00-9:00	Registration
9:00-10:00	**New Methods of Pulsed Excitation** Requirements of modern pulse programmer for new pulse sequences. Understanding of pulse sequence language and terminology. Spin-echo fundamentals and polarization transfer. Phase alteration and cycling effects. Use of composite (sandwich) pulses. Selective excitation. Multiple quantum excitation.
10:00-10:30	Break
10:30-12:00	**Multinuclear NMR** Consideration of nuclear properties, such as spin, T_1, T_2, NOE, regarding observed sensitivity, resolution and potential applications. Hardware considerations. Use of quadrapole echo. Practical guidelines. Examples are application of ^{15}N, ^{2}H, ^{29}Si and other nuclei.
12:00-1:00	Lunch
1:00-2:00	**NMR of Solids: Fundamentals** Fundamental approaches to solids. Magic-angle spinning, cross-polarization and dipolar decoupling. Multiple-phase techniques. Relaxation effects. Quantitation and methods of selective emphasis based on relaxation. Dynamics in the solid state. Cross-polarization vs. gated decoupling—when is one preferable? Carbon discrimination. Sideband suppression by convolution and/or echo methods. Effect of ^{14}N on solids spectra. Field dependence considerations. Sensitivity vs. sidebands—what is the optimum operating field? Resolution enhancement techniques. Contact time dependence of intensity.
2:00-2:30	Break
2:30-3:30	**NMR of Solids: Applications** Examples of the use of CP/MAS techniques in the areas of polymers, fossil fuels, pharmaceuticals, crystal morphology. Other nuclei applications: ^{15}N, ^{29}Si, ^{27}Al.
3:30-4:00	**NMR of Solids: Discussion and Questions**
4:00-5:00	**Applications of INEPT** Use of INEPT in sensitivity enhancement, determination of degree of protonation, elimination of solvent resonances, determination of heteronuclear couplings with high sensitivity and determination of proton T_1s. Other nuclei enhancement with examples of ^{15}N and ^{29}Si. Routine utilization techniques.

SECOND DAY

8:30-9:30	**Two-Dimensional NMR Spectroscopy: Fundamentals** Principles and methods. Hardware and software requirements. Data system considerations. Output devices. Pulse sequences. J-resolved and correlation methods for homonuclear and heteronuclear systems. Use in structure determination and as a substitute for homonuclear spin decoupling. Use of heteronuclear correlation for unraveling a proton spectrum. Techniques for minimizing time requirements for 2-D studies. How to do "routine" 2-D "real-life" problems.
9:30-10:00	**Optimal Data Handling** Efficient use of weighing functions and data points in FT NMR. Zero-filling, reverse transform, optimal sensitivity- and resolution-enhancement, convolution-difference, apodization methods.
10:00-10:30	Break
10:30-11:00	**High Dynamic Range Techniques** Fundamental requirements for very high dynamic range (>100,000). Instrumental limitations and data system limitations. The "word-size problem." Integer and floating-point mathematics considerations. Example in ^{13}C NMR of high polymers and ^{1}H NMR in H_2O solutions. How to handle mixed solvent or high concentration situations.
11:00-12:00	**Two-Dimensional NMR Spectroscopy: Applications** Examples of the use of 2-D for solving structural problems, assignment techniques, and correlating chemical shifts. Use of 2-D in polypeptide analysis, pharmaceuticals and other areas.
12:00-1:00	Lunch
1:00-2:00	**^{13}C Satellite COSMIC Analysis and ^{13}C-^{13}C Double Quantum 2-D** Use of ^{13}C satellite excitation and data analysis. Automatic spectral analysis using COSMIC to assign bonds, J(CC) values and isotope shifts. Use of the multiple-quantum 2-D analog of the experiment to generate unequivocal atom connectivities. Practical considerations.
2:00-2:30	**Optimizing the T_1 Experiment** Methods of pulse excitation and analysis. Homogeneity of ^{1}H rf fields. Sample size considerations. Use of composite pulses. Data analysis methods. Caveats in the use of T_1 data.
2:30-3:00	Break
3:00-4:00	**Biological Applications and FT NMR Methods** *Working In Aqueous Solutions:* Solvent suppression, solvent elimination, via selective excitation; NOE and transient NOE; 2-D methods. *Heteronuclear Decoupling:* Sample heating in salt solutions, bi-level techniques, modulation effectiveness, tradeoffs in preserving sample integrity vs. performance. *Isotopic Substitution Strategies:* Genetic engineering techniques, living cell cultures. *In Vivo Studies:* Topical NMR, whole body imaging.
4:00-5:00	**Invited Speaker** A guest lecturer will speak on a modern application of NMR techniques in an area of current research.

278-37

FACULTÉ DES SCIENCES
Université de Nantes - U E R DE CHIMIE

CHIMIE ORGANIQUE PHYSIQUE
E.R.A. nº 315 - C.N.R.S.

NANTES, October 12, 1981

Professor B.L. SHAPIRO
Department of Chemistry
Texas A & M University
College Station

TX 77843 U.S.A.

title : FMR and GERM meeting

Dear Barry,

We should like to announce the organization of a joint meeting of the Fachgruppe Magnetische Resonanz der GDCh and the Groupe d'Etudes en Résonance Magnétique (GERM) in 1982. It will be held from March 10 to March 12, in the Ancienne Abbaye des Prémontrés, in PONT-à-MOUSSON, France.

Twelve invited lectures and two poster sessions will cover applications of NMR in France and Germany. Lectures will be in English, but posters can be presented in English, French or German.

For further details contact GDCh, Postfach 900440, 6000 Frankfurt 90, Germany or Dr. P. SERVOZ-GAVIN, C.E.N.G., 85 X, 38041 GRENOBLE Cedex, France.

Yours sincerely.

Gérard J. MARTIN

Téléphone (40) 74.50.70 - 2, rue de la Houssinière - 44072 NANTES-CEDEX (FRANCE)

Dr. W. Bremser c/o
BASF Aktiengesellschaft

BASF

BASF Aktiengesellschaft · D-6700 Ludwigshafen

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

U S A

22.10.1981 WBr/CK
D-ZHV - B 9
Tel. 0621/60-28401

NMR IN FRANCE AND GERMANY

Dear Barry,

we herewith announce to all interested readers a joint conference of the Groupe d'Etude de Resonance Magnétique and the Fachgruppe Magnetische Resonanz Spektroskopie, which will serve to enhance scientific cooperation across the borders and may show the broad spectrum of applications of nmr in these two countries. In addition the seclusion of a beautiful old monastry and the opulent French cuisine should strengthen the personal contacts among devoted scientists. The meeting will take place in the Centre Culturel des Prémontrés, Pont-à- Mousson, France (situated between Metz and Nancy) from the evening of march 9 till noon of march 12, 1982. The conference language is English, however, posters can be presented in English, French or German. Plenary lectures will be given by Binsch, Cavagna, Courtieu, Delpuech, Gagnaire, Gueron, Köhler, Mannschreck, Nechstein, Pouzard, Spieß, and Ziessow. Further details can be obtained from Prof. Servoz-Gavin, Grenoble, or the German Chemical Society, or myself.

Best regards,

Wolfgang

W. Bremser

Telefon (06 21) 60-1 (Vermittlung)
Telex 4 64 811 basf d (Zentrale)
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6700 Ludwigshafen, Girokonto 545 07300
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Aufsichtsratsvorsitzender: Bernhard Timm
Vorstand: Matthias Seefelder, Vorsitzender;
Hans Moell, stellv. Vorsitzender;
Hans Albers; Ernst Denzel;
Erich Henkel; Wolfgang Jentzsch;
Horst Pommer; Karl August Wetjen;
Herbert Willersinn; Hans Joachim Witt
Registergericht: Amtsgericht Ludwigshafen,
Eintragungsnummer: HRB 2000

Lg.-Nr 9030506 59776 200M 380

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, october 23, 1981.

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

Title: Help! I need a Tape!

Dear Prof. Shapiro:

May I please ask you to publish this request for help in a rather silly problem of mine? Thank you!

For some years we have been using in this laboratory a Nicolet NMR-812 minicomputer, also called 1080 System,and only last year we have been able to get funds to complete our system with a Diablo NIC-294 Disk (low density).

After month and month of "red tape" we received (at last!) the disks (two of them) together with a new teletype and two big programs:one for the automated measurement of T_1 and the other for Correlation Spectroscopy.

Unfortunately the Nicolet people forgot that,to be able to use the disk one should be able to inicialize them and the computer must be tought to command the disks.For this purpose a rather small, though special tape, is needed.It is called DEMON - II .

At nowadays rate of technology's development there seems there is today nobody at Nicolet who remembers about this tape.Of course I do not blame them.They are so busy with megabyte buble memories and 3-D Colour F.T. to bother about such small things like a disk software! At least, at this conclusion I reached after several letters, telexes and phone calls.

May some reader of this letter, and owner of a NIC-294 disk system,commiserate with the undersigned and bother to make a duplicate tape of the DEMON - II and send it to the adress given below? If,beside this,he could find some time to make also duplicates of the IMP (Integrated Monitor Package) that is:Disk Editor, Disk Command Interpreter,Disk Assembler,Disk Loader,Disk Move Program and Disk I/O Supervisor,it would be extremely appreciated.But,please! Do not take too much trouble.I would be satisfied with the DEMON - II tape.At least I would be able to use the disks!

Thanking all of you,readers, for your attention,I remain very truly yours.

V. Kowalewski

Dr. V.J.Kowalewski.
Facultad de Ciencias Exactas.
(1428) Buenos Aires.
Argentina.

STATE UNIVERSITY OF NEW YORK AT BINGHAMTON

Binghamton, New York 13901

Department of Chemistry
Telephone (607) 798-2298

October 28, 1981

c/o Kay Struzick
TA+MU NMR Newsletter
B. Shapiro, Editor
Department of Chemistry
Texas A&M University
College Station, Texas 77843

VARIAN HA-100D NMR SPECTROMETER AVAILABLE

Twelve year old instrument is in excellent working condition. Has N.M.R. specialties heteronuclear capability (D^2, C^{13}, N^{15}) with decoupling and Varian variable temperature probe. Terms negotiable for mutual convenience. Contact David C. Doetschman (607)798-2298.

David C. Doetschman

David C. Doetschman

Department of Chemistry
State University of New York at Stony Brook
Long Island, NY 11794
telephone: (516) 246-5050

StonyBrook

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

POST-DOCTORAL POSITIONS AVAILABLE

Dear Barry:

Two or three post-doctoral positions will be available in my laboratory, beginning December 1, 1981 for work on advanced NMR zeugmatographic imaging techniques. Candidates should have experience with NMR hardware, such as the design and construction of probes and other components, and with the underlying principles. Knowledge of digital devices and computer programming would also be very useful. Those interested should write to me as soon as possible and arrange for at least two letters of recommendation to be sent at the same time. We are an Equal Opportunity/Affirmative Action Employer.

Yours truly,

Paul

Paul C. Lauterbur
Professor of Chemistry and
Research Professor of Radiology

278-41

THE JOHNS HOPKINS UNIVERSITY

SCHOOL OF MEDICINE

725 N. WOLFE STREET · BALTIMORE, MARYLAND 21205

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY

TELEPHONE 955-5000
AREA CODE 301

October 5, 1981

Used Varian Equipment Available

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

Dear Barry:

Sorry to be slow in responding -- my excuse is the recent move of my laboratory to the Johns Hopkins Medical School. All went well during the move, with the important exception that our Varian E-4 EPR spectrometer console was dropped in the moving van -- fortunately it was insured and has been repaired. The moral of the story is to fully insure everything during a move for replacement cost.

As a result of the move we have inherited some Varian NMR equipment which we probably will not use and can offer for sale. These components are:

1. Model V3506 12" Magnet Flux Stabilizer
2. Model V3507 Slow Sweep Unit for 12" magnet
3. Model 4365 Field Homogeneity Control Unit for 12" magnet
4. Model 920091 Spinner Speed Tachometer and Lock Level Meter
5. Model V4367 Field Homogeneity Controller for 15" magnet.

Any offer will be considered.

Yours sincerely,

Al

Al Mildvan

Joe

Joe Schaffer

Oxford Research Systems Limited
Ferry Hinksey Road, Oxford OX2 0DT, England
Telephone 0865 43294 Telex 83413

OXFORD RESEARCH SYSTEMS

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

Date 21 October 1981

Our Ref. DS/SIE

Your Ref.

RE: NMR SPECTROSCOPISTS REQUIRED

Dear Barry,

Oxford Research Systems is a company within the Oxford Instruments Group who manufacture Topical Magnetic Resonance spectrometers. These spectrometers are nulti-nucleus FT NMR spectrometers designed for biochemical and medical research, which can obtain high resolution spectra from localised parts of the sample. The spectrometers use ultra wire-bore superconducting magnets which can accommodate animals or people.

We are in the process of expanding our application/development capabilities both here at our production facilities in Oxford and also in the USA.

May I use your Newsletter to encourage anyone interested in joining us to contact me at the above address?

Best Wishes.

Yours sincerely,

DR. DEREK SHAW
Marketing Director

278-43

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

October 26, 1981

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

Dear Barry:

We would like to bring to the attention of readers of the NMR newsletter, the availability of National Research Council-National Bureau of Standards Post-doctoral Research Associateships at the National Bureau of Standards. These associateships are competitive, depending on evaluation of qualifications and a research proposal submitted by the applicant.

A booklet that describes application procedures, research opportunities, and research advisers may be obtained by writing or calling Dr. Robb Thomson, National Bureau of Standards, Washington, DC 20234, Telephone 301/921-2103, or one of the undersigned people.

Final applications must be postmarked not later than January 15, 1982, and received in the Associateship Office not later than January 25, 1982. The Associateship Office will notify applicants of the disposition of their applications in March 1982. Appointments usually begin after September 1, but may begin during the period April 1, 1982 to February 1, 1983. The NRC-NBS Associateships are for U.S. citizens only; the current salary is $24,736 for engineers and metallurgists, and $23,566 for others; and costs of travel and transportation of household effects within the U.S. are paid on appointment.

The NMR instrumentation available at NBS includes a Bruker WM-400 with four fixed frequency probes and one broad-band probe, and a Bruker CXP-200 wide-bore with a fluorine probe, two broad-band probes, and a carbon-13 CP-MAS probe. The people involved and their principal interests and telephone numbers are listed below.

Early contact of interested applicants with a potential research adviser is advisable so that the adviser may assist with the writing of the research proposal.

Yours sincerely,

Bruce

Bruce Coxon
Organic NMR
301/921-2867

Rolf

Rolf B. Johannesen
Inorganic NMR
301/921-3419

Dave

David L. Vanderhart
Polymer NMR, principally solids
301/921-3344

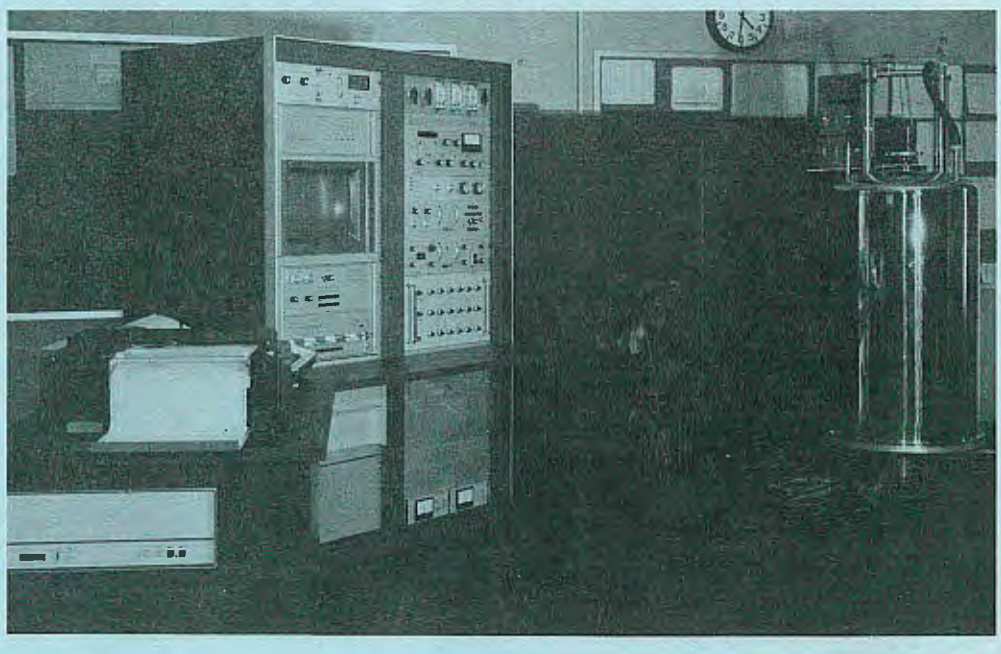
Nicolet Supercon FT-NMR Spectrometers

Uncompromising performance, limitless adaptability.

Our spectrometer systems have been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, they represent a completely modular approach to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding Nicolet features include these:

- **A full range of superconducting magnets from 4.7T to 11.7T (200MHz to 500MHz proton frequency range), in both wide-bore and narrow-bore configurations.**
- **Multinuclear observation with a wide variety of fixed-tune and broadband probes.**
- **Simultaneous acquisition, processing, and plotting for greater sample throughput.**
- **Simplified control of spectrometer operations and parameters by using easy keyboard commands.**



- **Advanced Nicolet 1180E Data System with 128K/20-bit memory, 256-step pulse programmer, and the most comprehensive FT-NMR software package available.**
- **Extended dynamic range performance with 40-bit acquisition and floating-point processing.**
- **An expandable pulse-sequence library, including T_1, T_2, Redfield, INEPT, homo- and hetero- 2D-FT, etc.**
- **Convenient computer control of field shimming, observe and decoupling frequencies, sample temperature, and probe-tuning.**
- **Precise digital plotting with full annotation of spectral parameters and flexibility of hardcopy format.**

The versatile Nicolet spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

Some of these are:

- **High resolution studies of solids with Waugh-Pines cross-polarization and magic-angle spinning.**
- **High sensitivity wide-bore ^{13}C studies of high molecular weight polymers.**
- **Automated T_1 and T_2 measurements.**
- **Chemical dynamics studies.**
- **Temperature-programmed experiments.**
- **^{31}P experiments on living organs.**

NICOLET MAGNETICS CORPORATION
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THE SOLID LEADER in NMR

With Multi-Nuclear/ Multi-Field Solid State Probes

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  ^{31}P (~80 MHz)
  ^{29}Si (~40 MHz)
  with one probe!
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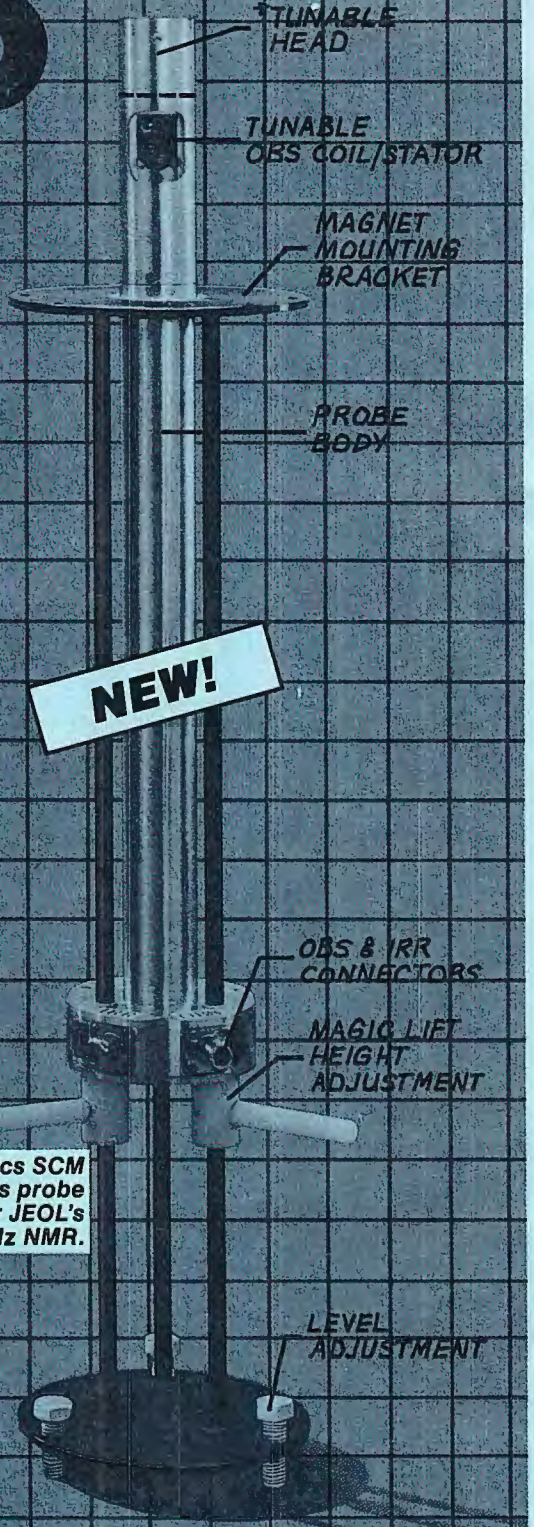
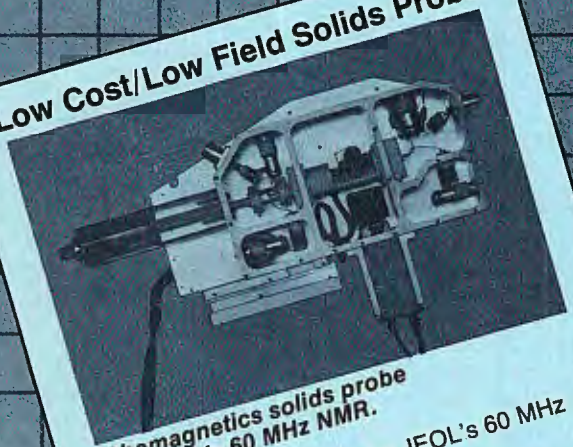


NEW!

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

Low Cost/Low Field Solids Probe



Chemagnetics solids probe for JEOL's 60 MHz NMR.

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- Best results for coal, shale oil & rigid polymers.
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- Probes available for observation of ^{13}C, ^{31}P and ^{29}Si!

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