

TEXAS A&M UNIVERSITY

NMR

NEWSLETTER

No. 342

March 1987

Samulski, E.T. and Janik, B. Dipolar Couplings in Hexane	2	Fleming, W.W. Mechanical Elimination of Spinning Sidebands, Etc.	24
Smith, W.B. Book Reviews.	4	van den Berg, E.M.M., van der Bent, A., Lefebvre, F., Erkelens, C., and Lugtenburg, J. A ^{13}C NMR Study of 9-Demethylretinal.	26
Glickson, J.D. Positions Available	7	Meynial, D., Arnal, M., Renou, J.P., and Bourdonneau, M. Heteronuclear $^{15}\text{N}/\text{H}$ Spin Echo NMR of Aqueous Leucine	28
Inglefield, P.T. and Cain, E.J. Dynamics of Sorbed $^{13}\text{CO}_2$ in Polymers.	8	Brisson, J.-R. and Bundle, D. PASCAL Program for CHORTLE Analysis	32
Jardetzky, O. Position Available	9	Wollenberg, K.F. Chiral Methyl Dithiophosphate Study Via ^{31}P NMR	34
Griffey, R.H., Brown, M.S., and Griffey, B.V. Deuterium T_1 Measurements in Imaging.	10	Canet, D., Brondeau, J., and Boudot, D. Quantitative Determination of Carbon-13 Isotopomers in Non-Uniformly Enriched Species by Polarization Transfer Experiments.	38
Roberts, J.D. Opportunity for NMR Research Fellowship in Lanzhou, China	12	Hunter, Jr., W.W. Position Available	40
Harris, R.K. and Nesbitt, G.J. Sodium-23 NMR in Solids	14	Addleman, B. Equipment Available	40
Suits, B.H. Circuit Design for a GPIB Interface Bus in a Home-Built NMR Spectrometer.	16	Smith, M.A.R. Position Available	41
Poupko, R. Deuterium Quadrupole Echo Spectra of Dynamic Systems	18	Cholli, A.L. Variable Temperature Studies of Peptides.	42
Cowburn, D. Easily Inspected and Repaired Probes.	20	Tschudin, R., Sklenár, V., and Bax, A. Coherence or Incoherence?	43
Hall, L.D. Non-Medical Imaging at UBC; Progress and Postdoctoral Fellowships at Cambridge.	23		

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AUTHOR INDEX ----- TAMU NMR NEWSLETTER, NO. 342, MARCH 1987

Addleman, B.	40	Hall, L.D.	23
Arnal, M.	28	Harris, R.K.	14
Bax, A.	43	Hunter, Jr., W.W.	40
Bent, A. van der	26	Inglefield, P.T.	8
Berg, E.M.M. van den	26	Janik, B.	2
Boudot, D.	38	Jardetzky, O.	9
Bourdonneau, M.	28	Lefebvre, F.	26
Brisson, J.-R.	32	Lugtenburg, J.	26
Brondeau, J.	38	Meynial, D.	28
Brown, M.S.	10	Nesbitt, G.J.	14
Bundle, D.	32	Poupko, R.	18
Cain, E.J.	8	Renou, J.P.	28
Canet, D.	38	Roberts, J.D.	12
Cholli, A.L.	42	Samulski, E.T.	2
Cowburn, D.	20	Sklenar, V.	43
Erkelens, C.	26	Smith, M.A.R.	41
Fleming, W.W.	24	Smith, W.B.	4
Glickson, J.D.	7	Suits, B.H.	16
Griffey, B.V.	10	Tschudin, R.	43
Griffey, R.H.	10	Wollenberg, K.F.	34

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Bruker Instruments, Inc. 29
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 Systems Group, NMR Instruments inside back cover
 JEOL outside back cover
 New Era Enterprises 15

Norell, Inc. 21
 Varian 5
 VCH Publishers, Inc. 37
 Wilmad Glass Company, Inc. inside front cover

FORTHCOMING NMR MEETINGS

8th International Meeting "NMR Spectroscopy" - July 5-10, 1987; University of Kent at Canterbury, England; For information, contact Dr. John F. Gibson, Royal Society of Chemistry, Burlington House, London W1V 0BN, England. See Newsletter #338, p. 55 for information and application.

29th Rocky Mountain Conference - August 2-6, 1987; Radisson Hotel, Denver, Colorado; Program Chair: Michael Reddy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002, (303) 236-3617; Nuclear Magnetic Resonance Symposium: James Haw, Department of Chemistry, Texas A&M University, College Station, Texas 77843, (409) 845-1966; Preliminary program and pre-registration information available from Sandy Grande, 8780 W. Quarto Circle, Littleton, Colorado 80213.

26th Eastern Analytical Symposium - September 13-18, 1987; New York Hilton Hotel, New York, New York; For information, contact J.P. Luongo, AT&T Bell Laboratories, Room 1A-352, Murray Hill, New Jersey 07974, (201) 846-1582.

FACSS XIV - October 4-9, 1987; Detroit, Michigan; For information, contact Dr. Stephen J. Swarin, Publicity Chairman, Analytical Chemistry Department, General Motors Research Labs, Warren, Michigan 48090-9055, 313-986-0806.

Fritz Haber International Workshop on Modern Techniques in Magnetic Resonance - December 13-17, 1987; Weizman Institute of Science, Rehovot, Israel; See page 7 of this Newsletter for additional information.

29th ENC (Experimental NMR Conference) - April 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Dr. Charles G. Wade, ENC Secretary, IBM Instruments, Inc., 40 West Brokaw Road, San Jose, California 95110, (408) 282-3641.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
 Should be Addressed to:

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

DEADLINE DATES

No. 344 (May) ----- 24 April 1987
 No. 345 (June) ----- 29 May 1987



Polymer Science Program
Institute of Materials Science
U-136
97 North Eagleville Road
Storrs, Connecticut 06268

January 29, 1987
(Received 4 February 1987)

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

"Dipolar Couplings in Hexane"

Dear Professor Shapiro:

We recently attempted quantitative simulations of deuterium quadrupolar splittings of alkane solutes dissolved in nematic solvents. Such simulations of flexible solutes require convolving a conformational ensemble average with an average over the orientation distribution of each conformer. The former average uses the classical rotational isomeric state (RIS) approximation while the latter involves a parameterized potential of mean torque. A by-product of these simulations is the direct dipole-dipole couplings between all pairs of spins. As there are many more dipolar couplings (relative to quadrupolar splittings) among both proximate and distant spins in the alkanes, these coupling should provide a more critical test of the RIS approximations and the potential of mean torque.

Recently Gochin et al. (1) reported the dipolar coupling constants D_{ij} of hexane in a nematic. In the table below we contrast these experimental D_{ij} with calculated D_{ij} derived our simulations. (2) It would appear from the agreement in the table that we are well on the way to a quantitative characterization of flexible chains in anisotropic environments.

Very truly yours,

E. T. Samulski

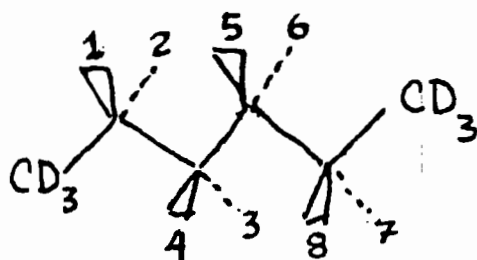
B.J.

B. Janik

ETS/yhc



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 ^1H Dipolar Coupling Constants for n-hexane- d_6

Expt (1)				Calculations (2)	
Sites	i	j	Dij (Hz)	Case A	Case B
E_1, E_1	1	2	3974	3854	4025
E_1, E_1	1	8	713	-901	-720
E_1, E_1	1	7	609	-660	-439
E_2, E_2	3	4	4487	4497	4478
E_2, E_2	3	6	190	-46	-559
E_2, E_2	3	5	43	32	-347
E_1, E_2	1	5	1616	-1483	-1168
E_1, E_2	1	6	1086	-980	-703
E_1, E_2	1	4	186	-40	197
E_1, E_2	1	3	81	8	136

ϵ for case A : 0.006495 see ref 2.
 ϵ for case B : 0.9221

References:

1. M. Gochin, K. V. Schenker, H. Zimmermann, and A. Pines
J. Ame. Chem. Soc. 1986, 6813-6814
2. B. Janik, E. T. Samulski and H. Toriumi
J. Phys. Chem. 1987 (March)

Texas A&M University NMR Newsletter - Book Reviews

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

"Applications of Dynamic NMR spectroscopy to Organic Chemistry"
(Methods of Stereochemical Analysis, Volume 4)

by
Michinori Oki

VCH Publishers, Inc., 303 N.W. 12th Ave., Deerfield Beach, Florida 33442
1985; 423 pages; \$74.00

Table of Contents: 1 - General Considerations; 2 - Restricted Rotations about a Partial Double Bond; 3 - Restricted Rotation about a Formal Double Bond; 4 - Racemization-Topomerization by Rotation about an sp^2 - sp^2 Bond; 5 - Restricted Rotation about a Trigonal to Tetrahedral Bond; 6 - Rotation about Tetrahedral to Tetrahedral Bonds; 7 - Conformational Changes in Ring Compounds; 8 - Stereodynamics of Amines and Imines; 9 - Application to Chemical Reactions.

This book is better described as a "what has been done" book rather than a "how to do it" book. The initial chapter gives a brief introduction to the techniques of dynamic NMR with a short consideration of the accuracy of data derived from such measurements. The remaining chapters are a survey of the literature of systems which have been studied. For the most part, there is no critical evaluation of the many works presented. If I wanted to know whether a system of interest had been studied, I'd start here.

"Applications of NMR Spectroscopy to Problems in Stereochemistry and Conformational Analysis"

(Methods of Stereochemical Analysis, Volume 6)

Edited by
Yoshito Takeuchi and Alan P. Marchand

VCH Publishers, Inc., 303 N.W. 12th Ave., Deerfield Beach, Florida 33442
1986; 221 pages, \$45.00

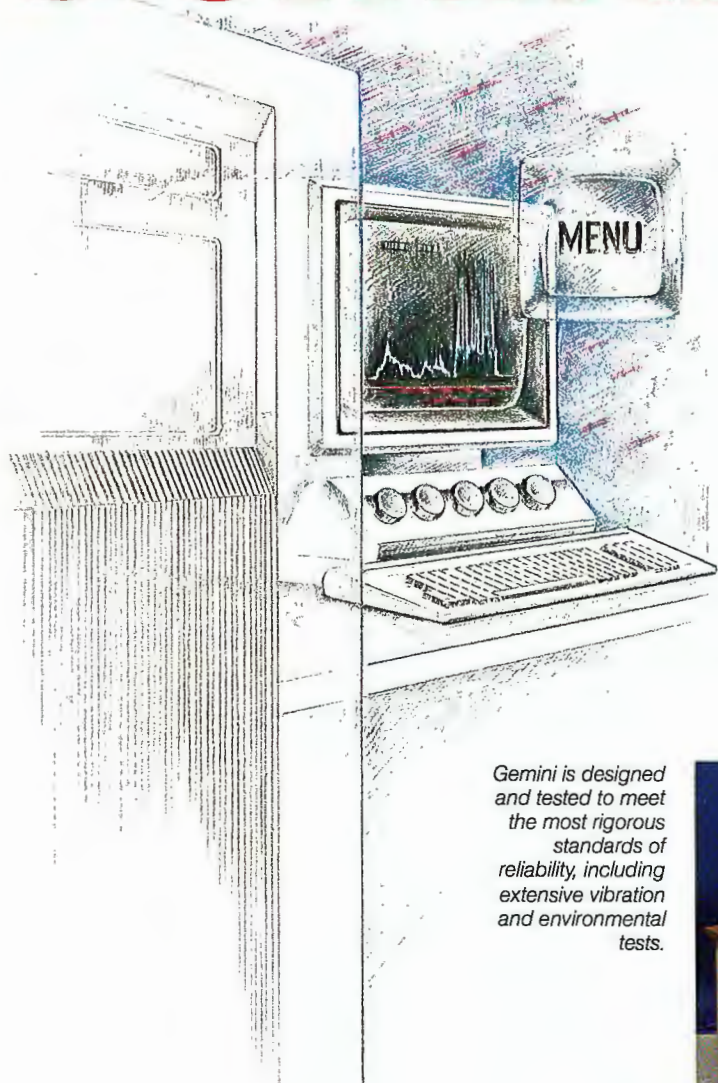
Table of Contents: 1 - Guest-Host Chemistry and Conformational Analysis, by Ian O. Sutherland; 2 - NMR Studies in Liquid Crystals: Determination of Solute Molecular Geometry, by P. Diehl and J. Jokisaari; 3 - C-13 Nuclear Spin Relaxation Study as an Aid to Analysis of Chain Dynamics and Conformation of Macromolecules, by Ryozi Kitamaru; 4 - Stereochemical Studies in the Solid State, by Takehiko Terao and Fumio Imashiro; 5 - Two-Dimensional NMR Techniques to Determine Molecular Skeleton and Partial Structures of Organic Substances, by Kuniaki Nagayama; 6 - Conformational Analysis of Peptides by Two-Dimensional NMR Spectroscopy, by Horst Kessler and Wolfgang Bermel.

As can be seen from the contents above, this is a series of "Special Topics" written by experts in the field. Each topic could as well have been the subject for an entire volume. However, the editors have done a good job in convincing the authors to present a short, pertinent introduction, followed by a series of examples of applications. They serve as good entres into the particular subject matter. Chapter 5 mainly provides introductory material for Chapter 6. The author of 5, however, uses a rather different approach than I've seen before in describing the magic of 2D NMR. This volume is a good value at \$45.00.

W.B.S.

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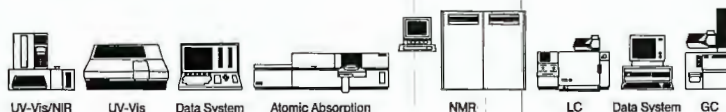
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In Australia 679 Springvale Road, Mulgrave, Victoria 3170 • In Japan 3rd Matsuda Bldg. 2-2-6 Ohkubo Shinjuku-ku, Tokyo 160
In Asia (South East) Mandarin Plaza, Rm 1018-20, Tower A, 14 Science Museum Rd., Tsimshatsui East, Kowloon, Hong Kong

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SCHOOL OF MEDICINE

Jerry D. Glickson, Ph.D.
Director, NMR Research
(301) 955-7490

Department of Radiology
NMR Research Laboratory
Traylor 311
720 Rutland Avenue
Baltimore, MD 21205

January 28, 1987

(Received 9 February 1987)

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

Dear Barry:

A number of postdoctoral positions are available in my laboratory and at the institutional NMR facility I direct. We are interested in people with expertise in NMR (previous experience in *in vivo* studies is not necessary but would be useful) and/or in physiology or metabolism.


Our laboratory has several programs currently underway, including investigations employing NMR spectroscopy and imaging methods for the study of tumor response to chemotherapy and radiation therapy. Plans are being implemented to reinstate a related program using NMR in the study of tumor response to hyperthermia. Ongoing projects also include investigations of the cardiotoxic effects of adriamycin, an anthracycline antineoplastic agent, as well as molecular studies of the conformation and dynamics of the glycopeptide antibiotic bleomycin. Available instrumentation includes spectrometer-imager systems of 1.5 T, 4.7 T, and 8.5 T. The institutional position calls for a fellow who will collaborate with various users at Hopkins in *in vivo* NMR spectroscopy, imaging, or microscopy (using the 4.7 T and 8.5 T instruments). Current user programs include studies of the heart, brain, pancreas, lung, liver, and kidney.

Please assist us by bringing this information to the attention of appropriate candidates. Interested individuals should send a C.V. and three references to:

Jerry D. Glickson, Ph.D.
The Johns Hopkins University School of Medicine
310 Traylor Building
Baltimore, Maryland 21205.

Best regards, and thank you for your kind consideration. Hope to see you at the Experimental NMR Conference or Society of Magnetic Resonance Meeting.

Sincerely yours,


Jerry D. Glickson, Ph.D.
Director of NMR Research



CLARK UNIVERSITY

950 Main Street Worcester Massachusetts 01610-1477

Department of Chemistry

Telephone (617) 793-7116

4 February 1987

(Received 9 February 1987)

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

RE: Dynamics of Sorbed $^{13}\text{CO}_2$ in Polymers

Dear Barry:

During the past year we have been involved in applying NMR to the problem of the state of sorbed gases in polymers. Much of our work has involved ^{13}C measurements of enriched $^{13}\text{CO}_2$ in glassy Bisphenol A Polycarbonate. We have made measurements as a function of both pressure and temperature at three different Larmor frequencies 22.6, 62.9 and 126 MHz using a NMR pressure-valve tube (Wilmad). At room temperature and five atmospheres CO_2 pressure we can clearly discern two chemical shifted peaks at 62.9 MHz corresponding to the free and sorbed CO_2 gas [figure 1]. Figure 2 shows experimental ^{13}C T_1 values for the sorbed gas peak as a function of temperature. From T_1 and NOE data three relaxation mechanisms can be identified. At high Larmor frequencies CSA is a major relaxation mechanism; at all frequencies spin rotation is important, and at 22.6 MHz intermolecular dipole-dipole relaxation between the labelled ^{13}C and the protons of the polymers contributes. Estimates of rotational and translational correlation times (3×10^{-11} s and 1.2×10^{-10} s respectively) are indicative of a very mobile CO_2 . However, the ^{13}C line width increases dramatically at low temperatures indicative of the presence of a slowly rotating species. The existence of more than one sorbed species present in rapid exchange has been postulated from other techniques.

The modification of the polymer motion due to the presence of CO_2 is also monitored by proton $T_{1\rho}$ measurements. The low temperature $T_{1\rho}$ minimum is shifted to higher temperature indicative of inhibition of the polymer motion and possible association between the CO_2 and a molecular site on the polymer repeat unit. It appears relaxation measurements can indeed be useful for probing the state of sorbed gases in such systems.

Regards,

Paul

Paul T. Inglefield

Edward J. Cain

Edward J. Cain

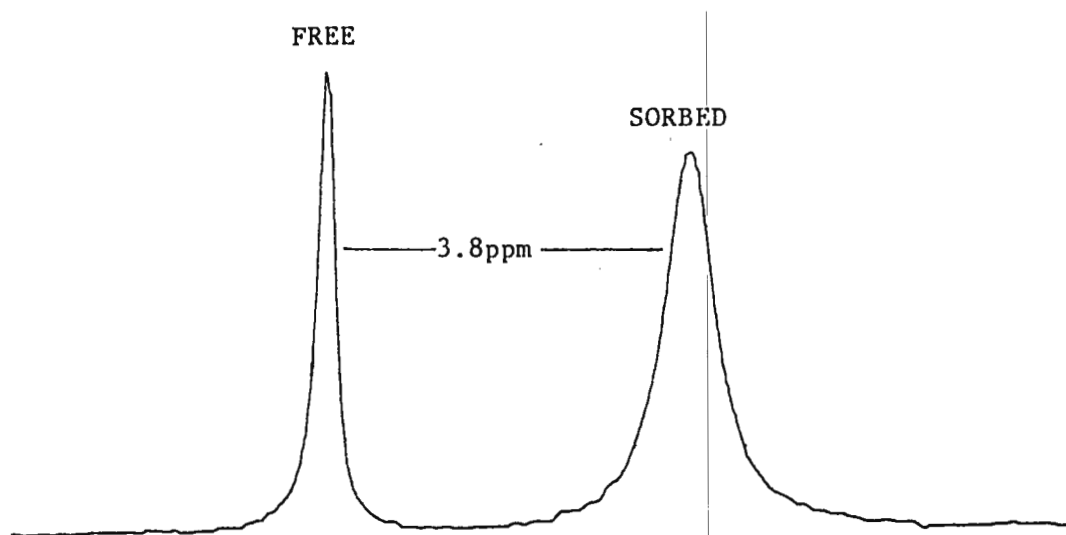


Figure 1: ^{13}C spectrum of $^{13}\text{CO}_2$ in BPAPC at 62.9 MHz.

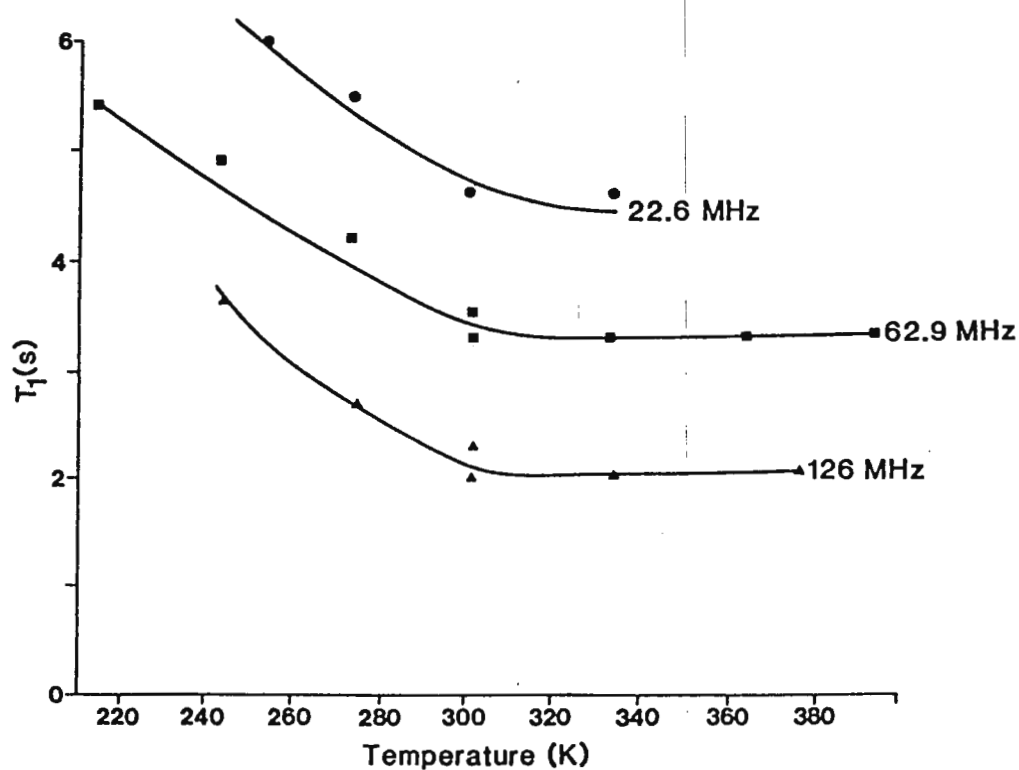


Figure 2: Experimental T_1 data for $^{13}\text{CO}_2$ sorbed in BPAPC polymer as a function of temperature.

NMR Physicist/Engineer with a good background in RF electronics and capable of probe design, to maintain and develop research on a newly installed in vivo spectrometer. Application and letters of reference should be sent to: Dr. Oleg Jardetzky, Stanford Magnetic Resonance Laboratory, Stanford University, Stanford, CA 94305-5055, U.S.A. Stanford University is an affirmative action, equal opportunity employer.



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(Received 2 March 1987)

Deuterium T₁ Measurements in Imaging

February 27, 1987

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

Dear Barry:

The utility of deuterons as a substitute for protons in magnetic resonance spectroscopy is well documented. Deuterons have served as negative labels in proton NOE experiments performed on macromolecules, since the difference in gyromagnetic moment makes deuteron-proton scalar couplings very small.(1) The T₁ relaxation of deuterons occurs through their quadrupolar moment, which is insensitive to the effects of neighboring protons, ie scalar and dipolar coupling.

We have been interested in determining the local correlation times of water in vivo. Such determinations are complicated by the intermolecular dipolar interactions between water, macromolecules, and other water molecules. The individual components are difficult to measure separately, which obscures the information on correlation times. The relaxation properties of deuterons described above make them an ideal probe, especially since deuterium can be incorporated at relatively high concentrations into rats by doping their drinking water with 10% deuterium oxide. We have calculated deuteron T₁ relaxation times using standard inversion recovery experiments on a 4.7 Tesla 33 cm bore chemical shift imaging system. A low-pass birdcage coil operating at 30.6 MHz provided high B₁ homogeneity, and a 180° pulse length of 150 usec.

A typical T₁ relaxation profile of a rat is shown below. The values of the T₁ relaxation time vary from 187 to 305 msec. Localized data was obtained using a 180° composite inversion pulse followed by a slice-selective 90° pulse over 10 mm portions of the rat. Four scans were summed for each of eight time points. The data was fit using the standard log-linear GE data reduction routine. No improvement in the fit was noted using a multiexponential algorithm.

Brown, Armitage, and Gore have developed a model for correlating the T₁ relaxation times of deuterons with those of protons, using solutions of polyethylene glycol to vary the effective correlation time of the water in the solution.(2) The value for the shortest deuteron T₁ described above yields a

correlation time of 9.05×10^{-12} sec, as calculated from Abragam. This value shows that even in the liver, the shortest T1 time is not very different from the values in the kidneys or intestines. We anticipate this model may have utility in cases where short proton T2 relaxation times preclude an accurate measurement of the T1 time, and in determining the presence or lack of local order among water molecules in vivo.

Sincerely,

Rich Griffey

Richard H. Griffey

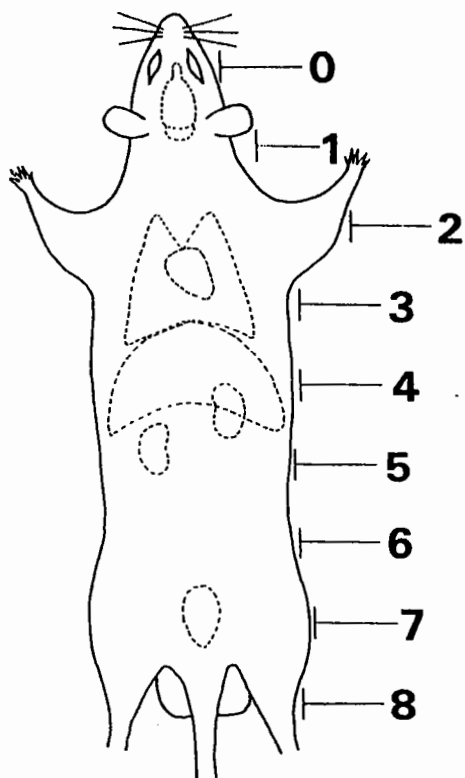
Mark S. Brown

Beatrice V. Griffey

Beatrice V. Griffey

(1) Sanchez, V.; Redfield, A.G.; Johnston, P.D.; Tropp, J.S.; Proc. Natl. Acad. Sci. USA (1980), 77:5659-5662.

(2) Brown, M.S.; Armitage, I.M.; Gore, J.C.; Magn. Reson. Med., submitted for publication.



<u>POSITION</u>	<u>AVERAGE DEUTERIUM T1 MEASUREMENTS</u>
0"	.224385 ± .013475
1"	.224885 ± .007841
2"	.218363 ± .008054
3"	.208936 ± .005832
4"	.187678 ± .007681
5"	.245148 ± .009246
6"	.304515 ± .0071392
7"	.209265 ± .0073972
8"	.220143 ± .0094375

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Division of Chemistry and Chemical Engineering
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John D. Roberts
Institute Professor of Chemistry

February 22, 1987

(Received 27 February 1987)

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

Opportunity for NMR Research Fellowship in Lanzhou, China

Dear Barry:

In the fall of 1985, I spent six weeks in China, four of them at Lanzhou University in Central China. Lanzhou is one of the top three or four best universities for teaching and research in organic chemistry in China. Thanks to a loan from the World Bank, they have a very well-equipped instrument center, with a lot of spectroscopic equipment not generally available in any but the most favored U.S. universities.

The purpose of this letter is to inform the readers of TAMUNMR that the Chemistry Department of the University would like to get one or more persons with a solid knowledge of NMR to come to Lanzhou for several months to carry on serious NMR research programs in their facilities. However, before I was willing to test the waters on this proposition, I wanted to have answers to the following questions (in boldface), for which Li Du, the Chairman of the Lanzhou Chemistry Department, has supplied excellent answers (in italics).

1. **Would the visitors work on their own problems or help your people with their problems? Would you expect the visitors to set up lines of research that your people would continue?**
2. **How much instrument time would be available, and what is the configuration of the high-field spectrometer as to frequencies, data and computer systems, accessories, and so on? What are the service arrangements to keep the machine going? Will visitors be able to run the instruments themselves or would your technicians run the spectra?**
3. **Would teaching be expected? At what level?**
4. **Would travel to Lanzhou be paid? What about families?**
5. **Would living expenses in Lanzhou be paid?**

1. *The visitors may work on their own problems with the hope that some of our people can join them. At the same time, they may act as consultants and help our people on our problems (as far as they can). If they can set up lines of research for us to continue, so much the better.*

2. *It is hard to say, at this moment, just how much instrument time will be available for visitors, but let me say 48 hours on the Bruker AM 400 each week at least, unless there are troubles with the machine. The visitors will be allowed to run the instruments themselves, or they may ask our technicians to run spectra for them.*

3. *Teaching on the graduate level will be appreciated. Instead, the visitors may give a series of talks on topics such as Fourier transform, ^{15}N NMR, 2D NMR, solid-state NMR or on some other research frontiers of NMR of their own choice. (About three hours per week.)*
4. *We will pay one-way airfare (to or from Lanzhou) for a visitor himself/herself, if he or she stays in Lanzhou for at least three months.*
5. *We will provide visitors and their families with accommodations in our campus guest house, free of charge.*
6. *A salary of 900-1200 chinese yen per month will be paid to a visitor.*

The NMR equipment at Lanzhou University includes:

1. *Bruker AM Spectrospin, with ^1H , ^{13}C , $\text{H}/^{13}\text{C}$ switchable, ^{19}F , ^{31}P , two broad-band probeheads covering most frequencies, X-nucleus decoupling unit, and ^1H flow-through probes. Variable temperature units covering -180 to $+200^\circ$. Aspect 300 computer, 24-bit word length, 256K main memory, array processor, 160 Mbyte hard disk. The software includes spin simulation, time sharing, and all programs necessary for 2-D NMR. There is also a CP-MAS unit for solid-state studies.*
2. *AC 80 Bruker-Spectrospin 80 MHz with probeheads as for the 400 MHz unit, variable temperature, 128 K memory, 24 Mbyte hard disk and also a probehead for ^1H CIDNP studies.*
3. *Varian FT-80A, for routine analysis.*
4. *Two JEOL 60 MHz spectrometers for the teaching laboratories.*

I can testify that Lanzhou and Lanzhou University have many fine features. The climate is dry, with a very short rainy season in the early fall. The elevation is a couple of thousand feet and the city is reasonably close to the Tibetan plateau which comes out fairly far into Central China. There are many wonderful trips possible to the Gobi Desert or the mountains. The University Guest House is relatively new, modern and, when we were there, the meals were excellent. Lanzhou is an industrial city with considerable air pollution, but the University is located rather far from the center of the industry, close to the banks of the Yellow River. Many of the staff speak good English and, although lectures really need to be interpreted, ordinary conversation is easy with most of the people with whom you have to deal. We made a quite a few trips, to Xi-ning, Dunhuang, Chinghi-ho, Urumuqui, Turpan and Kashgar. Travel in China is now rather easy and is inexpensive by US standards, if you are not on a tour. We took graduate students, post-docs, or staff from the University with us on trips (at our expense), they loved the experience and they helped with hotels and travel (not so easy to arrange yourself).

I would be glad to hear from anyone who is interested in this wonderful opportunity to see a part of China not usually on the heavily traveled tourist route, be able to participate and help the really wonderful people in Lanzhou. Even if I know you, please send a CV, publication list and a short statement of your research interests in NMR. I can supply a good deal of further information about the University, the city and getting around in the area.

With all good wishes,

Very truly yours,

Jack

University of Durham

Department of Chemistry

Science Laboratories, South Road, DURHAM,
GREAT BRITAIN, DH1 3LE
Telephone: Durham (0385) 64971

Professor of Chemistry:

Robin K. Harris

3rd February, 1987.

(Received 12 February 1987)

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

Dear Barry,

SODIUM-23 NMR IN SOLIDS

Help! the final catastrophe seems to have struck and we must have been cut off the TAMUNMR mailing list (since we failed to respond to the recent final ultimatum). We hope this letter will reinstate RKH on the right side of your ledger.

We have recently obtained some interesting ^{23}Na NMR spectra of solids using magic-angle spinning (MAS). These have proved to be more informative than we had expected, and we thought TAMUNMR readers might be interested in some of the basic methods. We use sodium borohydride as a test material because we can obtain spectra readily in both cross-polarization (CP) and single-pulse excitation (SPE) modes. Figure 1 shows typical spectra. The sodium is expected to be at sufficiently symmetrical sites that we observe the whole intensity and not just the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ central transition. Cross-polarization works well, with an optimum contact time of 5-10 ms. The enhancement over SPE is small (ca. 1.2).

Borax provides a good example where the quadrupole coupling constant (χ) is sufficiently large that only the central $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is observed, and this has the typical reduced powder pattern expected from MAS operation in the presence of second-order quadrupolar effects. In fact, two such patterns are observed (Figure 2), and this is consistent with the known crystal structure. The low-frequency band has the larger value of χ . Once more, cross-polarization is feasible, but the two environments respond somewhat differently to variation in the contact time. In other cases (for example, the mineral kenyaite) the CP experiment distinguishes even more clearly between different sodium sites.

We conclude that high-resolution ^{23}Na NMR of solids can be very useful, and that CP experiments can give additional or complementary information to SPE spectra.

Incidentally, we should tell you that although Geoff remains with this University he will be working in future on NMR projects of interest to the ICI Chemicals and Polymers Group.

Best wishes,

Yours sincerely,

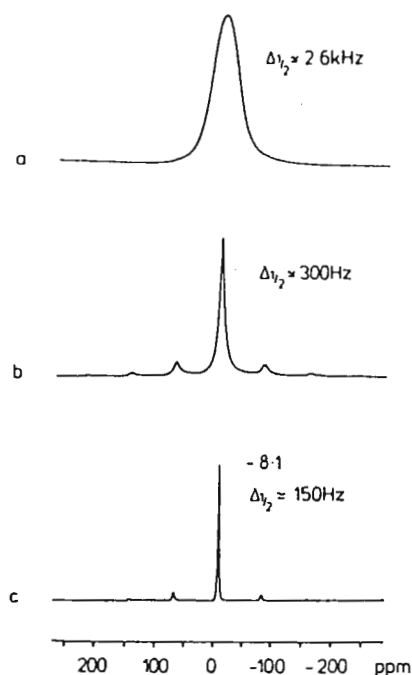


R.K. Harris



G.J. Nesbitt

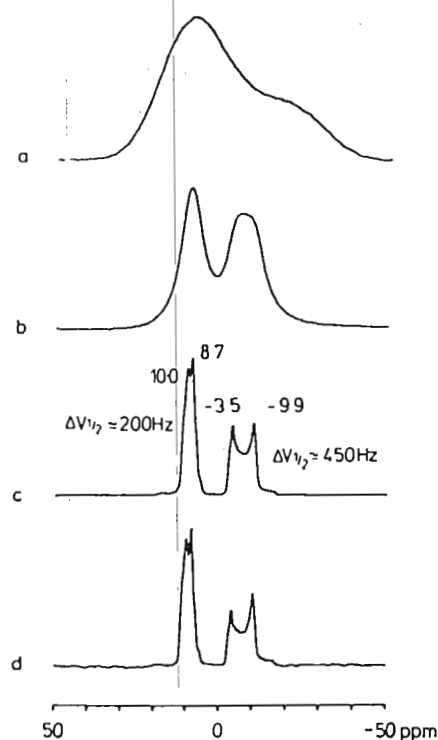
Figure 1



Sodium-23 spectra of Sodium Borohydride
8 transients, 30 s recycle, 4 μ s 90° pulse.

- a) static decoupled
- b) MAR (4.0 kHz) coupled
- c) MAR (4.0 kHz) decoupled

Figure 2



Sodium-23 spectra of Borax
16 transients, 30 s recycle, 2 μ s t_p

- a) static decoupled
- b) MAR (4.0 kHz) coupled
- c) MAR (4.0 kHz) decoupled
- d) CP MAR (4.0 kHz) 10 ms contact

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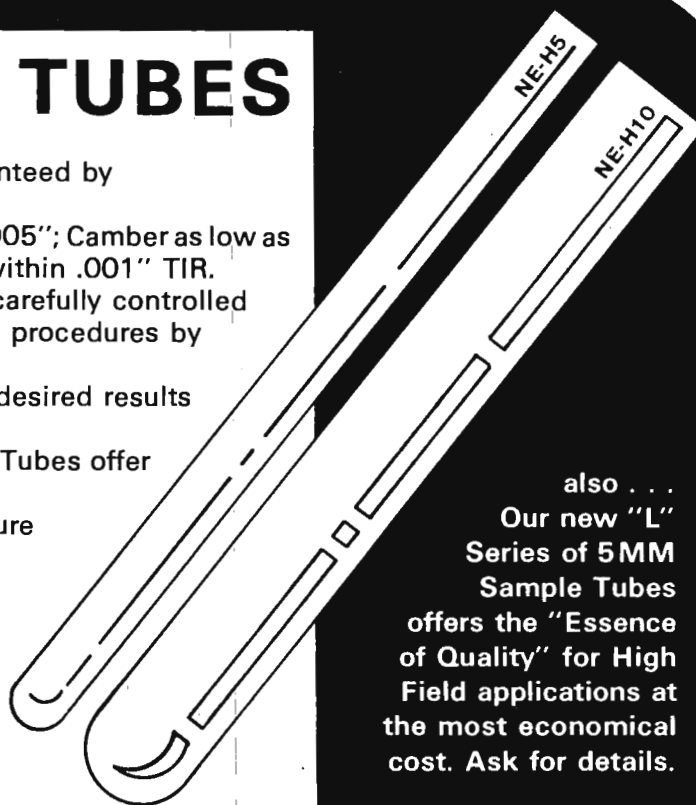
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College of Sciences and Arts
Department of Physics
906/487-2086

February 13, 1987

(Received 17 February 1987)

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

Circuit Design for a GPIB Interface
Bus in a Home-Built NMR Spectrometer.

Dear Professor Shapiro:

We are now constructing a versatile home built NMR spectrometer. In an attempt to have many pieces of commercial equipment easily incorporated into the system, we are using the IEEE-488 (GPIB) interface bus for most of the computer controlled equipment. Thus we have the flexibility to change any piece of the spectrometer, including the computer, with minimal down time. Several Commercial NMR machines also have connections for this bus as an option.

However, some NMR specific equipment is not compatible with the GPIB interface and some we want to build ourselves. We have designed a circuit which acts as a receiver for data on the GPIB bus. We will be using this circuit for homebuilt pulse programmers, gradient control systems and an oscilloscope display. A circuit diagram is attached.

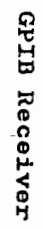
The circuit can be wire-wrapped or built on an etched board. We have had satisfactory experience with this circuit even at very high transfer rates (1 Byte/2 usecs) and have observed no interface with other devices on the system. IC4 can be used to limit the maximum transfer rate and should be adjusted for the particular application in mind.

The circuit is capable of responding to up to four GPIB address. The address is programmed using jumper wires J0-J5. Jumpers J0 and J1 determine a base address which is a multiple of 8. Jumpers J2 to J5 determine the offset from the base address. If fewer than four are needed, simply omit the corresponding jumper to IC 10.

Sincerely,

Bryan H. Suits

BHS/jw





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טלפון ישיר:

February 6, 1987

(Received 16 February 1987)

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

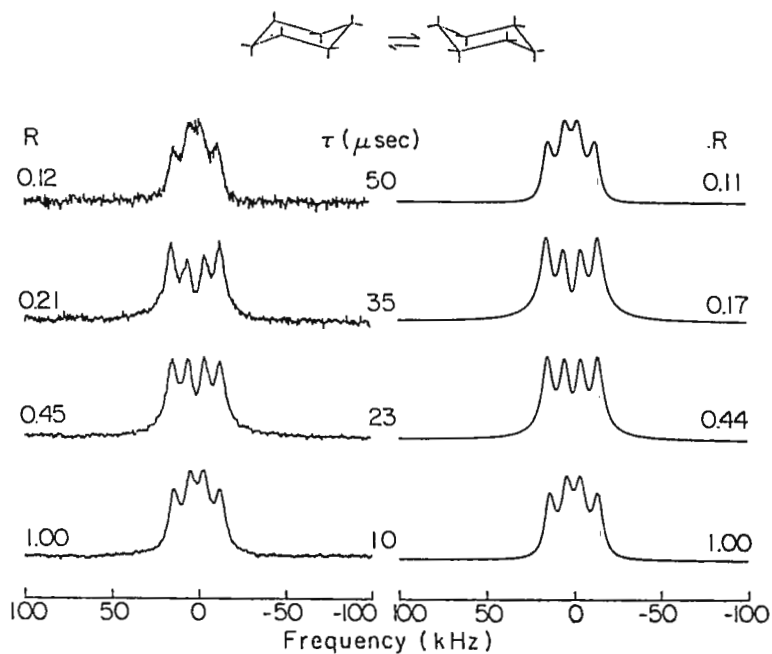
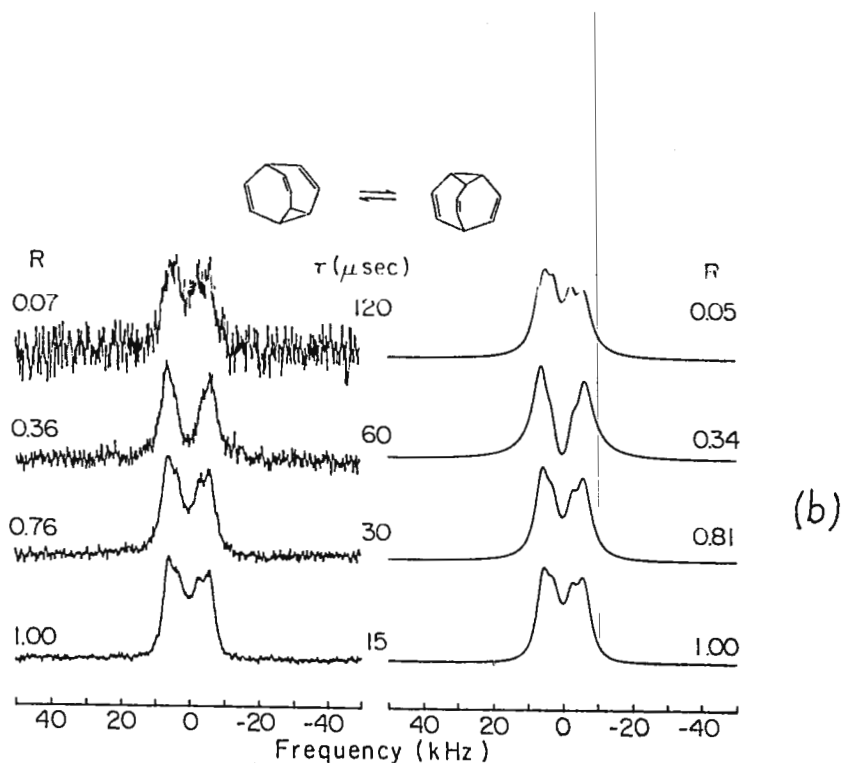
Deuterium Quadrupole Echo Spectra
of Dynamic Systems

Dear Professor Shapiro,

Deuterium quadrupole echo spectra in systems undergoing dynamic processes reflect not only the relaxation effects during the detection period, that is during the decay of the echo signal, but also the irreversible dynamic dephasing which takes place during the preparation period. Consequently the resulting spectra differ from those obtained by single pulse experiments. (H.W. Spiess and H. Sillescu, J.Magn.Reson. 42, 381 (1981); A. Vega, J.Polym.Prepr. (Am.Chem.Soc.Div.Polym.Chem.) 22, 282 (1981)). The effect, usually referred to as "echo distortion" may be useful for the characterization of dynamic processes and accurate determination of their kinetic parameters. Echo distortion may be quite conspicuous in powder samples where a large dispersity of the quadrupole interaction occurs. We have observed that considerable echo distortions take place also in (dynamic) liquid crystalline systems which are oriented by the magnetic field. Two such examples are shown in the figure. They correspond to cyclohexane- d_{12} and bullvalene- d_{10} dissolved in suitable liquid crystalline solvents. These solutes undergo dynamic processes which modulate the average quadrupole interaction of the various deuterons, resulting in characteristic dynamic lineshapes. In the figures are shown quadrupole echo spectra of the two systems at particular temperatures, but recorded with different time intervals between the 90° pulses. It may be seen that both the intensity of the spectra and their shape are strongly dependent on the time interval between the pulses in the range $10\mu s$ to $100\mu s$. The spectra, can readily be simulated as shown in the accompanying calculated spectra. The calculation take into account not only the quadrupole interaction but also differences in the chemical shifts of the various deuterium sites. More details on the experiments and on the method of simulation will soon appear in the Journal of Chemical Physics (R. Poupko, Z. Luz, A.J. Vega and H. Zimmermann, in press).

Sincerely yours,

R. Poupko



On the left are deuterium quadrupole echo of (a) 2.6 wt% solution of cyclohexane- d_{12} in Merck phase IV at -4°C , and (b) 4.5 wt% solution bullvalene in Merck ZLI2452 at 62°C . The time interval between pulses and the spectral relative intensities are indicated. On the right hand side are simulated spectra using the parameters, for cyclohexane: $k=2.18 \times 10^4 \text{ sec}^{-1}$, $\nu_{01}=4.96 \text{ kHz}$, $\nu_{02}=-14.9 \text{ kHz}$, $\delta_1=\delta_2=0$, $k=2.18 \times 10^4 \text{ sec}^{-1}$, $1/T_2=10^3 \text{ sec}^{-1}$; for bullvalene: $k=4.0 \times 10^4 \text{ sec}^{-1}$, $\nu_{01}=16.6 \text{ kHz}$, $\nu_{02}=-8.9 \text{ kHz}$, $\nu_{03}=6.04 \text{ kHz}$, $\nu_{04}=26.0 \text{ kHz}$, $\delta_1=-103 \text{ Hz}$, $\delta_2=\delta_3=103 \text{ Hz}$, $\delta_4=-116 \text{ Hz}$, $1/T_2=314 \text{ sec}^{-1}$.



THE ROCKEFELLER UNIVERSITY

1230 YORK AVENUE • NEW YORK, NEW YORK 10021-6399
5 February 1987

(Received 23 February 1987)

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

Dear Dr. Shapiro:

Easily inspected and repaired probes

One of the frustrations of repairing and modifying NMR probes is the disassembly and re-assembly, especially of the outer can. The older NT probes are normally glued together, and require special tools for disassembly. Inspection for physical damage or arcing can require a day's work. A simple and, to date, effective remedy is to replace the solid aluminum can with a can substantially cutout, as shown on the enclosed machinist's drawing. Probes modified this way can be immediately inspected for physical damage, or arcing. The turnable capacitors can be readily replaced or additional ceramic capacitors added. The can modification does not reduce sensitivity or degrade homogeneity of the two probes so modified.

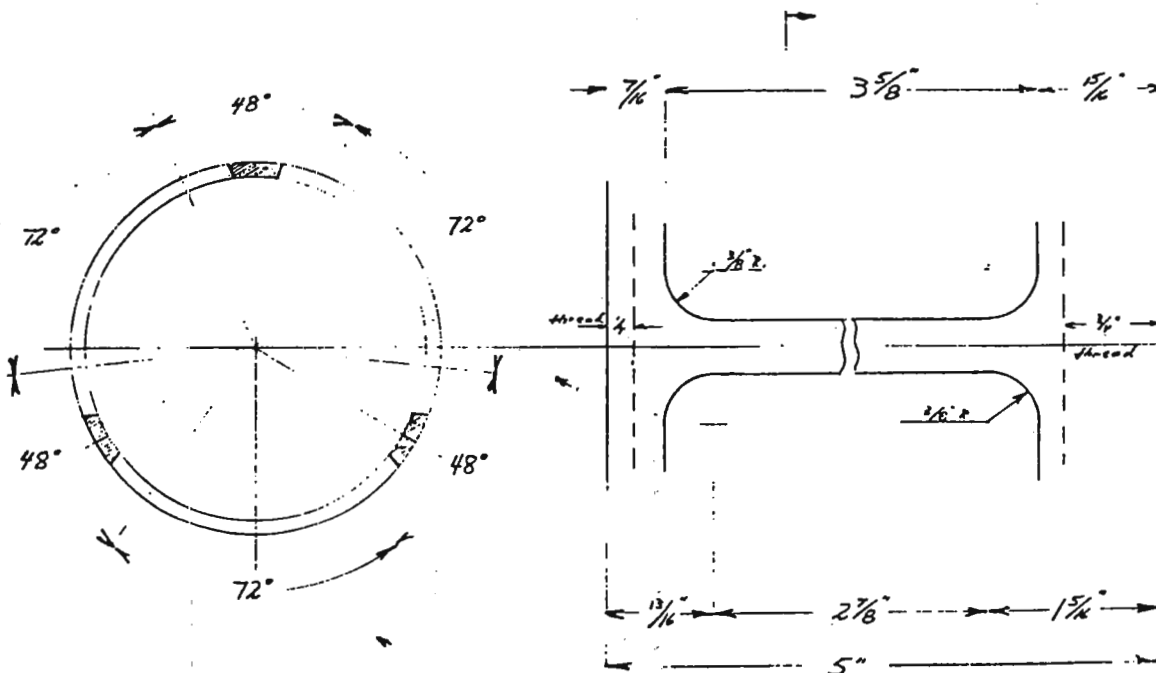
Similar modifications may not be so useful in other designs of probes. Nonetheless for spectroscopists interested in modified probes, it is well worth considering whether the total enclosure of the probe, as now generally practiced, is really the most convenient design.

Sincerely,

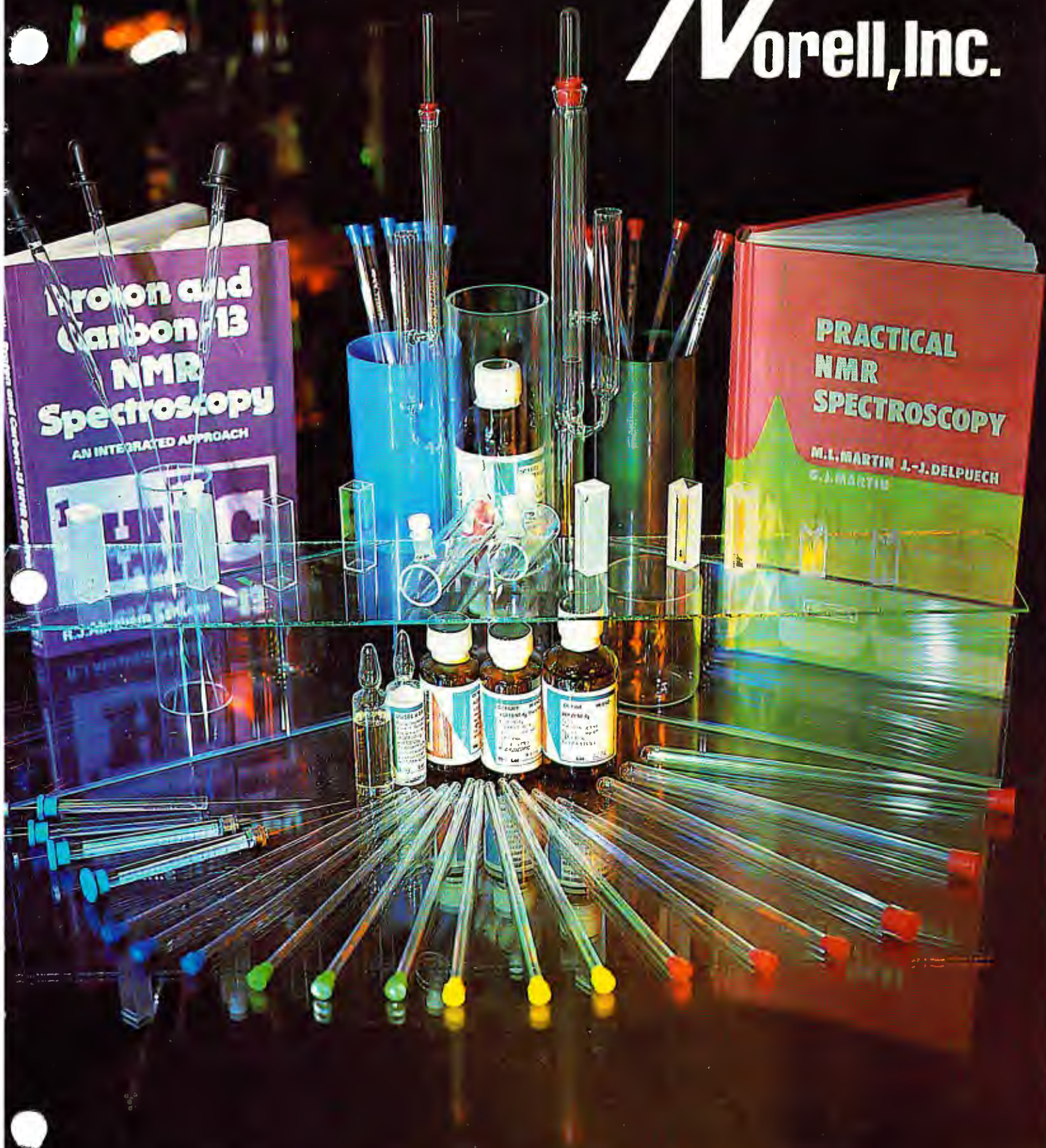
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Professor B L Shapiro
Editor, TAMU NMR Newsletter
Texas A and M University
Dept of Chemistry
College Station
Texas 77843-3255
USA

9th February 1987
(Received 16 February 1987)

Non-medical Imaging at UBC; Progress and Postdoctoral Fellowships at Cambridge

During the last year we have been continuing our work at UBC, and setting up here at Cambridge. The first building of my new Institute was completed last October, and the second will be ready this fall. We now have a 2 Tesla, 31cm bore system fully working; this is based on an Oxford Instruments Magnet and an Oxford Research Systems console. We hope to have two further imaging-spectrometers operational by this April, but more of them in a later letter. In addition, the new building for our 2 Tesla body scanner is on schedule, and the instrument should be running patients by this June.

I have funds for two Postdoctoral Fellows here, commencing immediately. Our needs are for people who have primary ability with, and interest in, NMR hardware and software, along with applications. The latter can be either clinical or non-clinical.

However, the main scientific purpose of this letter concerns the none-medical imaging programme at UBC, which is still going ahead rapidly. In particular, Dr Vasanthan Rajanayagam has been able to use our 1.9 Tesla system to demonstrate a wide array of studies of wood and wood products. Besides the expected findings, delineation of annual growth rings etc, we have been able to study impregnation by wood preservatives, and also kiln drying. Perhaps the most interesting findings however, involved the detection of pronounced zones surrounding areas infected by "rot"; we are not sure if these represent "pre-infection" or "defence". We also have some delightful results from oil and water mixtures in porous media, with sub-millimeter resolution.

Should anyone wish to have further information, please write to me at this address.

With all best wishes

Laurance

L D Hall



International Business Machines Corporation

February 9, 1987

(Received 13 February 1987)

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

William W. Fleming
Polymer Science and Technology, K91/801
IBM Almaden Research Center
650 Harry Road
San Jose, California 95120-6099
Tel. (408) 927-1611

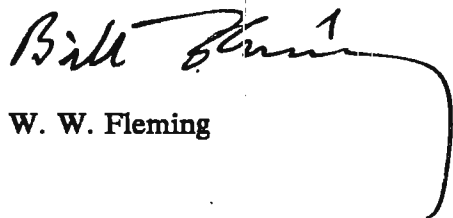
Subject: Mechanical elimination of spinning sidebands, etc.

Dr. Shapiro,

In the process of tuning probes on our 500 MHz spectrometer, I have found that a sweep generator is very useful as a complimentary tool. During recent checks of tuning using this sweeper, I noticed that the "peak" seen on the oscilloscope will vibrate when the sample tube is spinning and that the vibration can be significant with some probes and with larger tubes. This is likely due to a lack of concentricity of the spinning axis of the tube and the gravitational field (i.e. the tube is is not spinning concentric with the gravity vector) or the tube axis is not concentric with the coil axis. Because this wobbling will cause spinning sidebands, "spin-balancing" the tubes might be useful for long term homogeneity. Since the spinning and room temperature shim assemblies should be aligned so that the center of the RT shims is optimized to the superconducting solenoid, the spinning has to be optimized by orienting the solenoid perfectly concentric with the gravitational vector (neat trick!) or slightly tilting the entire magnet. The later can easily be done using leveling screws or wooden "shims" at the base of the magnet! I recall stories about using wooden shims to improve homogeneity a long time ago so I don't think this can be patented, and I have not actually done this myself. However, for those who are obsessive compulsive, it is worth thinking about!

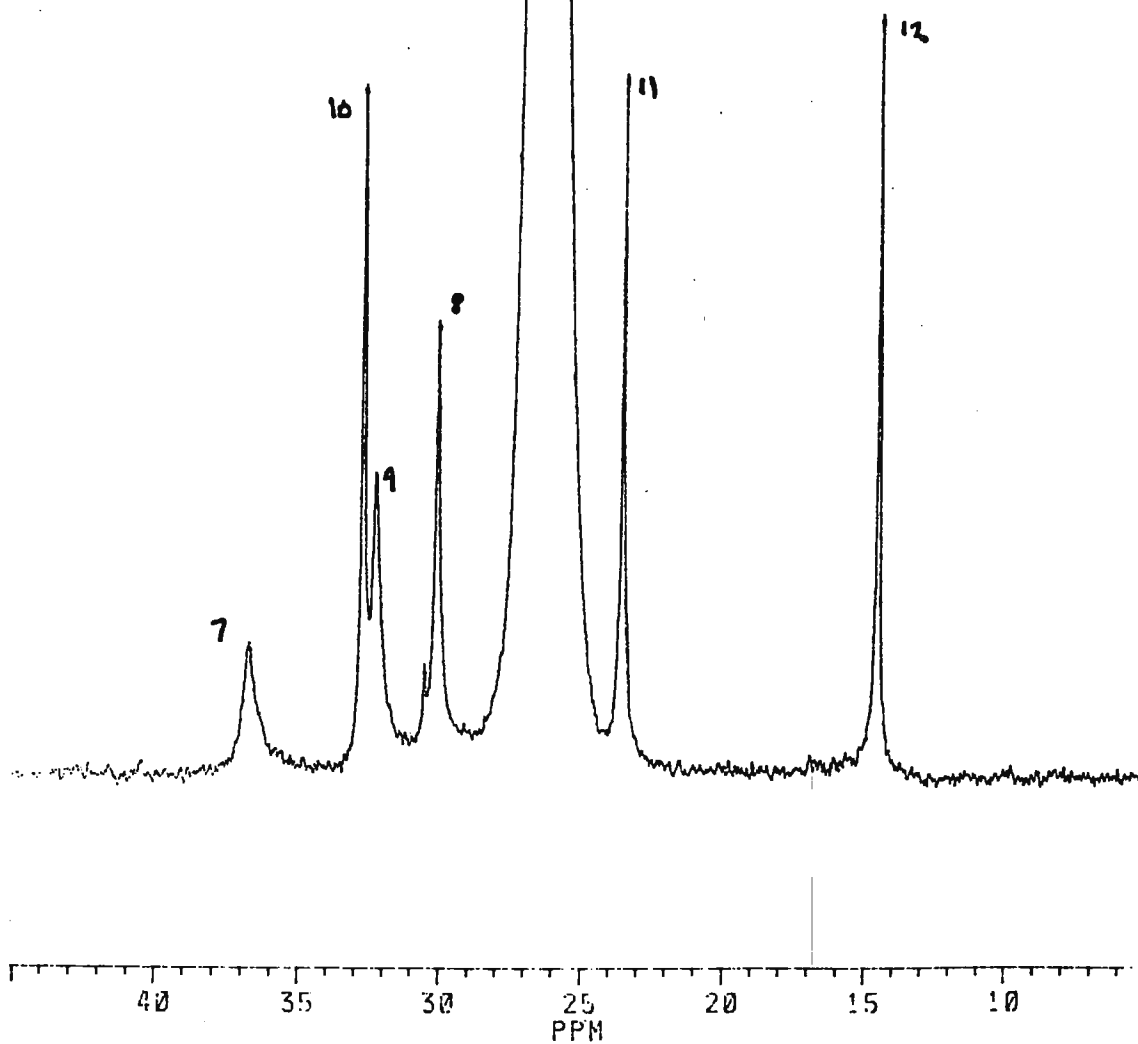
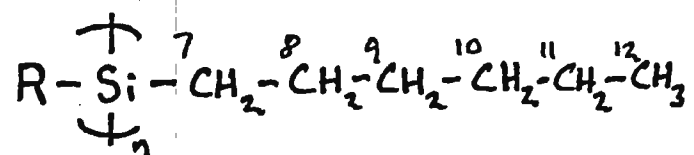
I have enclosed a ^{13}C spectrum at 125 MHz of poly(di-n-phenylhexylsilane) at room temperature. It is interesting that the line width changes as the carbon resonance gets closer to the silane backbone. Indeed, it is difficult to see the phenyl resonances even at elevated temperatures. The dynamics of short chains or end groups might be studied with such polymers since the rigid backbones make the molecules more like a "fixed wall" than conventional hydrocarbon polymers.

Sincerely,



W. W. Fleming

Poly(di-4-n-hexylphenylsilane)



(Received 16 February 1987)

Subject: A ^{13}C NMR study of 9-demethylretinal

Further NMR investigations on demethylretinals are in progress.

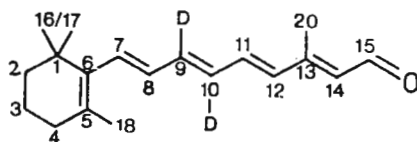


fig. 1

1. M. Muradin-Szweykowska, A. D. Broek, J. Lugtenburg
Recl. Trav. Chim. Pays-Bas 102, 42 (1983)

fig. 2:
75,4 MHz noise decoupled ^{13}C NMR spectrum
of 9,10 D_2 , 9-demethylretinal

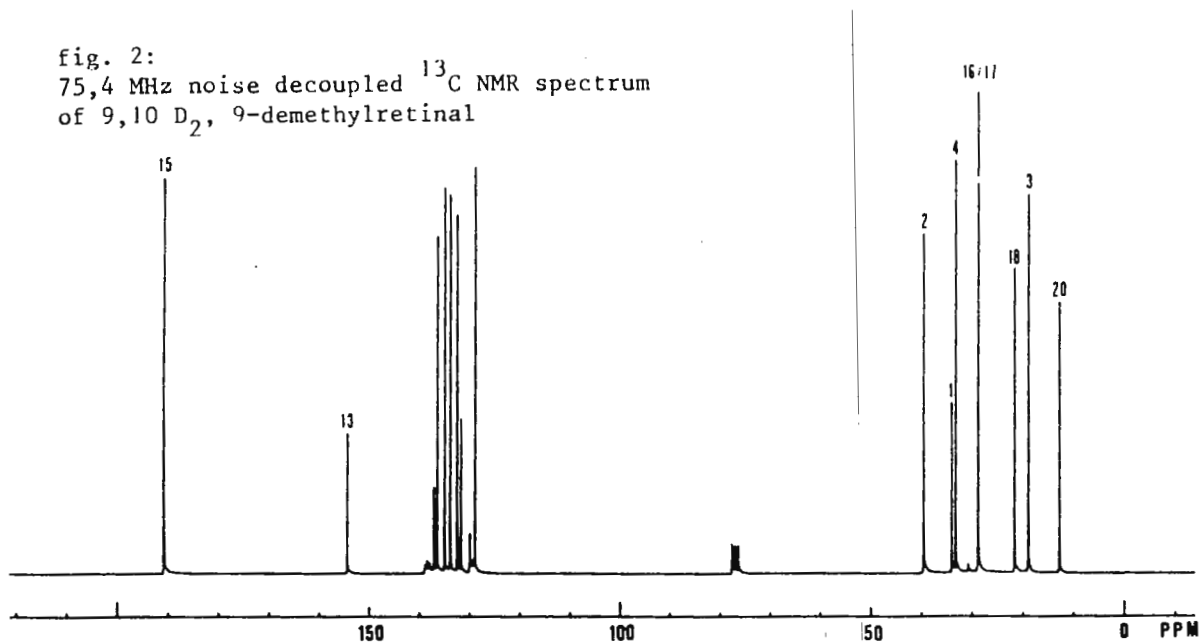
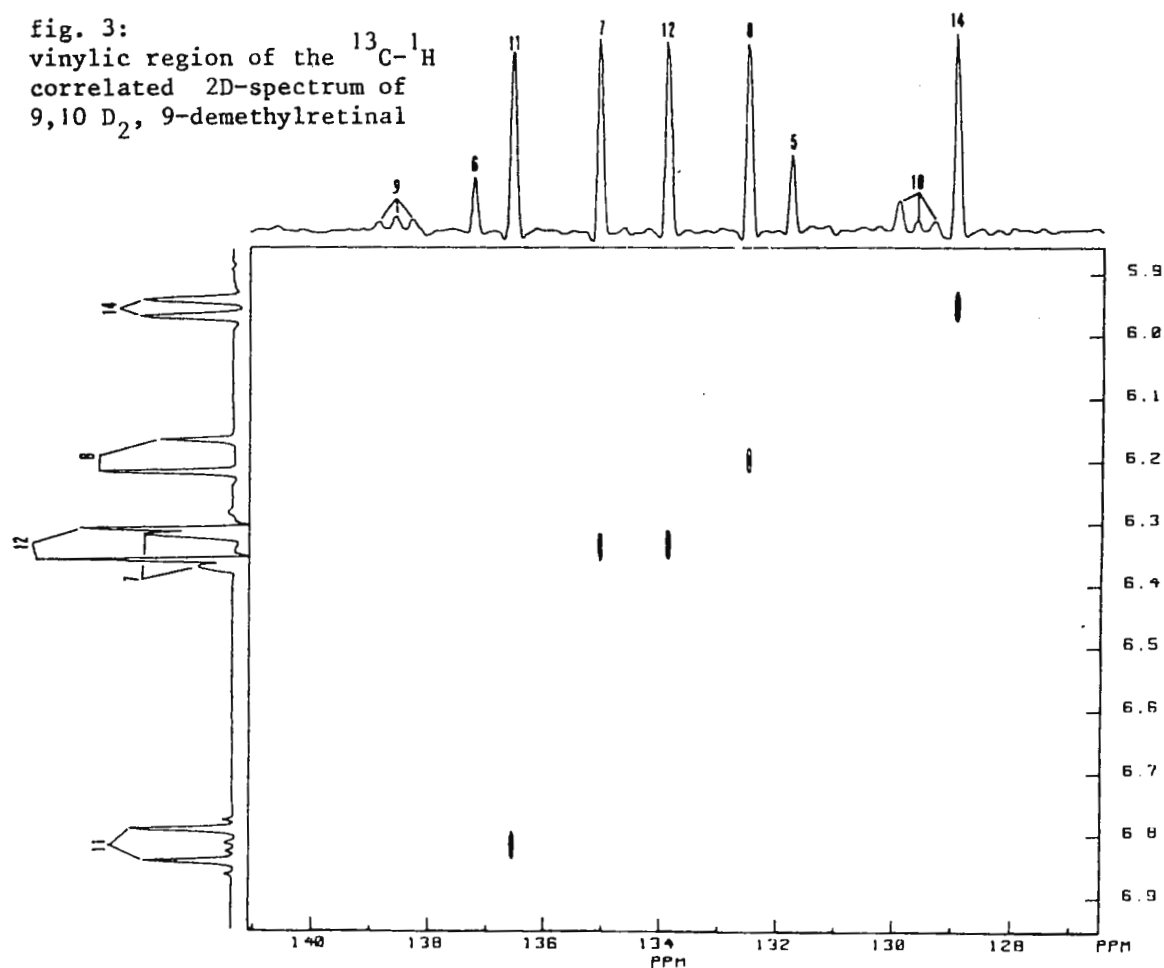


fig. 3:
vinylic region of the ^{13}C - ^1H
correlated 2D-spectrum of
9,10 D_2 , 9-demethylretinal



Sincerely yours,

E. M. M. van den Berg *A. van der Bent* *F. Lefeber* *C. Erkelens* *J. Lugtenburg*

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Professor Bernard L. SHAPIRO
TEXAS A&M UNIVERSITY
Department of Chemistry
College Station
Texas 77843-3255

Heteronuclear $^{15}\text{N}/\text{H}$ Spin

12 February 1987

Echo NMR of Aqueous Leucine

(Received 2 March 1987)

Dear Pr Shapiro:

Branched-chain amino acids (BCAA) are considered to be regulators or precursors for a variety of metabolic reactions. In muscle, BCAA undergo transamination. Nitrogen from BCAA is transferred in the first step, to α -ketoglutarate. NMR can be a suitable method to follow metabolism pathways.

To overcome the low sensitivity of ^{15}N nucleus, this can be observed in the ^1H spectrum through the effect of J coupling (K. Brindle et al., 1984)*.

In aminoacids, protons directly bonded to ^{15}N are in rapid exchange with water protons and much smaller couplings ($2J$, $3J$), have to be detected. The proton of leucine is labil. At $\text{pH} \approx 14$, however, the ^{15}N -H coupling ($2J$) is approximately 3 Hz and the heteronuclear $^{15}\text{N}/\text{H}$ spin echo NMR experiment can be carried out (figure 1) :

$90^\circ(^1\text{H})$, $1/2J$, $90^\circ_{+x}(^{15}\text{N})$, $180^\circ(^1\text{H})$, $90^\circ_{\pm x}(^{15}\text{N})$, $1/2J$, $\text{Acq}(\pm)$.

The C_β protons display large multiplicity due to homonuclear coupling, but they have no exchange. They would allow detection at physiological pH. Our investigations have focused on detection of leucine released in the perfusing medium of muscle.

Yours sincerely,


D. MEYNIAL

M. ARNAL

J.P. RENOU

M. BOURDONNEAU
Bruker France

* K.M. Brindle, R. Porteous, I.D. Campbell (1984) J. Magn. Res. 56, 543



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K1A 0R6

January 27, 1987

(Received 9 February 1987)

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

PASCAL PROGRAM FOR CHORTLE ANALYSIS

Dear Professor Shapiro:

CHORTLE, a C-H chemical shift correlation from one-dimensional polarization transfer ^{13}C NMR spectra (G.A. Pearson, J. Magn. Reson. 64, 487-500 (1985)) has proven very useful in our laboratory. We use it extensively on polysaccharides whose proton lines are broad. Since with CHORTLE, total evolution time is less than 6 ms, only four proton evolution times are needed and no resolution enhancement is employed to process the data, better sensitivity is usually achieved compared with standard 2D C-H correlations.

With CHORTLE, C-H correlations are obtained from the BASIC program CHFIT of G.A. Pearson which does a non-linear squared fit of the ^{13}C intensities as a function of proton evolution times. However, data analysis was fairly tedious since all peak intensities had to be entered by the user. This inconvenience was circumvented by using the file oriented version of CHFIT from Jan Ulrich Thomsen and Klaus Bock (Dept. Chemistry, Technical University of Denmark, 2800 Lyngby, Denmark). This version uses the file generated by the T1 subroutine of BRUKER's DISNMRP program (Table 1). Their communication package, ASCOM, was also used to transport the input data file from the ASPECT 3000 computer to an IBM PC where data analysis was performed.

To make CHORTLE more versatile, the BASIC CHFIT program was translated to TURBO PASCAL for the IBM PC and Apple/2E computers. Then, it was ported to the Aspect 3000 computer and modified to run with the PASCAL PASCAL compiler. Hence, now data analysis can be performed directly on a BRUKER spectrometer with minimum data entry which consists of the input and output filenames, the spectrometer frequency and the ^{13}C reference. An example of the output generated by CHFIT is shown in Table 2.

Since, CHFIT is now in PASCAL implementation on other NMR spectrometers should be much easier. Copies in TURBO PASCAL for the IBM PC or APPLE computers or in PASCAL for the ASPECT 3000 computer are available free of charge if you send an appropriate formatted floppy diskette.

Sincerely,

Jean-Robert Brisson

David Bundle.

Canada

TABLE 1. INPUT FILE GENERATED BY THE T1 SUBROUTINE

TAU	CURSOR	FREQ	PPM	INTEGRAL	INTENSITY
.2500	4769	13025.066	103.604	14.275	78.174
.2500	4771	13023.613	103.593	-1.309	-10.497
.7500	4769	13025.066	103.604	12.469	61.687

--- etc.

TABLE 2. OUPUT GENERATED BY CHFIT

H-1 NMR frequency is 500.13 MHz.

4 H-1 evolution times of .250 .750 2.400 3.200 ms.

The C-13 reference line is no. 1 with its H-1 at 4.500 ppm.

The decoupler is at 4.756 +/- .004 ppm.

C-13 line no. 1	Cursor = 4769	103.604 ppm
-----------------	---------------	-------------

H-1 offset = -128.1 +/- 2.1 Hz.

H-1 shift = 4.500 +/- .006 ppm.

Tau(ms)	Cosine int.	error/s.dev.	sine int.	error/s.dev.
.250	78.174	-1.1	-10.497	-1.1
.750	61.687	.1	-41.341	-.3
2.400	-22.552	-1.0	-73.255	.7
3.200	-62.569	-.2	-34.749	-1.4

Io= 75.2 +/- 2.0

No. of iterations = 2

Standard deviation of fit= 4.1

Minimum detectable splitting is 75 Hz. or .150 ppm.

C-13 line no. 2	Cursor = 15727	40.271 ppm
-----------------	----------------	------------

H-1 offset = -1277.0 +/- 3.5 Hz.

Splitting = 520.5 +/- 4.9 Hz.

H-1 shifts = 1.682 and 2.723 +/- .009 ppm.

---- etc...

Table of C-H chemical shifts (ppm).

No	C-13	H-1	+/-	H(1)	H(2)	+/-
1	103.6	4.500	.006			
2	40.3	2.203	.008	1.682	2.723	.009

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January 14, 1987
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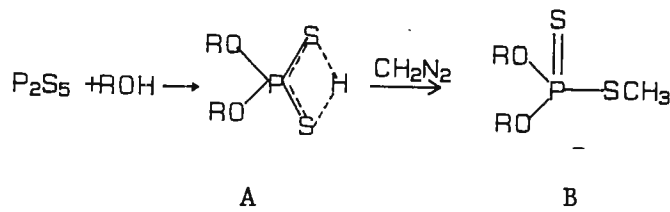
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Professor Shapiro:

Subject: Chiral Methyl Dithiophosphate Study Via ^{31}P NMR

We have studied the general stereochemistry of dialkyl dithiophosphoric acids A and the corresponding S-CH_3 dithiophosphate esters B derived from chiral alcohols (scheme 1) by ^{31}P and two dimensional NMR techniques.

(scheme 1)



Compound	ROH
A-1, B-1	(-)-menthol
A-2, B-2	racemic menthol
A-3, B-3	racemic 4-methyl-2-pentanol

We have observed doublet multiplicity in the ^{31}P NMR spectra for a variety of A compounds produced from chiral alcohols. Furthermore, we have observed triplet multiplicity for the corresponding B isomers with pronounced chemical shift differences ($\Delta\delta$) relative to the A isomers (Table I). Figure 1 illustrates the A-2 doublet and the B-2 triplet which have been assigned as a meso-isomer and a d,l pair and as two meso-isomers and a d,l pair, respectively. The chemical shifts of A-2 and B-2 were assigned on the basis of A-1 and B-1 prepared from pure (-)-menthol to yield the single R/R enantiomer as shown in Figure 1. Similar spectral results are shown for A-3 and B-3 in Figure 2. The two meso diastereomers and d,l pair structures for B-3 are illustrated in Figure 3 by Fischer projections.

We propose the application of scheme 1 and subsequently compound B as a possible derivative for enantiomeric excess (ee) determinations of chiral alcohols via ^{31}P NMR analysis. Previous studies have shown that both chiral and achiral^{2,3} derivatizing agents can be used for ee determinations of chiral alcohols by ^{31}P NMR analysis. Thiophosphoric acids have also been alluded to as potential ee derivatives. However, the larger $\Delta\delta$'s as well as narrower line shape of the B isomers (Table I) should yield more precise ee determinations⁴ as a result of more accurate integrations. The methylation procedure is quite simple and our preliminary results show the methyl addition not to be stereoselective.

The ^{13}C and ^1H NMR spectra of A and B are complex due to stereoisomer mixtures as well as diastereotopic alkyl groups on the meso-isomers. We are presently preparing a manuscript discussing the ^{13}C and ^1H NMR analysis of dithiophosphoric acids and dithiophosphate esters derived from chiral alcohols.

Please credit this contribution to Dr. Horton Dunn.

Sincerely,

K F Wollenberg

K. F. Wollenberg
Research Chemist

KFW/dabe

References

1. C. R. Johnson, R. C. Elliott and T. D. Penning, J. Am. Chem. Soc., 106, 5019 (1984).
2. B. L. Feringa, A. Smaardijk, H. Wynberg, J. Am. Chem. Soc., 107, 4798 (1985).
3. B. L. Feringa, A. Smaardijk, H. Wynberg, Tetrahedron Lett., 27, 997 (1986).
4. T. A. Tauli, J. Chromatogr. Sci., 7, 671 (1969).

Table I

Ratio of d,l pair: meso-isomer and d,l pair: meso-isomer pair (meso₁, meso₂) for A and B, respectively, derived from ROH in scheme 1. Chemical shift difference ($\Delta\delta$) of d,l pair to meso-isomer for A and meso₁ to d,l pair and d,l pair to meso₂ for B.

<u>Compound A</u>	<u>Racemic</u>	
	<u>Racemic Menthol</u>	<u>4-Methyl-2-Pentanol</u>
d,l pair: Meso	1.0:1.0	1.0:1.0
peak width (Hz)	1.06, 2.19	0.79, 0.85
$\Delta\delta$ (Hz)	56	10
<u>Compound B</u>		
meso ₁ : d,l pair: meso ₂	1.0:2.0:1.0	1.0:2.0:1.0
peak width (Hz)	0.93, 0.35, 1.03	0.54, 0.56, 0.71
$\Delta\delta$ (Hz)	250, 423	133, 165

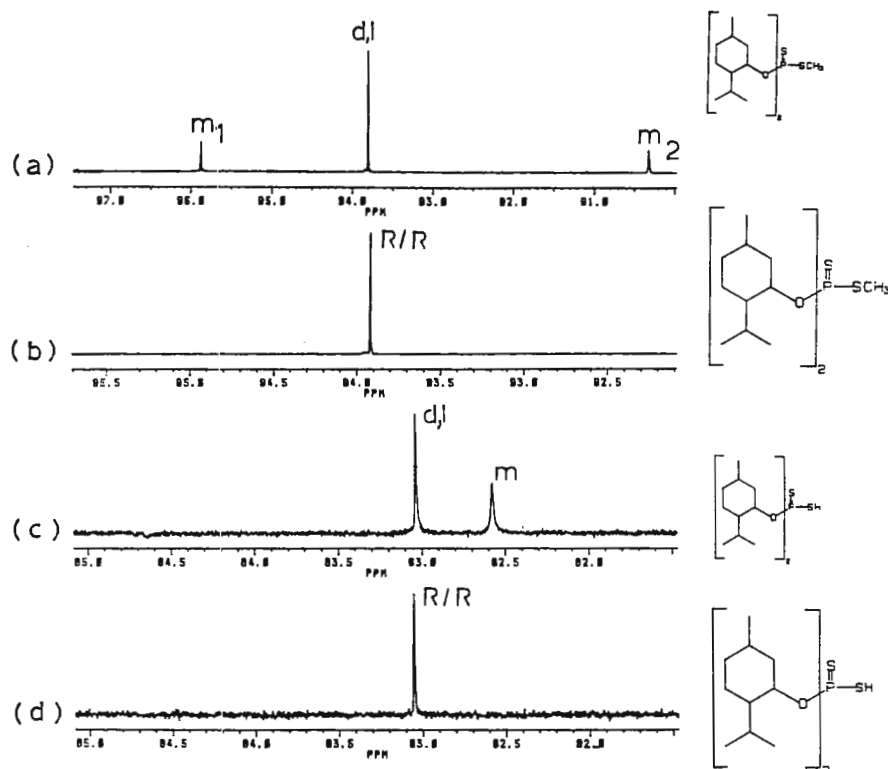


Figure 1: ^{31}P NMR (121.51 MHz), 85% H_3PO_4 ($\delta=0.00$) as external standard, Bruker AM-300 (a) B-2 [95.9 ppm (M_1), 93.8 ppm (d,l), 90.3 ppm (M_2)] (b) B-1 [93.8 ppm (R/R)] (c) A-2 [83.0 ppm (d,l), 82.6 ppm (m)] (d) A-1 [83.0 ppm (R/R)], m refers to meso-isomer, d,l refers to enantiomeric pair, and R/R refers to single enantiomeric isomer derived from (-)-menthol

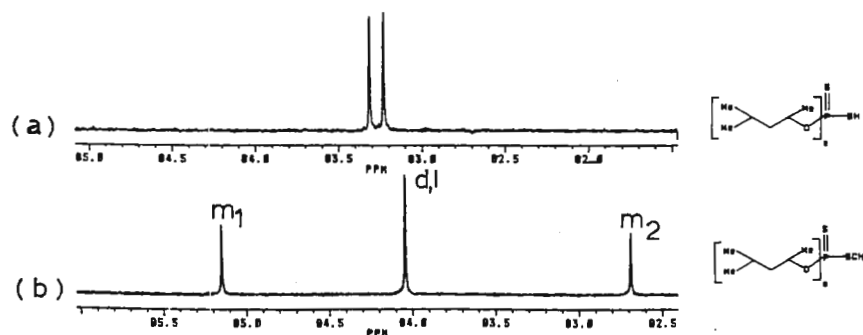


Figure 2: ^{31}P NMR spectra of (a) A-3 and (b) B-3 prepared by scheme 1 from racemic 4-methyl-2-pentanol

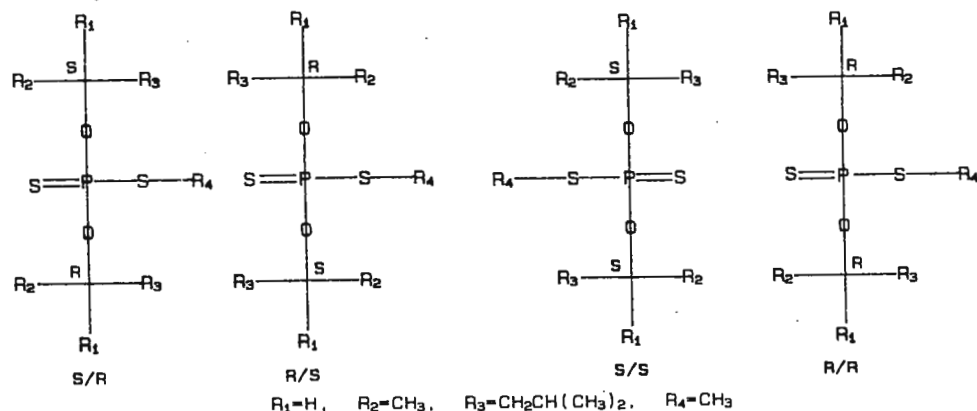


Figure 3: Fischer projections of B-3, two meso-isomers (S/R, R/S) and d,l pair (S/S, R/R), derived from racemic 4-methyl-2-pentanol.

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D. CANET
Professeur

Professor B.L. SHAPIRO
Texas A&M University
Department of Chemistry
COLLEGE STATION, Texas 77843-3255
U.S.A.

Title: *Quantitative determination of carbon-13 isotopomers in non-uniformly enriched species by polarization transfer experiments.*

February 20, 1987
(Received 27 February 1987)

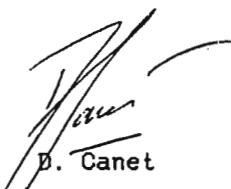
Dear Professor Shapiro:

In reply to your "ultimatum" of last december, we would like to mention a simple homonuclear polarization transfer experiment aimed at separating carbon-13 isotopomers. This is of some interest in biochemical systems obtained from a ^{13}C enriched precursor. Labeling is not uniform and the relative intensity of each isotopomer can be indicative of biochemical pathways. The sequence we have used is the simplest one:

$(\pi/2)_x - \tau - (\pi/2)_y$ - Acquisition

The carrier frequency is set at the resonance of a given carbon. Transfer from that carbon is made selective by varying τ by $\pm 20\%$ around a particular value τ_0 ($1/2J$ or $1/4J$) and coadding the relevant fid's. The joined figure provides an example of the information attainable from such experiments. The lower trace shows the normal ^{13}C spectrum of an extract involving several metabolites. The sequence has been applied to the C_3 carbon of glutamate (middle trace: $\tau_0 = 1/2J$; upper trace: $\tau_0 = 1/4J$). These spectra include signals at the position of carbons J-coupled to C_3 . It can be shown that their analysis enables to quantify all isotopomers indicated in the figure (a star denotes ^{13}C labeling at the corresponding carbon).

Sincerely yours,

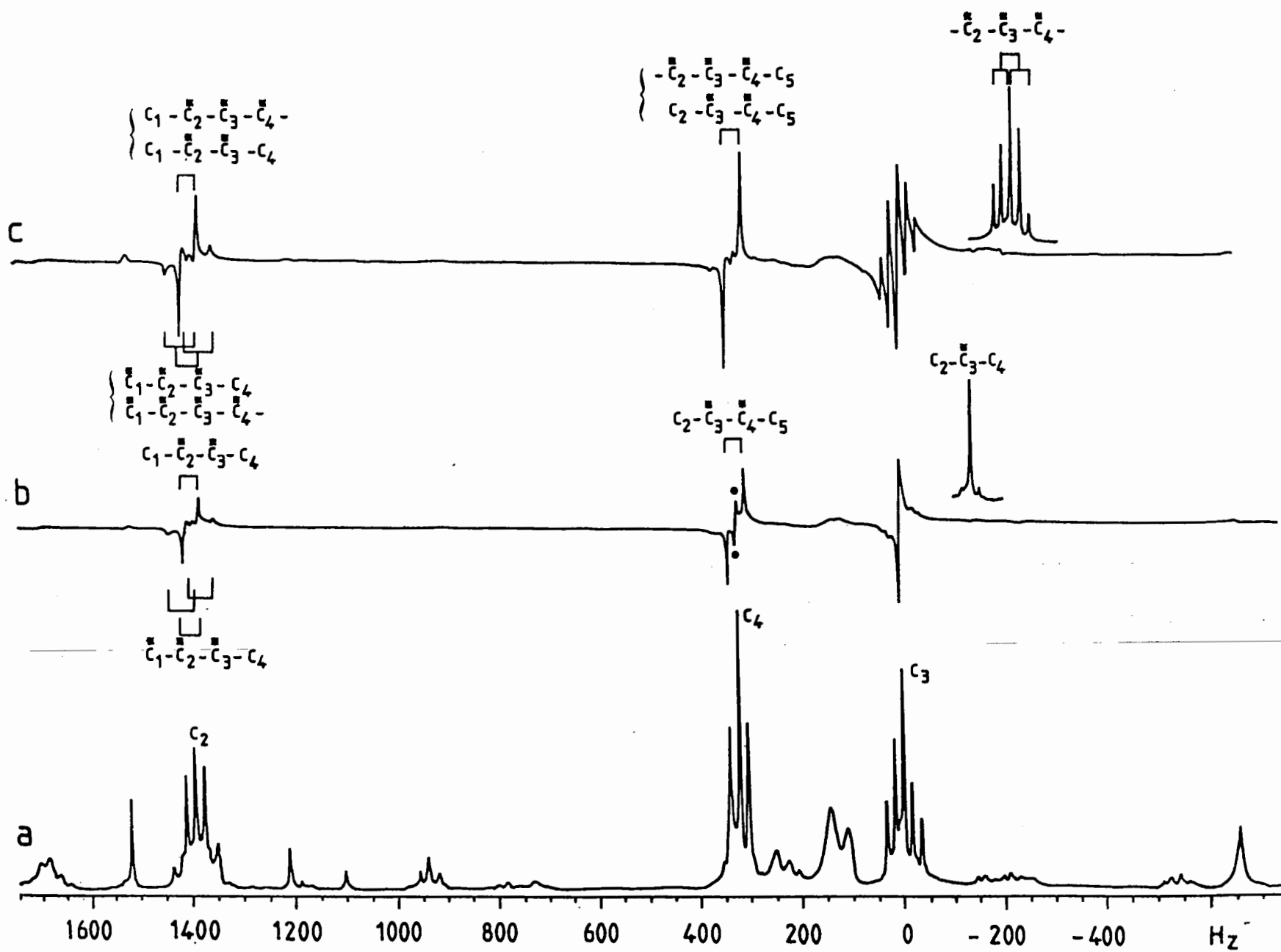


D. Canet



D. Brondeau

D. Boudot



(Received 27 February 1987)

NMR RESEARCH SCIENTIST - POST-DOCTORAL

PROGRAM AND ROLE: The Ohio State University has instituted a major interdisciplinary program to develop methods for obtaining localized proton spectra from an organ or tissue which provides diagnostic and therapeutic monitoring information related to the pathophysiology of a disease. Imaging by means of magnetic resonance (MRI) which can identify the region-of-interest has become a standard medical tool at the University Hospitals. The NMR Research Scientist will be responsible for continuing development and implementation of the basic technology. Exploration of clinical applications such as atherosclerosis, neoplasia and dementia will ensue in conjunction with a team of medical scientists and physicians.

SUPPORT FACILITIES AND PERSONNEL: Our modern facility, designed to insure magnetic field homogeneity, is equipped with a 1.5 T MRI unit including a spectroscopy module [General Electric Co.]. An adjacent 4000 sq. ft. support laboratory facility is newly constructed. The facility is integral with one of the largest academic medical centers in this country. A fulltime administrative director, a physician and a physicist provide core support for the program. Resources for this medically oriented program include scientists of many disciplines on this large and congruent campus. Important resources for advanced NMR instrumentation and technology include the Campus Chemical Instrument Center (A. G. Marshall, Director).

OPPORTUNITY: A post-doctoral position as a NMR Research Scientist with a one or two year appointment in the Department of Radiology, College of Medicine is immediately available. The nature of our program combined with technological growth also creates the genuine potential of a career opportunity. Starting salary is \$19-21,000 per annum and open for adjustment based on qualifications and performance. The position will provide experience in medical applications.

QUALIFICATIONS: A Ph.D. in chemistry with strong academic and practical experience in NMR spectroscopy are prerequisite. NMR experience in the biological sciences is preferred. The Ohio State University is an equal opportunity employer.

APPLICATION: A letter summarizing experience and specific interests, curriculum vitae and two letters of recommendation should be directed to:

William W. Hunter, Jr., M.D.

Tel. 614/293-8181

OSU MR Facility

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3. A Varian XL-100-15 nmr system with Nicolet & Transform Technology FT system for ^1H , ^{31}P , ^{13}C , ^{17}O . This system is fully functional.

Please contact Bob Addleman, nmr supervisor, at (812) 335-1639 if you have any interest.



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Vice President
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enclosing a copy of your *curriculum vitae*. We hope to invite shortlisted candidates for interviews in April. The position has a targeted starting date of May 1, 1987. In accordance with Canadian immigration requirements, this advertisement is directed to Canadian citizens or permanent residents. Candidates of either sex are equally invited to apply.

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Jan 4, 1987

(Received 9 February 1987)

Variable Temperature Studies of Peptides

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

Dear Professor Shapiro :

We are interested in using high resolution multi-nuclei NMR spectroscopy to study molecular dynamics of anesthetic related compounds. A combination of various NMR techniques enabled us to study the structure and dynamics of both diketopiperazine ring (DKP) and side chain of cyclic peptide, c-(Gly-Kynureninyl). Variable temperature NMR study of this compound show a unique observation of non-equivalence of CH₂ protons of the kynureninyl side chain at elevated temperature and equivalence of these protons at room temperature (Figure 1). This unusual behavior of protons in the side chain, is reversible with temperature, and is interpreted in terms of molecular dynamics¹. Based on our study, We also conclude that, i) DKP ring is planar ($\beta = 0^\circ$), ii) no folding over of the kynureninyl side chain on the backbone (DKP ring), and iii) hydrogen bonding is observed between carbonyl and NH₂ group of the kynureninyl side chain of the cyclic peptide.

Sincerely Yours,

Ashok

Ashok L. Cholli

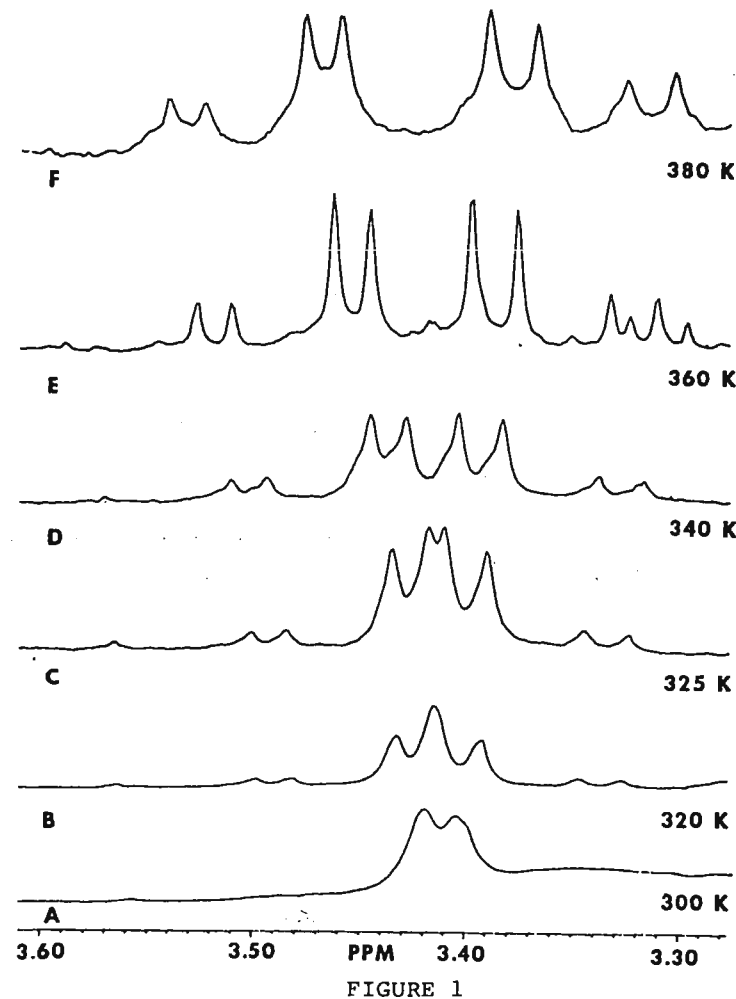


FIGURE 1

1. A.L. Cholli, A.Galdes, D.Pennino, and Z. Kosarych, to be published



DEPARTMENT OF HEALTH & HUMAN SERVICES

342-43
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Bethesda, Maryland 20892

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

February 1, 1987
(Received 10 February 1987)

Dear Barry:

Coherence or incoherence ?

As was clearly demonstrated by Zuiderweg et al. (1), for 2D NMR experiments in H_2O with presaturation it is advantageous to make the presaturation irradiation and the observe frequency phase-coherent. Since on nearly all spectrometers decoupler and observe frequencies are derived from two phase-locked synthesizers one would expect that setting the decoupler and observe frequencies to identical values would be sufficient to accomplish phase coherence. Zuiderweg and friends comment on the fact that this is not the case for the GN-500; the same was found for our NT spectrometers and a number of different brands. Rolf Tschudin set out to investigate this puzzling "phase incoherence". Here is what he found:

Trying to make the observe carrier frequency (SF) equal to the decoupler frequency (F2) generally (but not always) will produce a difference in these frequencies by a fraction of a Hz. Also, the entered frequency often will differ from the confirmation.

For example: F2 entered 500,090,000
 confirms 500,090,001
 produces 500,089,998.4

The reason appears to be the floating point arithmetic used by the program to calculate the synthesizer frequencies. To represent the decimal digit on a 500 MHz instrument (10 significant figures) requires 33 bits (plus a sign bit). The floating point package has only 29 mantissa bits plus a sign bit available and round-off errors will occur. To overcome the problem without a lengthy rewrite of the program we simply disabled the 0.1 Hz remote lines into both synthesizers. After this modification, if identical values are entered for F2 and for SF, identical frequencies are usually generated. Sometimes the generated frequencies still differ by exactly 1.0 Hz; this then is easily corrected by a 1 Hz change of either SF or F2.

A comparison of the spectra with and without the fix is shown in the accompanying figure. One interesting feature in the "incoherent" spectrum is that the wings of the H_2O t_1 -noise appear to be regular, or better, non-random. To understand this, one has to realize that these wings come from magnetization generated by the decoupler field (and are coherent with the decoupler rf). If, for example, in a 1D experiment FID's are acquired at 1 s intervals and the decoupler and observe differ by 0.25 Hz, the decoupler generated signal will cancel after 4 scans. If the time between scans is increased to 1.33 s, the decoupler generated signal will cancel after 3 scans, i.e. scan#4 remains uncanceled. Something similar occurs in a 2D experiment when t_1 is incremented, i.e., the time between scans becomes longer. t_1

incrementation occurs in a regular fashion and therefore the corresponding artifacts are regular too. Introduction of a random delay (e.g., the random disk access time upon completion of a t_1 value), long relative to the reciprocal of the frequency difference, removes the regularity of the wings and decreases their intensity. The better solution, however, is to synchronize the frequencies or use a DANTE for presaturation (1).

Best wishes,

R. Tschudin

Rolf Tschudin

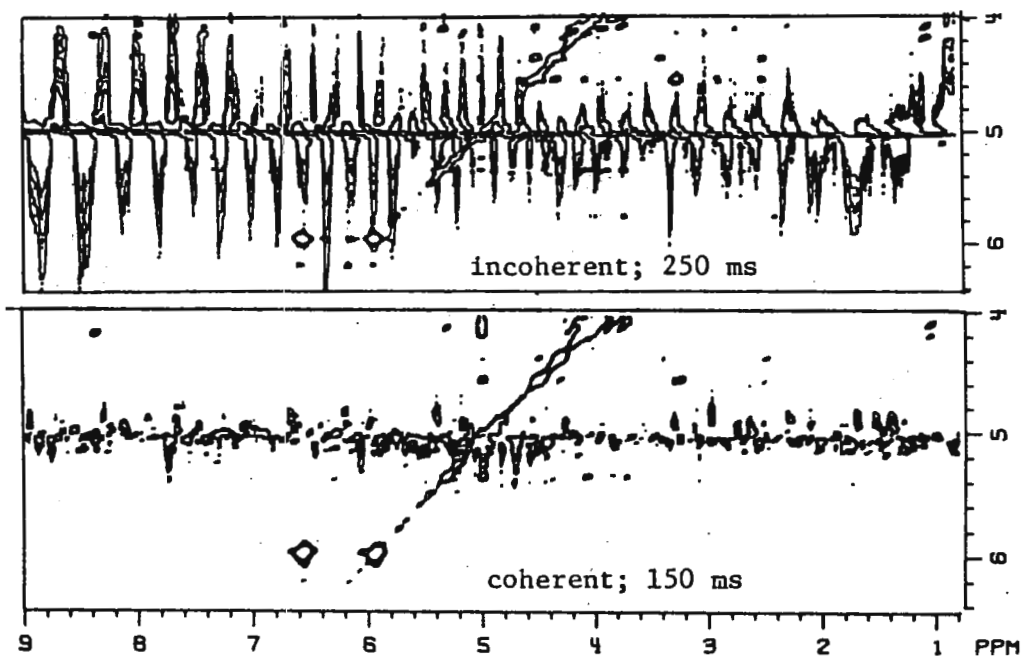
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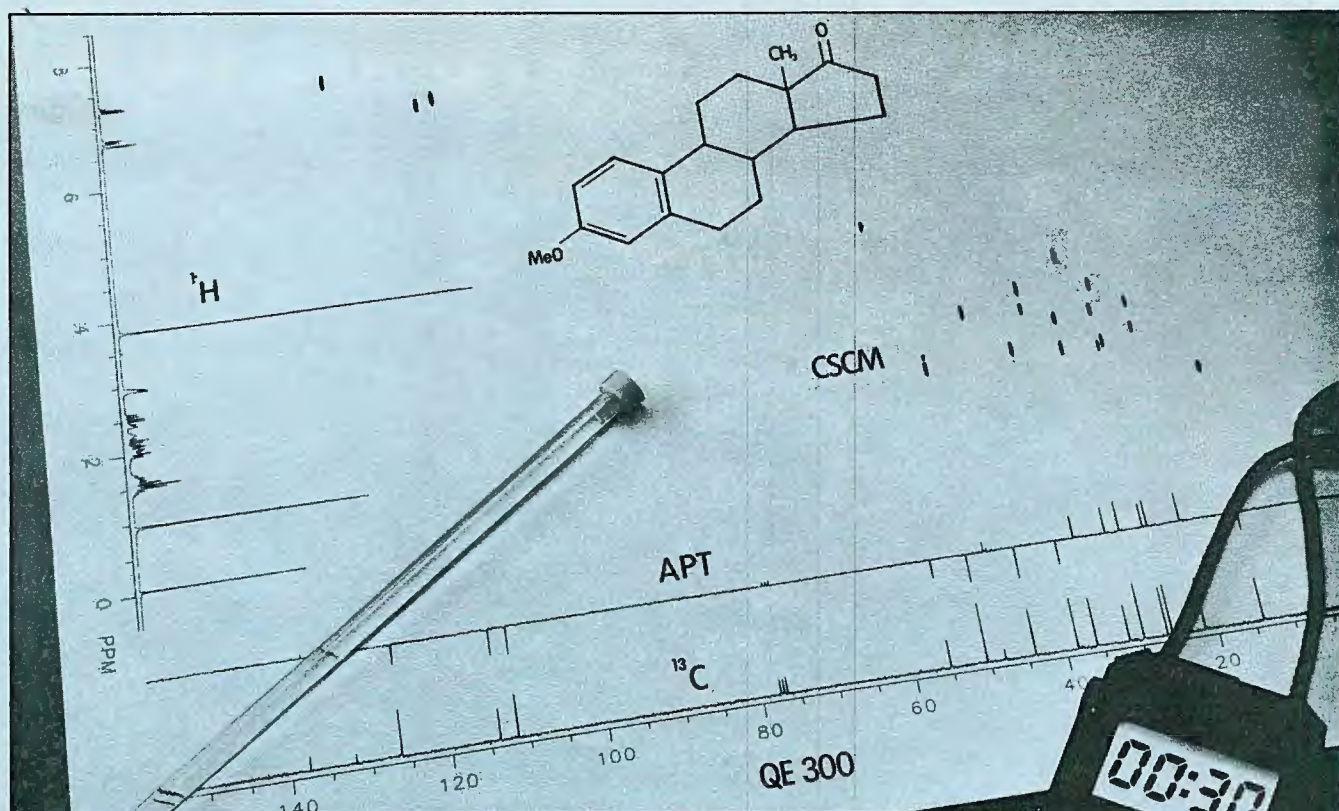
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(1) E.R.P. Zuiderweg, K. Hallenga and E.T. Olejniczak, J. Magn. Reson. 70, 336 (1986).



A comparison of two sections of two 2D NOE spectra recorded with and without (top) synchronization of decoupler and observe frequencies. The mixing times are 250 (top) and 150 ms (bottom).



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most advanced automation.**

This performance is made possible by the QE-300's automated software, hardware, and powerful MACRO programming capability.

Set-up starts with *Autolock*. Lock on as little as 10% CDCl₃ in a 5 mm tube.

Use *Compushim* for touching-up spinning shims or complete shimming with both spinning and non-spinning gradients using

the lock signal or observe FID.

Autogain optimizes the receiver gain independently for sequential ¹H and ¹³C acquisition.

After data acquisition, *Auto-phase* accurately phases ¹H and ¹³C spectra.

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

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

**And the most complete package
of hardware accessories.**

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

**Structural
elucidation simplified.**

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

**High throughput and
performance demonstrated.**

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

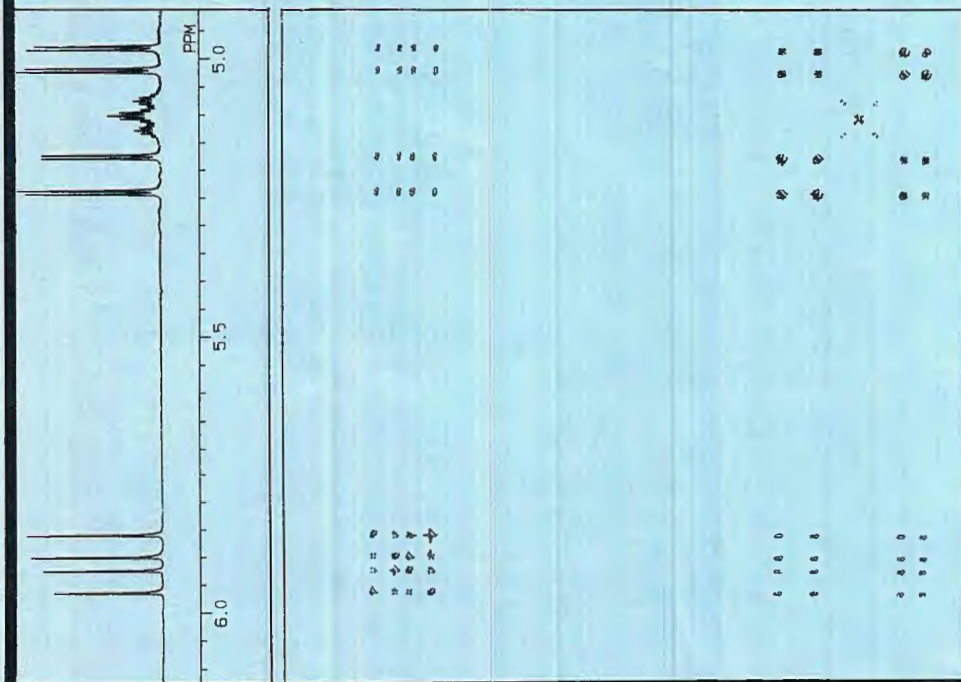
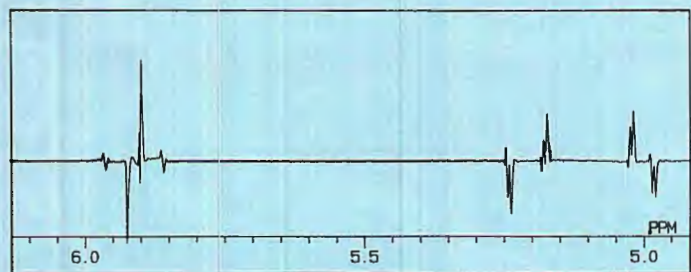
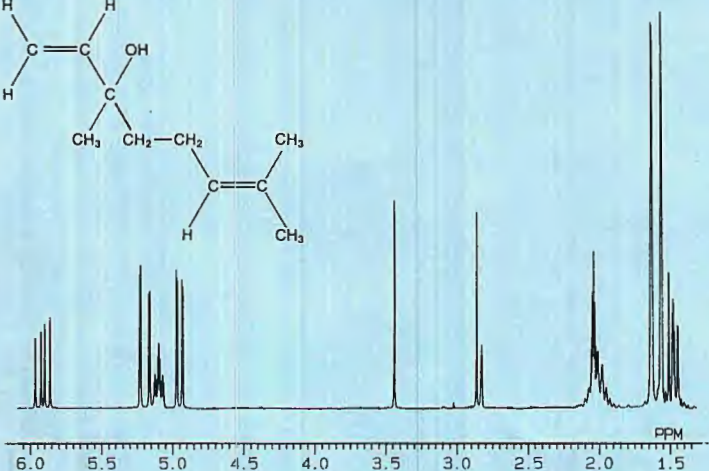
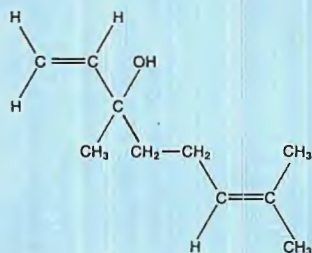
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JEOL'S GX-FT NMR Systems

Subject: Automation

One of the more than 200 (and growing) automated routines available on the GX-Series; the data illustrates a Double Quantum Filter Phase Sensitive Cosy on the downfield section of Linalool run on a GX-270WB (89mm) MHz spectrometer. From the moment you

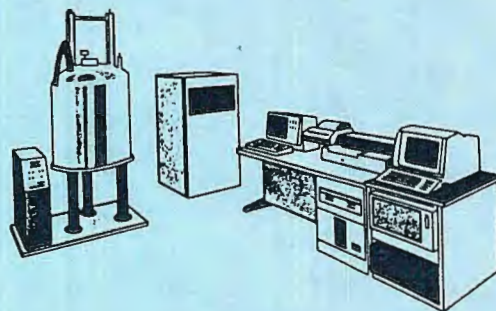
Linalool



load the sample, spinning, lock, shimming, acquisition, transform, phase correction, and plotting are totally automated. Should you need something not already in our menu a few strokes on the keyboard will put it there.

So whether your requirements are for routine or research, the GX-FT NMR is an instrument that you should consider when evaluating FT-NMR Systems.

The GX Series FT-NMR Spectrometer



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