

NMR

NEWSLETTER

NO. 317

FEBRUARY 1985

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Forthcoming NMR Meetings (Additional listings are solicited)

New Directions in Chemical Analysis, the 3rd Annual Symposium of the Industry-University Cooperative Chemistry Program, Texas A&M University, College Station, Texas, April 1-3, 1985. Papers to be presented by T.B. Hirschfeld, R.D. Macfarlane, C.A. Fyfe, R.L. Swofford, G. Guiochon, A.G. Marshall, A.T. Hubbard, A.C. Parr, J. Ruzicka, J. Callis, N. Winograd, D.H. Williams, M.V. Novotny, W.P. Rothwell, J. Schaefer. For further information, write Prof. E. A. Schweikert, Department of Chemistry, Texas A&M University, College Station, Texas 77843 U.S.A.; (409) 845-2341.

26th ENC - April 21-25, 1985, Asilomar, Pacific Grove, California; Chairman: P. Mark Henrichs, Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

Seventh International Meeting on NMR Spectroscopy - July 8-12, 1985, University of Cambridge.

12th FACSS Meeting - Sept. 30-Oct. 4, 1985, Philadelphia, PA; NMR Program Chairman: Rodney D. Farlee, E.I. du Pont de Nemours & Co., Inc., Experimental Station, Building 328, Wilmington, Delaware 19898; see page 9.

Attention All Newsletter Recipients:

When discussing advertising possibilities with potential advertisers, I am always asked the circulation figures for the TAMU NMR Newsletter. There are in fact two numbers which ought to be provided to potential advertisers, one being the number of issues we actually mail out. The other number of interest is how many people actually read the Newsletter on a routine basis. We are therefore conducting one of our periodic surveys of this latter number. Enclosed with this issue is a postcard on which I would greatly appreciate your indicating the actual number of readers who routinely read, inspect, or have the opportunity to make significant use of the copy of the Newsletter which you actually receive. Please indicate this number on the attached postcard and return it to me at your earliest convenience. (I regret that it is not possible for us to include postage for foreign recipients of the Newsletter, but please return the postcard by airmail. Thank you.)

The postcard will also afford space for you to relay any comments or suggestions to us, as well as to verify in detail your mailing address as indicated on the card.

Thank you very much for your cooperation with this very important request.

B.L. Shapiro

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

All Newsletter Correspondence
Should be Addressed to:

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

DEADLINE DATES

No. 319 ----- 1 April 1985
No. 320 ----- 5 May 1985

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January 7, 1985

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

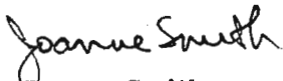
Title: ^{13}C Assignments For 1,1-Di(4-hydroxy-3,5-dimethylphenyl)-
2,3-dimethylbutane Using 2D NMR

Dear Barry:

The ^{13}C spectrum of the title compound contains four methyl carbon resonances due to the chiral center at C-2 (see Figure for structure). The chemical shift difference between the magnetically non-equivalent C-5 and C-6 is substantial and both resonances occur in the same region as C-4. We were unable to unequivocally assign these resonances based on chemical shift arguments alone. Homonuclear ^1H decoupling experiments demonstrated that H_c was coupled to both H_e and H_f , which showed that these were the isopropyl methyl protons. Also, irradiation at the resonance labelled "b,g" caused H_d to collapse to a singlet which indicated that methine proton H_d was hidden under the xylyl methyl protons, H_g . The heteronuclear 2D correlation spectrum is shown in the Figure. The contour plot shows that C-5 and C-6 correspond to protons H_e and H_f , respectively, which assigns these as the nonequivalent methyl carbons of the isopropyl group. C-4 likewise must correspond to H_d from the 2D spectrum. The observation from the homonuclear decoupling experiments that H_b must lie under H_g is also confirmed in the 2D spectrum.

The title compound was synthesized by Victor Mark of our Lexan Products Dept. The parameters for the 2D experiment included spectral widths of 16000Hz (^{13}C , 75.4MHz) and 3000 Hz (^1H , 300MHz), 256 increments of 64 transients each, relaxation delay of 4s, refocusing delay of 2.5ms, mixing delay of 4ms and a 512x2048 data matrix. Only the aliphatic region is shown in the Figure.

Sincerely,



Joanne Smith



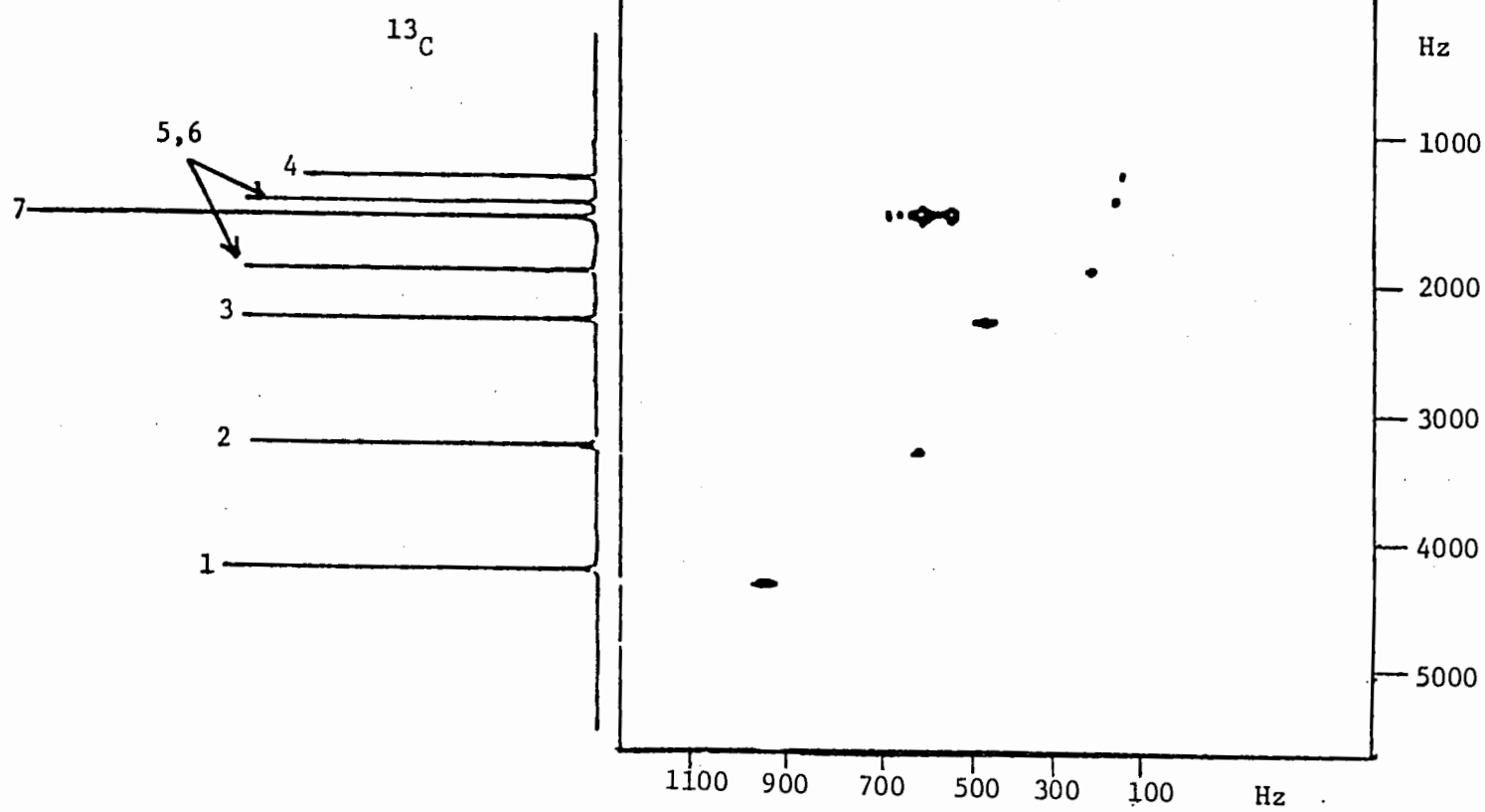
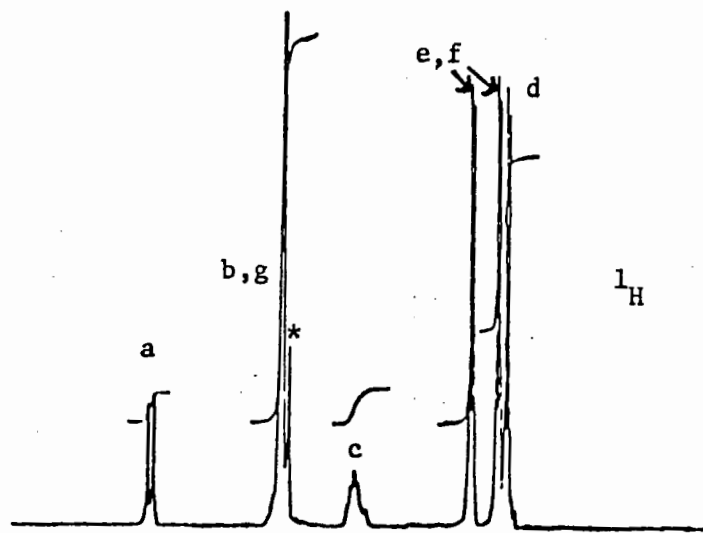
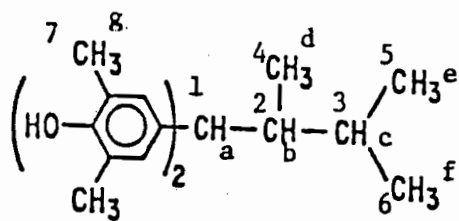
Paul Donahue



Liz Williams

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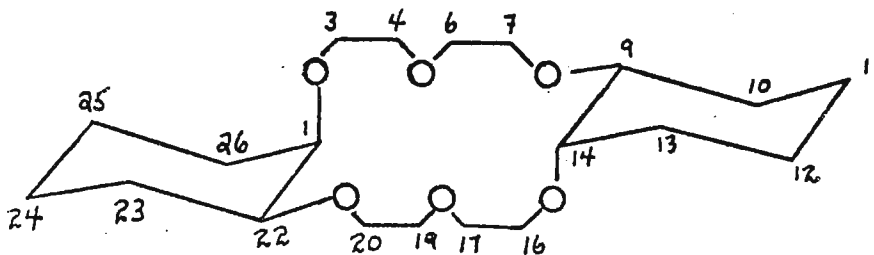
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January 9, 1985.

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

Title: "Crown Ether Conformations Detected By 100 MHz ^{13}C NMR at 173 K"

As a sequel to our recent work⁽¹⁾ we wish to report detection of minor stereoisomers for both the cis-syn-cis and cis-anti-cis isomers of dicyclohexano-18-crown-6. ^{13}C spectra for the cis-anti-cis isomer (below) at 173 K are shown in the Figures.



Clearly, a second conformation which is populated to the extent of ca. 30% is present. At 173 K, $-\Delta G^0 = 0.31 \pm 0.05$ kcal/mole for this isomer in CD_2Cl_2 . In MeOD, $-\Delta G^0 = 0.11 \pm 0.04$ kcal/mole. We suggest that the second isomer arises from restricted rotation in the macrocyclic portion of the ring. The barrier for this process is ca. 8.5 kcal/mole, which is ca. 1.5 kcal/mole lower than that found⁽¹⁾ for the overall ring inversion process, which necessarily involves cyclohexane ring reversal.

Best wishes to all for the new year.

Sincerely,

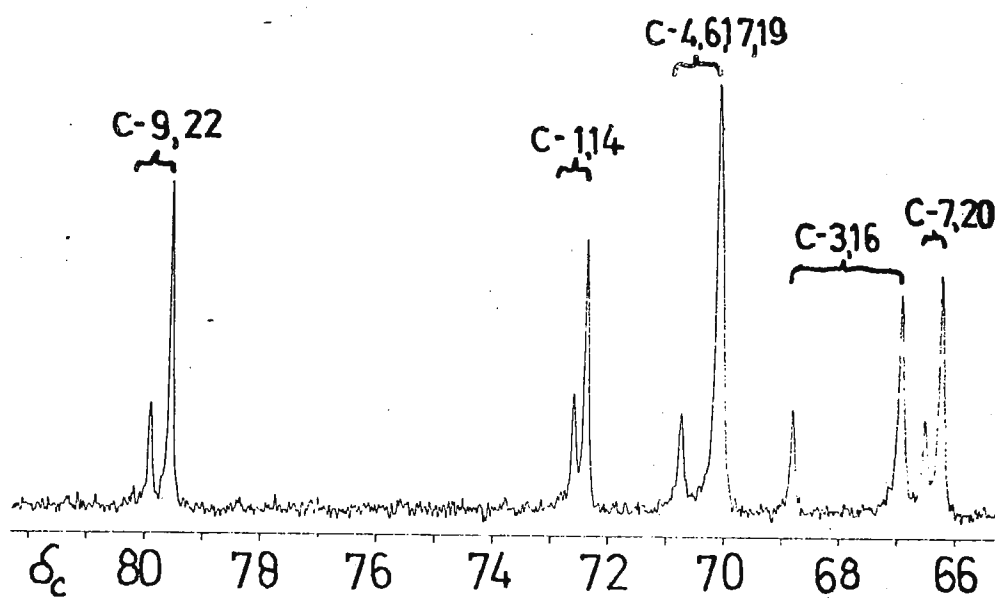
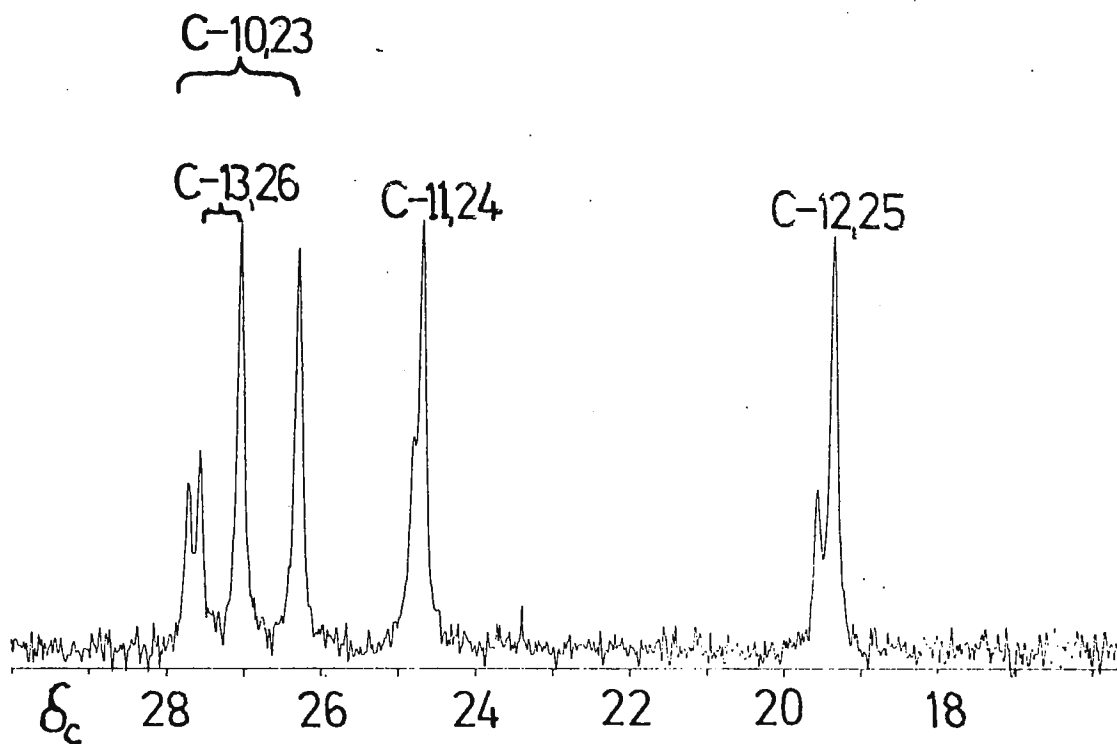
G.W. Buchanan,
Professor of Chemistry.

Reference

(1) G.W. Buchanan, K. Bourque, J.W. Bovenkamp, A. Rodrigue and R.A.B. Bannard. Tet. Letters 3963-3966 (1984).

MCS





100.6 MHz ^{13}C Spectra at 173 K. (cis-anti-cis) isomer
in CD_2Cl_2

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

5900 Siegen, January 4, 1985
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$^2\text{H}/^1\text{H}$ Isotope Effects on $\delta(^{13}\text{C})$ in Ethane, Ethylene, and Acetylene

Dear Barry,

in connection with our studies on deuterium-induced ^{13}C isotope shifts we thought that the data for the three basic hydrocarbons ethane, ethylene, and acetylene would be of general interest. Here they are, measured at -100°C (1,2) and -60°C (3) in $\text{CD}_2\text{Cl}_2/\text{CS}_2$ 1:1 (1,2) and acetone- d_6 (3):

	$\text{H}_3\text{C}-\text{CH}_2\text{D}$	$\text{H}_2\text{C}=\text{CHD}$	$\text{HC}\equiv\text{CD}$
$^1\Delta(^{13}\text{C})$ (ppb)	284.0	273.6	226.7
$^2\Delta(^{13}\text{C})$ (ppb)	93.5	131.2	500.4
$^1\text{J}(^{13}\text{C}, ^2\text{H})$ (Hz)	19.2	24.0	38.0
$s(\text{i})$ (%)	25.0	31.2	49.5

There is for the second time ⁽¹⁾ a good linear correlation between $s(\text{i})$, the fractional s-character of the CD bond as derived from the modified Muller-Pritchard relation $s(\text{i}) = 6.5144 \times ^1\text{J}(^{13}\text{C}, ^2\text{H})/500$, and $^1\Delta(^{13}\text{C})$:

$$^1\Delta(^{13}\text{C}) \text{ (ppb)} = -239.9 s(\text{i}) + 349.9 \quad (R = 0.9973)$$

A preprint with the details will shortly be available.

We hope this letter beats your "Ultimatum". With best wishes for 1985

D. Moskau
D. Moskau

xxx
J. R. Wesener

H. Günther
H. Günther

(1) A similar correlation was established for the phenyl-substituted systems already by J. R. Wesener (J. R. Wesener, Diploma Thesis, Siegen 1982).

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January 10, 1985

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

Dear Professor Shapiro:

Square-Law Dependence of $^2\text{H } T_1^{-1}$ Rates on Segmental Order Parameter For Multilamellar Lipid Dispersions

We have recently performed ^2H NMR studies of a homologous series of 1,2-diacyl-sn-glycero-3-phosphocholines, with perdeuterated saturated chains ranging in length from C12:0 to C16:0. Randomly oriented, multilamellar dispersions containing 50 wt.% water in the liquid crystalline (L_α) phase have been investigated. The ^2H spin-lattice relaxation times (T_1) and C- ^2H bond segmental order parameters (S_{CD}) of each of the resolved acyl chain components with different quadrupolar splittings were measured as experimental observables. ^2H NMR spectra were acquired with a phase-cycled quadrupolar echo sequence at $\omega_0/2\pi = 55.4$ MHz, using a Nicolet NT-360 spectrometer, Henry Radio Tempo 2006 r.f. boost, homebuilt horizontal solenoidal probe yielding $<3-4 \mu\text{s } 90^\circ$ pulses, and Nicolet Explorer 2090 fast transient digitizer. Michael Sefcik and Dennis Torchia provided much helpful assistance.

Figure 1 shows a typical set of partially relaxed ^2H NMR spectra. No first order phase correction was applied and both quadrature data channels were used. The measured T_1^{-1} rates for each of the resolved splittings are plotted versus the square of the corresponding S_{CD} values in Figure 2. As can be seen, the results are consistent with a square-law dependence of the apparent T_1^{-1} rates on the corresponding S_{CD} values (1). This observation is very interesting -- it implies the existence of a contribution from relatively slow fluctuations in the local ordering of the bilayer acyl chain segments to the relaxation.

The suggested correlation between the observed $^2\text{H } T_1^{-1}$ and S_{CD} values can be summarized by the following expression (1):

$$T_1^{-1} = T_{1\text{fast}}^{-1} + B f(\omega_0) |S_{\text{CD}}|^2$$

In the above, B is approximately constant and $f(\omega_0)$ describes the frequency dispersion of T_1^{-1} . The first term on the left represents the contribution from local motions of the acyl chain segments to the relaxation, and is similar to that obtained for liquid n -paraffins (2). The second term describes the influence of collective motions such as twist, splay, etc., which are not observed in simple paraffinic liquids.

In summary, the results suggest that two broad classes of motion influence the ^2H T_1^{-1} relaxation of lipid bilayers: rapid local motions, most likely due to bond rotational isomerizations and long-axis rotational diffusion of the lipid chains, as well as slower director fluctuations as postulated for other liquid crystalline mesophases (2). We hope that these data will contribute to a better understanding of the molecular dynamics of anisotropic systems such as liquid crystals, lipid bilayers, and biomembranes.

Yours sincerely,

James M. Beach *Gerald D. Williams*
James M. Beach Gerald D. Williams

Steven W. Dodd *Michael F. Brown*
Steven W. Dodd Michael F. Brown

1. M.F. Brown, *J. Chem. Phys.* **77**, 1576-1599 (1982); *ibid.* **80**, 2808-2831 (1984a); *ibid.* **80**, 2832-2836 (1984b).
2. M.F. Brown, A.A. Ribeiro, and G.D. Williams, *Proc. Natl. Acad. Sci. USA* **80**, 4325-4329 (1983).

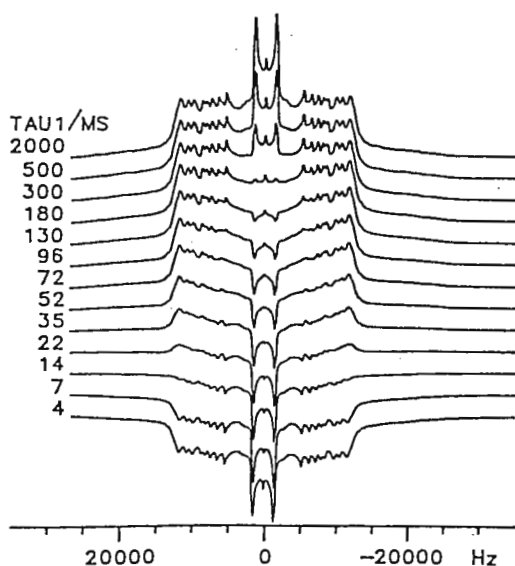
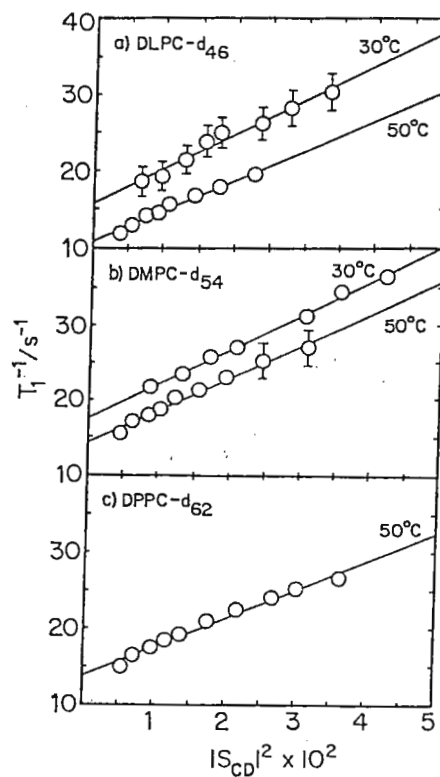


Fig. 2. Plots of ^2H spin-lattice relaxation rate T_1^{-1} vs. $|S_{CD}|^2$ for homologous series of chain perdeuterated 1,2-diacyl-sn-glycero-3-phosphocholines in the L_α phase at the indicated temperatures. (a) DLPC- d_{46} (C12:0 acyl chains); (b) DMPC- d_{54} (C14:0 acyl chains); (c) DPPC- d_{62} (C12:0 acyl chains).

Fig. 1. Partially relaxed ^2H NMR spectra of multilamellar dispersion of DLPC- d_{46} , containing 50 wt.% H_2O in the L_α phase at 30°C , obtained using quadrupolar echo method.





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1985 January 9

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

Dear Barry,

Call for Papers: 1985 FACSS Meeting

The 12th FACSS Meeting will sponsor an expanded NMR program, broadly covering fundamental research and new applications of NMR. It will be held on September 30 through October 4 at the Marriott and Adam's Mark Hotels in downtown Philadelphia. The symposia and their organizers are listed below.

"Solid State NMR of Synthetic and Biopolymers", Alan English, DuPont.

"NMR: Catalysts, Surfaces and New Methods", Kurt Zilm, Yale Univ.

"Novel Applications of NMR Imaging", Allen Garroway, Naval Research Labs

"Analytical Applications of NMR", Robert Santini, Purdue Univ.

"Biological Applications of NMR", Walter Gerasimowicz, USDA

"High Resolution NMR of Polymers", Martha Bruch, Syracuse Univ.

There will also be a general session and a poster session on NMR. Contributed papers are welcomed. The deadline for titles is March 15, and for abstracts is June 1.

Sincerely,

Rodney D. Farlee
NMR Program Chairman

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
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TELEPHONE (0223) 66499

TPPI in Pure Phase Two-Dimensional Correlation

Experiments

The advent of pure-phase two-dimensional correlation spectra is probably one of the most significant advances in two-dimensional NMR to date, and we therefore feel it important to comment on a recent contribution (TAMU 313 p.38) concerning the use of Time Proportional Phase Incrementation (TPPI) in two-dimensional correlation experiments, as originally described by Marion and Wüthrich (1).

The only effect of the TPPI procedure is to add an apparent offset of $1/2$ (SW1) to all the observed f_1 frequencies. The purpose of this is to shift the apparent spectral width in f_1 from $-1/2$ (SW1) $\longrightarrow +1/2$ (SW1) to $0 \longrightarrow +$ (SW1), so effectively avoiding the need to discriminate the signs of the f_1 frequencies (this is entirely analagous to the method of Redfield and Kunz for achieving quadrature detection in one-dimensional experiments while using real Fourier transforms (2)).

This shift of $1/2$ (SW1) is entirely "transparent" to the user - a spectrum acquired using TPPI in t_1 , and with the transmitter placed centrally, appears identical to one acquired using echo selection, except for the all-important replacement of phase-twisted lineshapes by pure-phase lineshapes. There is no restriction on the relative values of SW1 and SW2, nor is there any reason to expect their values to be connected. The value of

SW1 used in the original paper of Marion and Wuthrich was chosen purely to optimize digital resolution in f_1 , and the relationship $SW1 = 2/3 SW2$ arose only through coincidence. In confirmation of this, several recent experiments from the Zurich group (e.g. 3-5) employ equal values for SW1 and SW2 in conjunction with the TPPI procedure, although in only one case is this stated explicitly (4).

We would also like to point out that the TPPI method, although superficially dissimilar, is in fact very closely related to the method of States, Haberkorn and Ruben (6). The former method is appropriate when a real Fourier transform is used in t_1 , whereas the latter generates data suitable for a complex Fourier transform with respect to t_1 . Both methods are generally applicable to any experiment in which cosine and sine amplitude modulated data sets can be obtained separately (i.e. correlation experiments). A manuscript dealing in detail with the experimental and theoretical aspects of these procedures has been submitted to JMR.

Please credit this contribution to Jeremy Sanders' account.

David Neuhaus

David Neuhaus

James

James Keeler

- (1) D. Marion and K. Wüthrich, Biochem. Biophys. Res. Commun., 113, 967 (1983).
- (2) A.G. Redfield and S.D. Kunz, J. Magn. Reson., 19, 250 (1975).
- (3) G. Wagner, J. Magn. Reson., 55, 151 (1983).
- (4) D. Neuhaus, G. Wider, G. Wagner and K. Wüthrich, J. Magn.

Reson., 57, 164 (1984).

(5) D. Neuhaus, G. Wagner, M. Vařák, J.H.R. Kagi and K. Wüthrich,
Eu. J.Biochem., 143, 659 (1984).

(6) D.J. States, R.A. Haberkorn and D.J. Ruben, J. Magn. Reson.,
48, 286 (1982).

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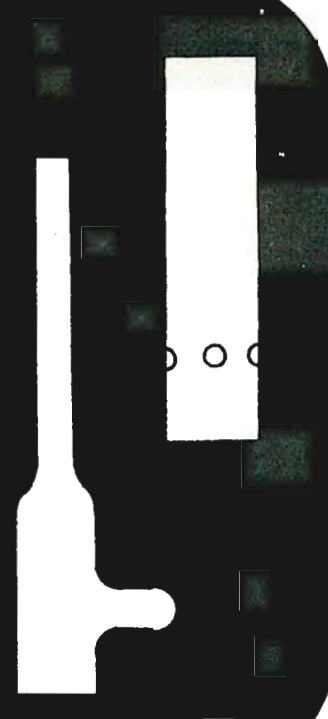
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RESEARCH AND DEVELOPMENT

December 31, 1984

C10
TAMU NMR Newsletter
Wha-6-84

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

Dear Dr. Shapiro:

CONTROL OF AN NMR SPECTROMETER FROM HOME

Since our spectrometers operate on a 24 hour basis, a remote terminal to monitor, control and program them from home "tis a consumation devoutedly to be wished". Toward this end, we have modified one of the terminals on our JEOL GX-270. The line to the main console terminal (TT0:) was converted into a dual access line by the addition of a modem splitter between the 25 pin DP connector on the back of the terminal. The splitter allows a third terminal to share the line via a modem and function as the console terminal (TT0:). The spectrometer makes no distinction between the in-lab terminal and home terminal, treating input from either one identically. (Note: Whatever is typed on one terminal shows up on the other terminal.)

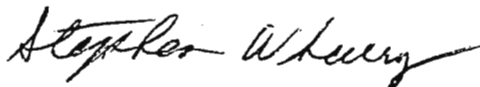
This particular modem splitter only passed the RS-232 lines, thus, two ports needed to be rewired to connect the lines necessary for graphics. Lines 9 through 13 and 21 through 25 were directly connected between the ports used for the spectrometer and the in-lab graphics terminal. Since the graphics are not transportable at this time over RS-232, it is not necessary or feasible to hook the graphics to the third terminal.

The port used for the third terminal is connected to a bi-directional printer buffer which is then connected to a modem. This is accessed over the telephone using a matching modem and a standard VT-100 emulating terminal. The whole system was rather inexpensive, costing just under \$2500 and can be set up by any layman slightly familiar with computer communications.

The third terminal can be used to monitor or control the spectrometer or perform any system work necessary such as pulse programming or building/testing indirect command files. It is even possible to shim the spectrometer over this line, though this is about 2.2 times slower than normal since the third terminal operates at 2400 baud.

As mentioned above, the graphics are output to the JEOL terminals over non-standard lines. Although this is necessary to increase the speed of data display to the screen, it severely hampers transport of the graphics over long distances. In fact, line 8 (used in some higher forms of RS-232 communications) is used to transport graphics information and must be disconnected in the line going to the modem; otherwise, the intensity of the graphics decrease to such a point that the spot and cursor features will not work.

Sincerely,



Stephen Wharry
144 Petroleum Laboratory
(918) 661-9793

Lines 1-7 and 20 connected to all ports.

Lines 8-13 and 21-25 connected to computer input and graphics terminal.

Line 8 must be disconnected for third terminal.

Microbuffer in-line from Inmac.

9600 baud input, 2400 baud output.

Input: Receive pin #2, transmit pin #3.

Output: Receive pin #3, transmit pin #2.

No hardware handshaking lines connected.

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DALHOUSIE UNIVERSITY
HALIFAX, CANADA
B3H 4J3

January 14, 1985

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

Dear Professor Shapiro:

Re: ^2H NMR Order Profiles of Long Chain Dicarboxylic Acids

A number of years ago,¹ it was reported that the di-K and di-Rb salts of docosanedioic acid form lamellar phases in the presence of 45-65% water at elevated temperatures. We have prepared tetracosanedioic acid (24 carbon atoms) and have found that its di-caesium salt forms a lamellar liquid crystal at room temperature in the presence of 50 wt% water. The ^2H NMR spectra at various temperatures are shown in the figure. The amphiphile is essentially totally deuterated at the carbons adjacent to the carboxylates and approximately 25% deuterated at all twenty other positions.

At 20°C, the spectrum collapses to an axially symmetric pattern with most deuterons giving rise to a splitting of 17.5 kHz although inner shoulders of 11 kHz are evident. The order profile of the chain is therefore essentially constant, and relatively low in comparison with the plateau regions of single headed amphiphiles in lamellar phases.

Spectrum f is that of the C24 diacid in bilayers of dilauroylphosphatidylcholine in the L_α phase. The main splitting is 26 kHz and there is also significant intensity in the central part of the spectrum. This whole pattern is superimposed on a much broader signal. The broad component decreases in intensity with increasing temperatures and is absent when the host is dimyristoyl-phosphatidylcholine. In light of previous work^{2,3}, the broad component is assigned to a conformation of the diacid which spans the bilayer and does not undergo rapid rotation about its long axis. The central portion is due to a horseshoe conformation with the chain bent back on itself such that the C-D bonds go through the magic angle. This demonstrates the feasibility of using this technique as a spectroscopic ruler of bilayer thickness, even in non-orienting systems. Both systems described here will be receiving further attention when our new Bruker MSL200 high power spectrometer arrives in late February. Please credit this contribution to Rod Wasylishen's account.

Sincerely,

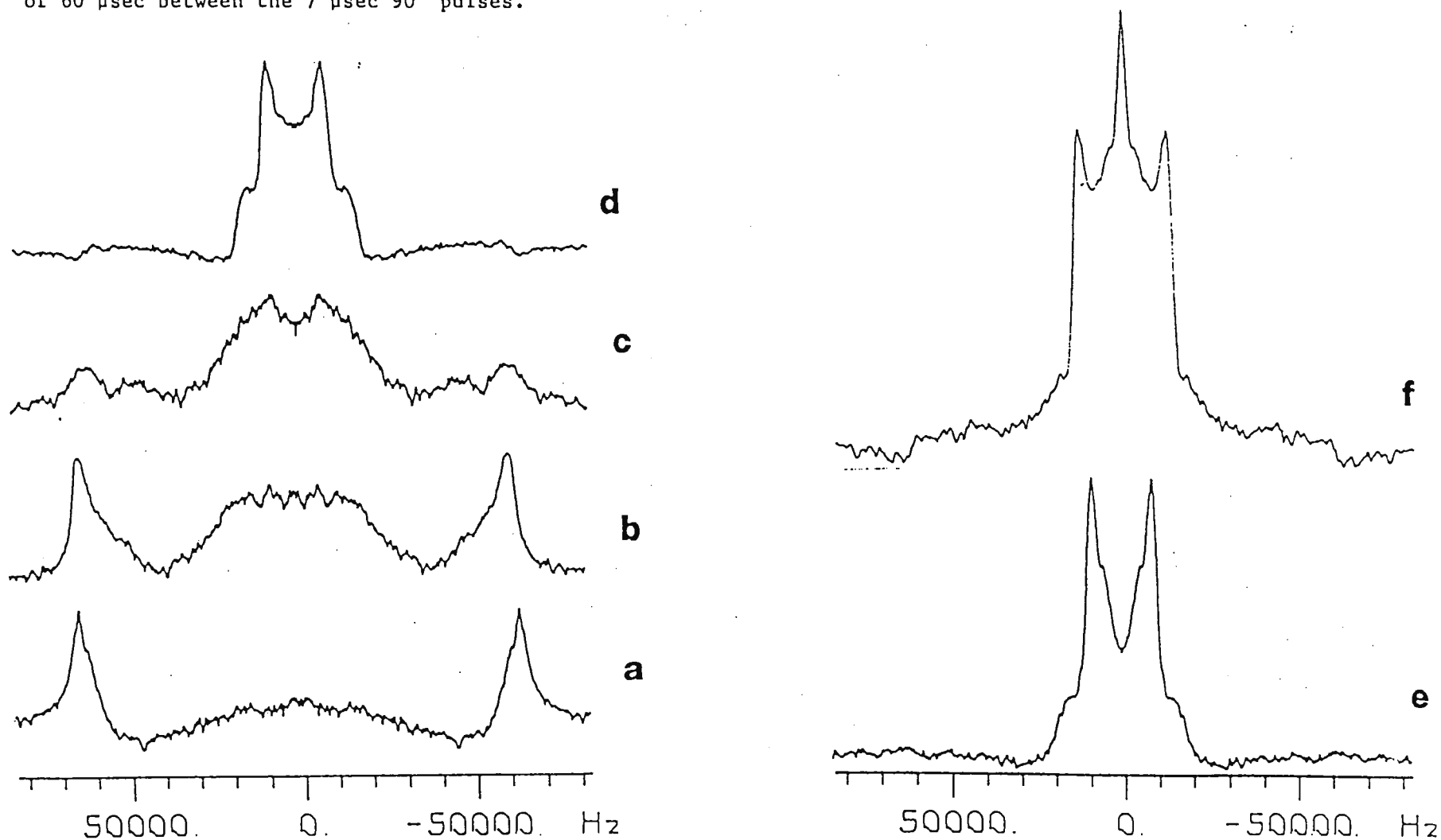
Bruce J. Forrest
Assistant Professor (Research)

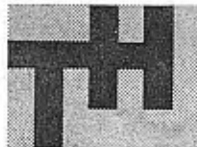
References

1. B.R. Gallot, Mol. Cryst. Liq. Cryst. 13, 323 (1971).
2. J. Seelig, H. Limacher, and P. Bader, J. Am. Chem. Soc. 94, 6364 (1972).
3. B.J. Forrest, L.H. de Carvalho, L.W. Reeves and C. Rodger, J. Am. Chem.

Figure Legend

^2H NMR spectra of dicesium tetracosanedioate (a-e) at -40, -20, -5, 5, and 20°C, respectively. Spectrum f is of the free acid in dilauroyl PC liposomes at 20°C. All spectra were taken on a Nicolet 360 NB spectrometer, which has a maximum spectral width of 167 kHz, using a high power ^2H probe (Probe Systems Inc.) and employing a quadrupole echo sequence with a delay of 60 μsec between the 7 μsec 90° pulses.





DELFT UNIVERSITY OF TECHNOLOGY

Laboratory of Organic Chemistry

Jullianalaan 136
~~2628~~ 2628 BL DELFT
 The Netherlands

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

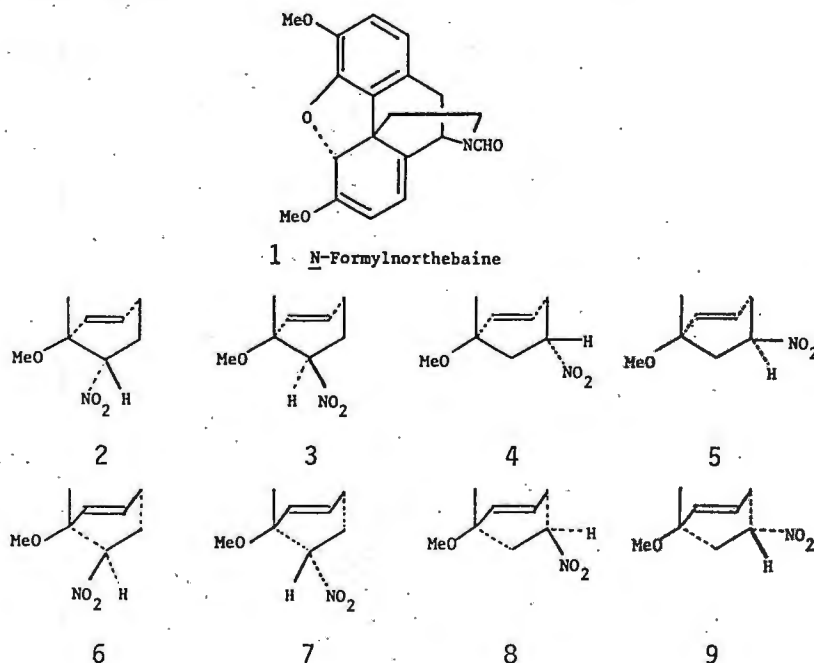
Delft, January 16, 1985
 LM/mk/39

Dear Professor Shapiro,

Detection of E- and Z-isomers in N-Formylmorphinans with the use of 2D-J-spectroscopy

We would like to report an important application of 2D-spectroscopy in structure elucidation.

In our search for new analgesics based on the modified morphinan skeleton, we prepared a Diels-Alder cycloaddition product from N-formyl-northebaine (1) with nitroethene. This reaction may give rise to eight isomers (Scheme 1).



Scheme 1

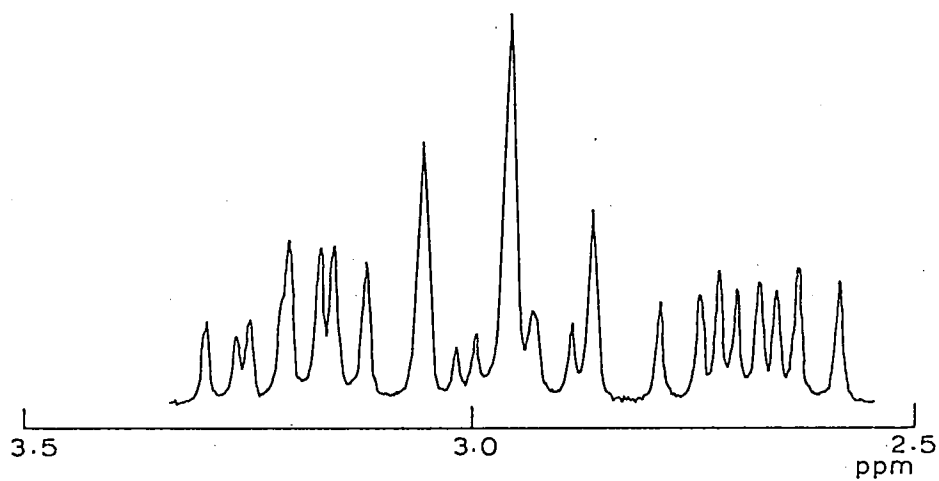
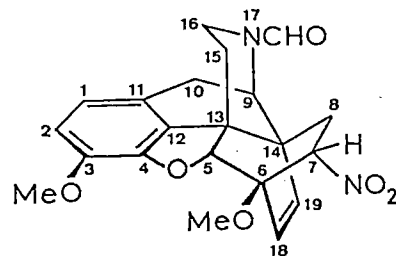
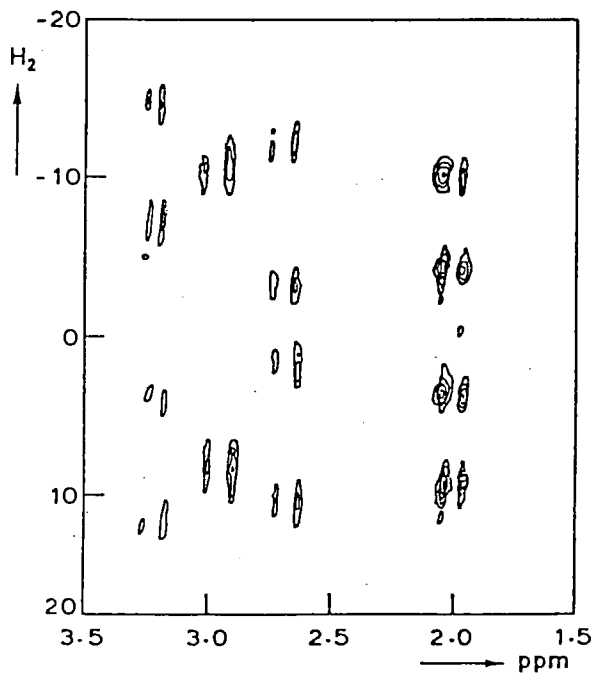


Fig. 1. Fragment of the ^1H NMR spectrum of compound 2.



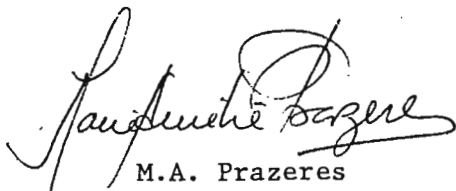
Compound 2 of Scheme 1.

Fig. 2. Fragment of the homonuclear 2D J-spectrum of compound 2 (counter plot) showing coupling patterns of H-10 α , H-10 β , H-8 β , and H-8 α , respectively.


In order to establish the position of the etheno bridge at C-6 and C-14 and of the nitro substituent, the product obtained was investigated using ^1H NMR. The ^1H spectrum of this type of compound is usually rather simple since the signals are spread out over a large shift range. In this case, only one aldehyde resonance was observed, so we expected the N-formyl group to be exclusively E or Z. However, some of the multiplets were rather puzzling to us at first sight (e.g. Fig. 1). The problem was solved by a 2D J-spectrum which showed several pairs of identical coupling patterns (Fig. 2). This may be attributed to the presence of both the Z and E isomers of the formyl group. It may be expected that the formyl function has a neglectable influence on the conformation of the ethenoisomorphinan skeleton. From the 2D-experiment, we also learned that the puzzling multiplets, actually, were overlapping multiplets of the Z and E isomers in a 1:1 ratio.

Then with the use of a COSY spectrum all signals of both the Z and the E isomer could be assigned and from an analysis of the ^1H coupling constants it could be concluded that the product consisted of a mixture of the Z and E isomers of 2 with the nitro group in position 7 α and the etheno bridge between C-6 α and C-14 α .

Sincerely yours,

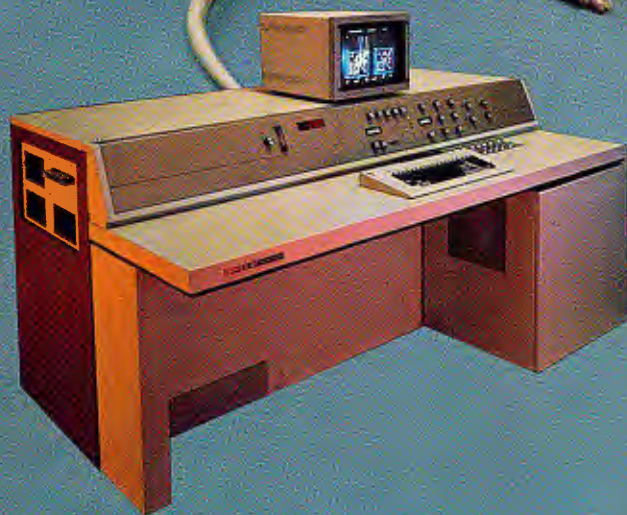
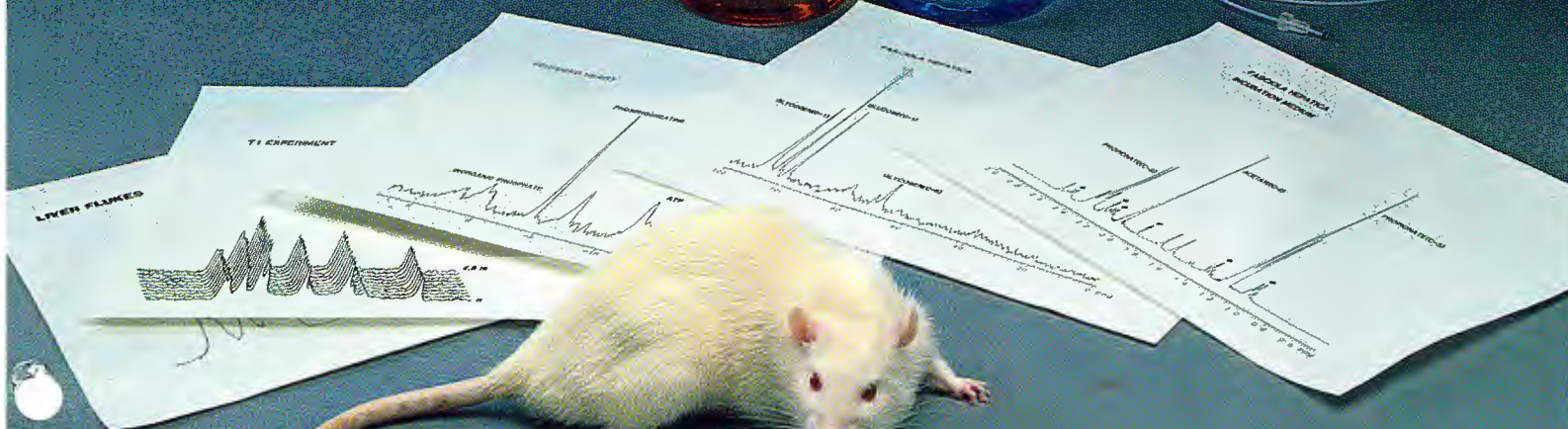

M.A. Prazeres


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Bern, January 7, 1985

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

Postdoctoral NMR position available at July 1, 1985

Dear Dr. Shapiro,

With the installation of our new 400 MHz NMR spectrometer a postdoctoral research associate position is available for an applicant with a Ph.D. in chemistry, with extensive experience in magnetic resonance, particularly modern pulse techniques, and a strong interest in chemical structure problems. The candidate should be cooperative and experienced in computational analysis as well as in interpretation of NMR data using larger computer systems.

The position opens at July 1, 1985 and is free for a 1-2 years period, provided that the working permit, which is obligatory on non-Swiss candidates, can be obtained and that the government agrees.

The candidate is expected to participate in NMR research projects and will have to solve complicated structural problems of the various research groups in our institutes. He will further assist in teaching and in maintenance of our NMR systems.

The NMR laboratory at the University of Berne - which is placed in a nice landscape in the center of Switzerland - includes a new 400 MHz (Bruker AM 400 WB) spectrometer, fully equipped for multinuclear operation, with an ASPECT 3000 data system and connected with an autonomous data station, a 100 MHz (Varian XL-100-15) machine and several low field CW-spectrometers.

Interested applicants should submit two letters of reference, a copy of their thesis, a list of publications, a summary of special interest in the field of NMR and a curriculum vitae.

Sincerely yours

Peter Bigler

mailing address:
Director of the Institute of organic chemistry
University of Berne
Freiestr. 3
CH-3012 Berne Switzerland



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January 17, 1985

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

Dear Barry,

Re: ^{31}P MAS NMR Spectra of Phosphine Complexes

In this letter we will describe some ^{31}P MAS and CP-MAS experiments that we have been doing on our CXP-200 equipped with a CP-MAS probe. We found that the spectra could be acquired using normal acquisition with high power decoupling but the necessary recycle times were very long (> 10 min). By using cross polarisation we can cut this down to about 10-30 s. With good tuning the spectra were always visible after one pulse.

In the figure, the bottom spectrum is that of a cis- $\text{PtCl}_2(\text{Phosphine})_2$ complex. Because of the fairly large anisotropy of the phosphorus atoms, the spinning side bands are about the same size as the ^{195}Pt satellites. Clearly this could be confusing in more complex spectra. The top spectrum is of the same compound but it was acquired using the side band suppression pulse programme TOSS.PPG*. Both spectra are the sum of four scans with a contact time of ~0.5 ms.

We feel that ^{31}P MAS and CP-MAS has much untried potential especially for compounds which are insoluble or are fluxional, and further work is underway in our lab on some complexes with known crystal structures.

Yours sincerely,

Bob Leninski
R.E. Leninski,
Manager

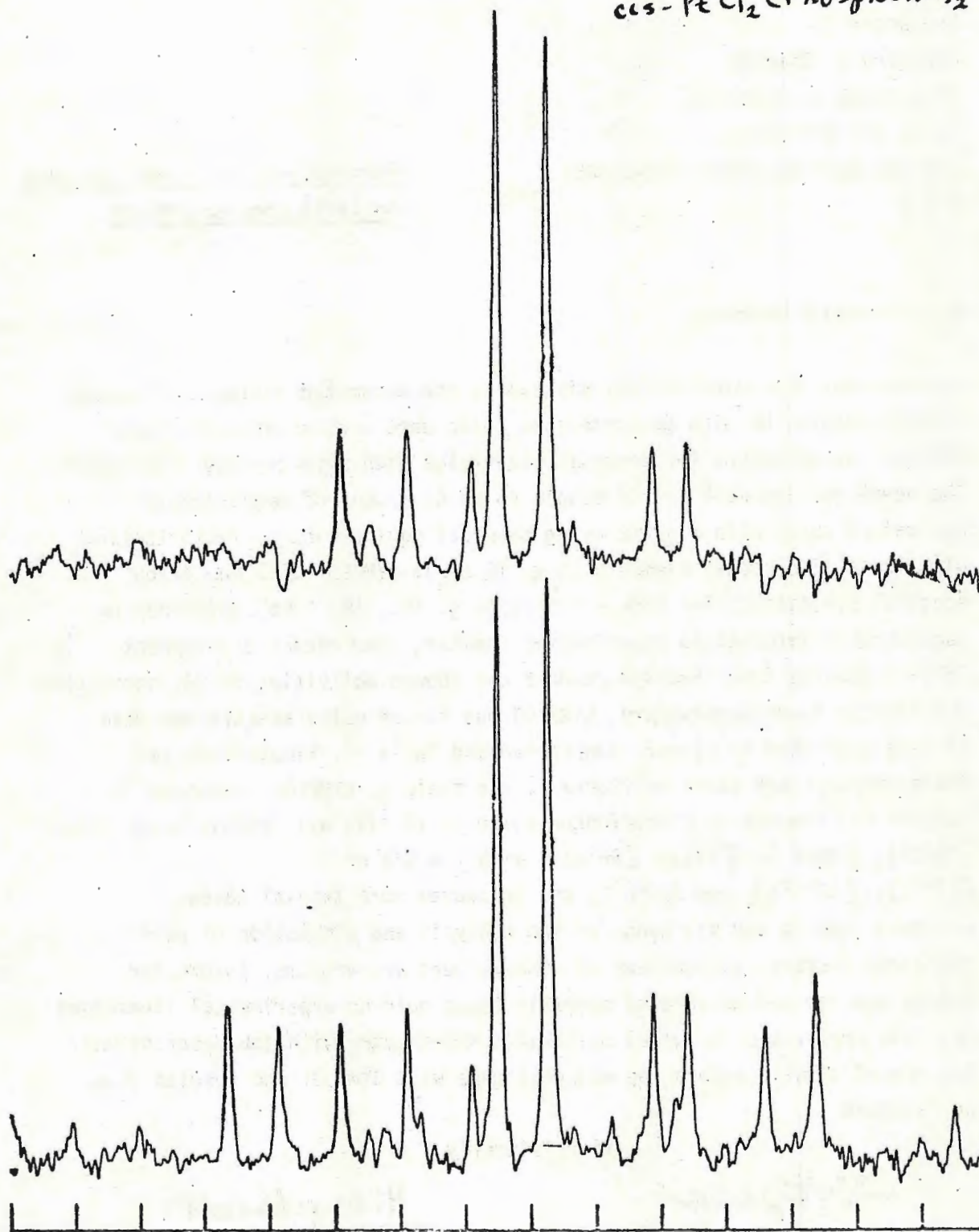
Tim Allman
Tim Allman

/la

* Tim Allman has written a Pascal programme which calculates and loads the required delays for TOSS.PPG based upon the 90° pulse and the measured spinning rate. It will appear in the next ABACUS catalogue but we will send the programme to those who are interested now upon receipt of an initialised floppy disk.



cis-PtCl₂(Phosphine)₂



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

Dipl. Chem. Michael Engelhardt

4000 Düsseldorf, den 21.01.1985
 Universitätsstr. 1/26.42.U1.32
 Telefon 0211 - 311-2289/2287
 Telex 8 587 348 uni d

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

Revised Version of the Spectral
Analysis Program CYMPLLOT

Dear Professor Shapiro,

we continued our interests for simulation and automated analysis of complex HR-NMR-spectra. We wish to present an up-to-date version of our program CYMPLLOT, which stands for composite particles with symmetry and plot option. The novel version will tackle single spins or groups of magnetically equivalent spins with $I \geq 1/2$ using chemical equivalence by factorization with up to 12 symmetry elements (e.g. in D_{3h}). CYMPLLOT will now allow spectral simulations for higher nuclei (e.g. 1H , ^{11}B , ^{93}Nb) which are of considerable interest to experimental chemists. Our recent development follows demands from TAMU-NMR-readers who showed activities in CD_3 -structures and similar Deuteronchemistry. CYMPLLOT was tested using spectra and data of B_2H_6 published by Farrar, Johannesen and Coyle ¹⁾. Simulations and NMR-parameters are shown in figure 1. and table 1. CYMPLLOT, designed in FORTRAN IV, running on a Telefunken computer TR 445, will handle cases like : $[ABCDE]_2$, $[ABCX_3]_2$, $[AX_3]_3$, $[ABX_9]_2$, with $I = 1/2$ or : $[A^{3/2}X]_3$, $[AB^{9/2}X]_2$ and $ABCDE^1X_3$ and of course more trivial cases. We would like to try our hands on the analysis and simulation of more practical systems, so problems of TAMU-readers are welcome. Interested groups are invited to send us magnetic tapes holding experimental lineshapes or, less preferable, original calibrated NMR-spectra with job descriptions. For reward we will return the magnetic tape with CYMPLLOT and results from our studies.

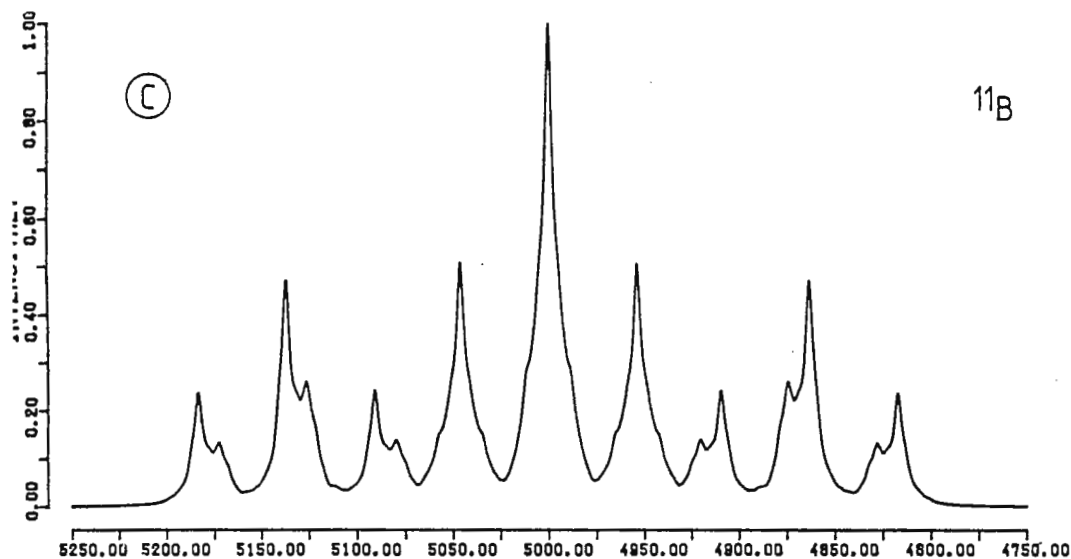
Yours sincerely



(G. Hägele)



(M. Engelhardt)



Parameters	Values [Hz] at 100 MHz
$\Delta(\nu_{H_t} - \nu_{H_b})$	450.
$1J_{H_bB}$	46.2
$1J_{H_tB}$	133.
$2J_{H_bH_t}$	7.2
$2J_{H_bH_b}$	0
$2J_{H_tH_t}$	3.
$1J_{H_tB}$	4.
$3J_{H_tH_t}$ cis	14.
$3J_{H_tH_t}$ tr	6.
$2J_{BB}$	-5.

Table 1. : NMR-parameters for simulation of figure 1. Data were taken from ref.1

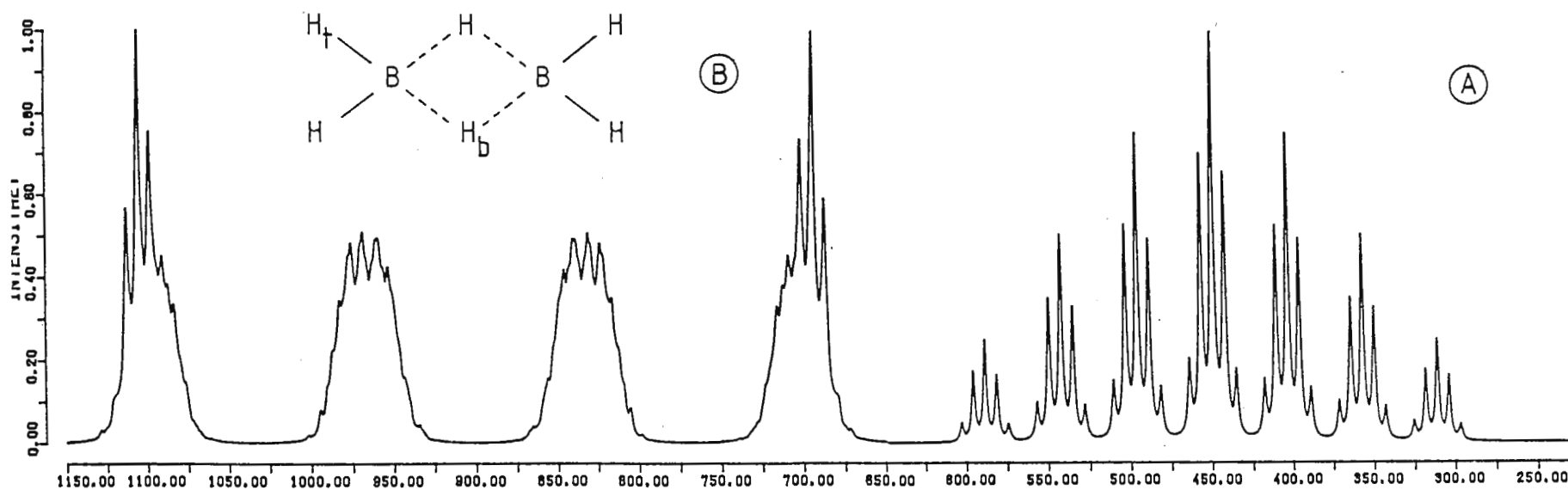


Figure 1. : Simulated spectra of B_2H_6 using the novel version of CYMPLLOT A) and B) were simulated with a half-height width of 2.5 Hz and C) with 4.5 Hz

A) bridging protons H_b B) terminal protons H_t C) boron spectrum

(ref. 1. : T.C. Farrar, R.B. Johannesen and T.D. Coyle, J. Phys. Chem. 49(1), 281 (1968)



UNIVERSITY OF MISSOURI-COLUMBIA

College of Arts and Science

Department of Chemistry

 123 Chemistry Building
 Columbia, Missouri 65211
 Telephone (314) 882-2439

January 22, 1985

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

2D Correlation Spectroscopy and
Coupling Constant Signs

Dear Professor Shapiro:

The heteronuclear chemical shift correlation spectroscopy with homonuclear decoupling in the proton dimension has been shown to provide a convenient way to measure the magnitude and relative sign of the coupling between proton and an additional nucleus X (e.g., JACS 1984, 100, 7046). This application is particularly advantageous in cases where the ^1H spectrum is unresolved and the nucleus X is of low abundance. The advantages are (1) The proton signals are decoupled and (2) They are separated by the ^{13}C signals in the other dimension thus eliminating most of the overlapping. The following examples illustrate how satellites can be conveniently detected by this technique.

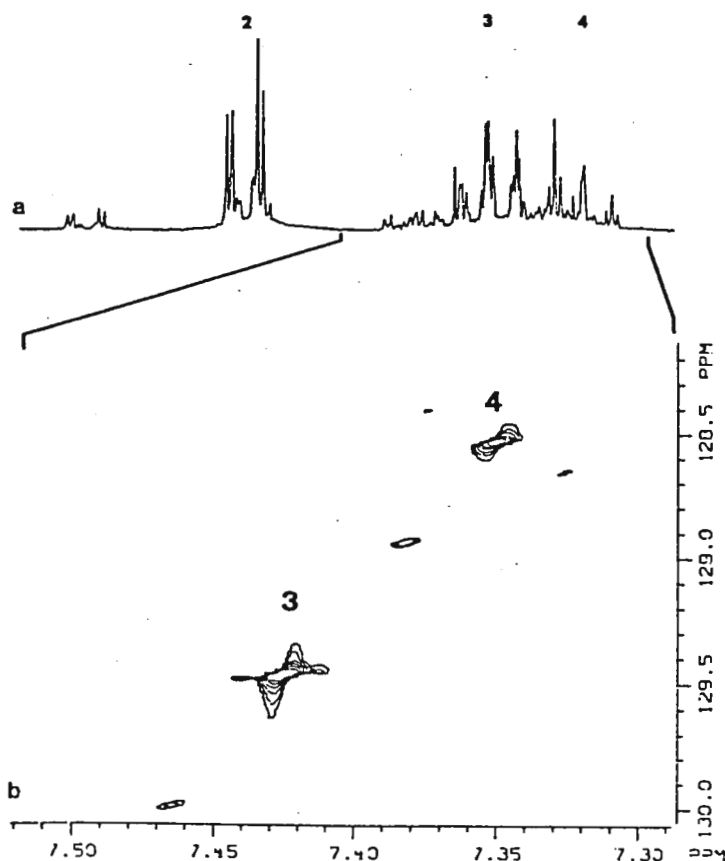


Fig.1 (a) The ^1H spectrum of tetraphenyllead; (b) The portion of the ^1H - ^{13}C COSY containing the signals of carbons and protons 3 and 4. Both the magnitude and the relative signs of the ^{207}Pb - ^{13}C and ^{207}Pb - ^1H coupling constants have been determined. For position 3, the Pb-C and Pb-H couplings are of the same sign, while for position 4, the couplings are of opposite sign.

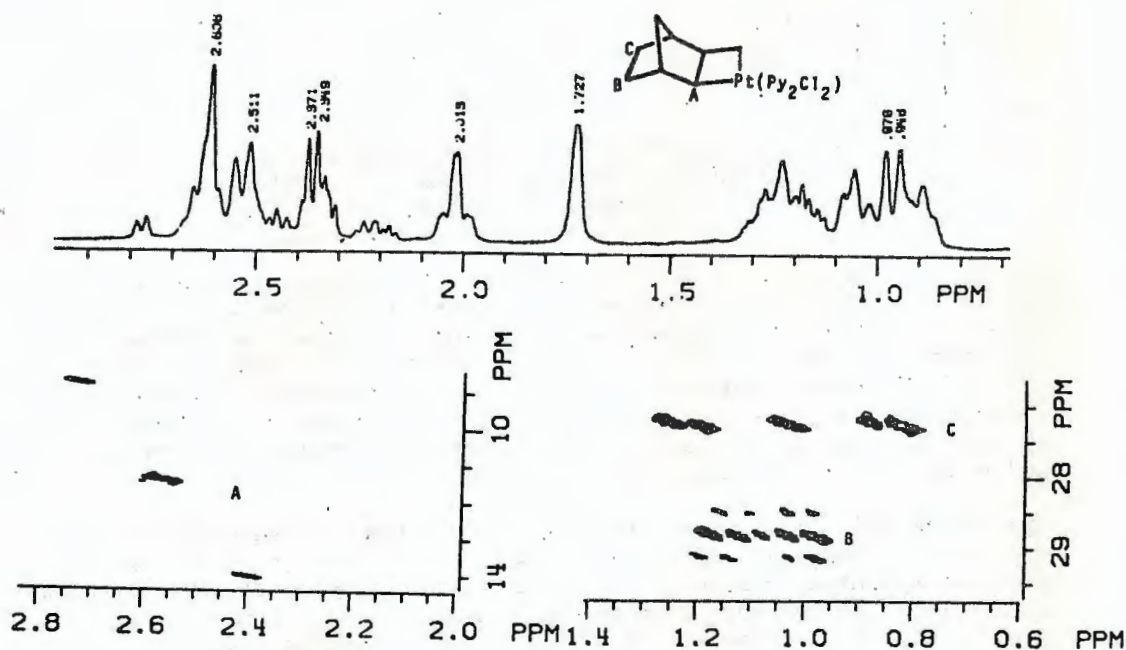


Fig. 2 Aliphatic portion of the 1-D ^1H spectrum for the Pt complex shown together with expansions of two sections of the ^1H - ^{13}C CPMG contour plot. Only one Pt-H coupling constant for the ^1H at 2.05 can be determined from the 1-D spectrum, however, all the Pt-H coupling constants are available from the 2-D experiment. Homonuclear J couplings have been eliminated except for nonequivalent geminal protons, i.e., B and C, by the selective flip of distant protons. Positions of peaks are determined by chemical shifts and heteronuclear J couplings with the ^{195}Pt spin. The contour maps show that J_{HAPt} and J_{CAPt} have opposite signs, while for position B the couplings are of the same sign. The protons on carbon C are not coupled to Pt, however, the geminal coupling constant is directly measurable.

Sincerely yours,

Dick

Richard B. Taylor
NMR Spectroscopist

Tuck C. Wong

Tuck C. Wong
Associate Professor
of Chemistry

245-273 Wellington Road
Mulgrave, Victoria, Australia 3170
P.O. Box 264, Clayton 3168
Telephone 560 7066

File: 107-80

Dr. B.L. Shapiro,
TAMUNMR Newsletter,
College of Science,
Texas A&M University,
COLLEGE STATION, TX. 77843. U.S.A.

11th January, 1985

Dear Dr. Shapiro,

re: TRANSMISSION OF SPECTRA BETWEEN A BRUKER
ASPECT COMPUTER AND A COMPUTER WITH A
FORTRAN 77 COMPILER

In our work using Bruker WP and CXP200 spectrometers, we have much recourse to storing large numbers of spectra on such media as magnetic tape, or to process the spectral data using other packaged software than that provided by Bruker. We have decided to use our in-house VAX 11/780 computer system for both and have developed a program, named VAXNET, which emulates the Bruker supplied program, SPECNET, on the VAX. As this program may be of general interest we describe below some of its features.

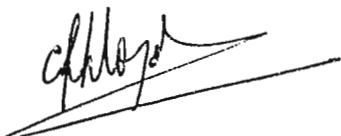
Apart from specific system routines, the program is essentially written in Fortran 77 and should be readily adaptable to different computer operating systems. It provides for multiple file transmissions from, and to, an Aspect using SPECNET. Multiple file transmission from an Aspect is accomplished using normal automation routines, while multiple file transmission to the Aspect is restricted to files with consecutive extension numbers starting from .001. A more comprehensive error message system than that supplied by SPECNET is provided. The data are stored as it is received in the user directory area of the VAX disc with the file name constructed from the file definition table transmitted by SPECNET. As the 24-bit data words are distributed over four 8-bit bytes in the files, this being the method of transmission by SPECNET, the data words of the original spectrum or f.i.d. will have to be reconstructed for data manipulation. This method of storage of the transmitted file has been adopted to facilitate the two-way transfer of spectra, as most of our spectra which will be transferred to the VAX will be stored on magnetic tape for later retrieval.

We have successfully used this program for bidirectional transmission of files ranging in size from 1-16k using both the FTQNM and DISCXP programs. The length of the RS232 transmission line has limited us, so far, to a baud rate of 2400.

We will be submitting this program to ABACUS, the Bruker users group, in source form only, with detailed release notes.

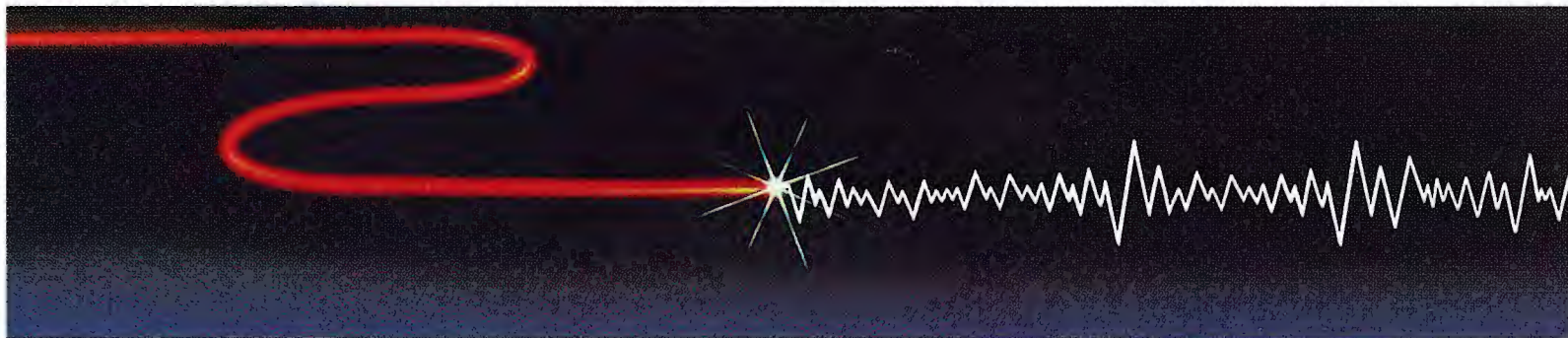
Please credit this letter to Professor Ian Rae's account.

Yours sincerely,



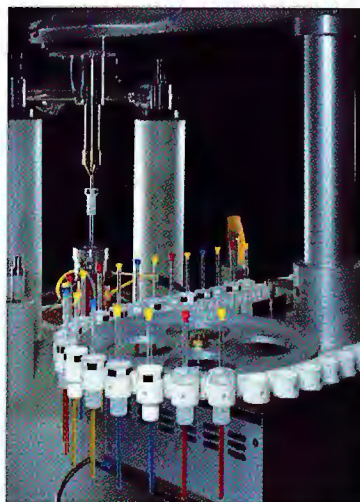
C.P. LLOYD
Senior Research Officer
BHP Melbourne Research Laboratories

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NMR Systems designed to solve problems.

HARVARD MEDICAL SCHOOL

BRIGHAM AND WOMEN'S HOSPITAL

Associate Professor of Physiology
and Biophysics in the
Department of Medicine
Director, NMR Laboratory

JOANNE S. INGWALL, Ph.D.

221 Longwood Avenue
Boston, Massachusetts 02115



75 Francis Street
Boston, Massachusetts 02115
Telephone (617) 732-1975

January 6, 1985

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

Re: ATP reaction rates in the isolated heart

Dear Professor Shapiro:

To assess the relationship between mitochondrial ATP synthesis and creatine kinase flux in the heart, we used the ^{31}P -NMR technique of magnetization transfer to study reaction rates in the isolated rat heart at five levels of cardiac performance. Isolated hearts, placed in the bore of an NT-360 spectrometer, were perfused with Krebs-Henseleit buffer (without phosphate) and designed to develop a rate-pressure product (RPP) that ranged from 0 to 45,000 mmHg/min. Spectra were obtained after saturation at the (CP) or (γ -P)ATP resonances for 0 to 4.8 seconds. When the (γ -P)ATP resonance was saturated (Figure 1A and 1C), CP magnetization fell exponentially with respect to time, reflecting in part the transfer of ^{31}P from CP to (γ -P)ATP. The slope of the exponential decay was greater for the hearts that developed a RPP of 45,000 mmHg/min (example given in 1C) than for the hearts subjected to KCl arrest with a RPP of 0 (1A). Also, inorganic phosphate (P_i) magnetization decreased with respect to saturation time at (γ -P)ATP, partly reflecting the rate of ATP synthesis (1C). When the CP resonance was saturated, (γ -P)ATP magnetization decreased (1B), due to the reverse direction of the creatine kinase reaction.

All data were fit to the 2-site chemical exchange model of Forsen and Hoffman (1963). The T_1 values for CP and (γ -P)ATP were 2.06 ± 0.13 and 0.75 ± 0.08 sec ($N=22$), respectively, and showed no dependence on cardiac performance. These results are in accord with those from Nunnally and Hollis (1979). As the RPP varied from 0 to 45,000 mmHg and oxygen consumption rose from 5.9 to 45.8 $\mu\text{mol O}_2/\text{gram dry weight/min}$, the rate constant for the forward creatine kinase reaction, $k(\text{for})$, increased from 0.27 to 1.30 and the reverse rate constant, $k(\text{rev})$, increased from 0.31 to 1.14 sec^{-1} . Figure 2 shows the relationship between creatine kinase flux and cardiac performance. The discrepancy between the forward and reverse fluxes was unexpected and probably apparent, owing to ATP participating in reactions other than creatine kinase. Indeed, simultaneous double saturation at both CP and P_i may generate new values for the reverse flux that match those for forward flux (Ugurbil et al, 1984).

Rates of ATP synthesis were estimated only for six hearts that developed a RPP greater than 23,000 mmHg/min because of the low P_i signal in hearts at low levels of cardiac performance. The mean T_1 value for P_i was 0.81 ± 0.26 sec. Estimates of ATP synthesis from NMR were similar to values calculated from oxygen consumption and an ADP:O ratio of 3:1.

These studies demonstrate that the NMR technique of magnetization transfer can be adapted to the study of ATP reaction rates in the intact heart. Our results suggest that the creatine kinase reaction is coupled to the rate of ATP synthesis in the heart at different levels of cardiac performance.

Sincerely,



John A. Bittl, M.D.



Joanne S. Ingwall, Ph.D.

References

Bittl, J.A., Ingwall, J.S. Reaction rates of creatine kinase and ATP synthesis in the isolated rat heart: a ^{31}P -NMR magnetization transfer study. J. Biol. Chem., in press.

Forsen, S., Hoffman, R.A. Study of moderately rapid chemical exchange reactions by means of nuclear magnetic double resonance. J. Chem. Phys. 39:2892-2901, 1963.

Nunnally R.L., Hollis, D.P. Adenosine triphosphate compartmentation in living hearts. A phosphorus nuclear magnetic resonance saturation transfer study. Biochemistry 18:3642-2646, 1979.

Ugurbil, K., Maidan, R.R., Petein, M., et al. NMR measurements of myocardial CK rates by multiple saturation transfer (M.S.T.). Circulation 107:II-84 (abstract), 1984.

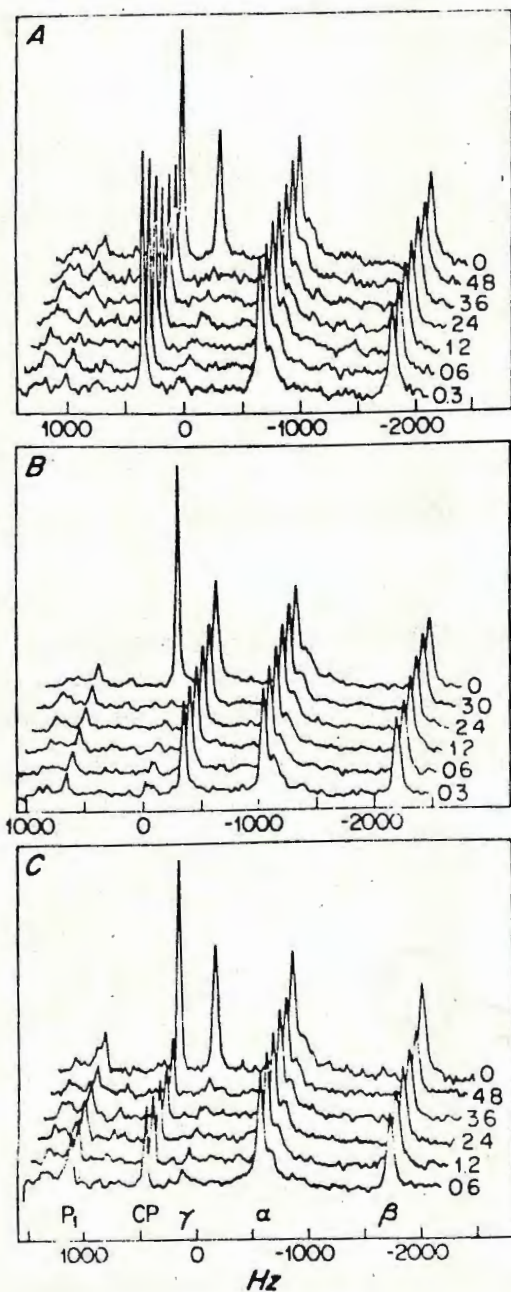


Figure 1: Stacks of NMR spectra after saturation at CP or (γ -P)ATP for 0 to 4.8 sec from KCl-arrested (A,B) and high workload (RPP=45,000 mmHg/min) hearts (C).

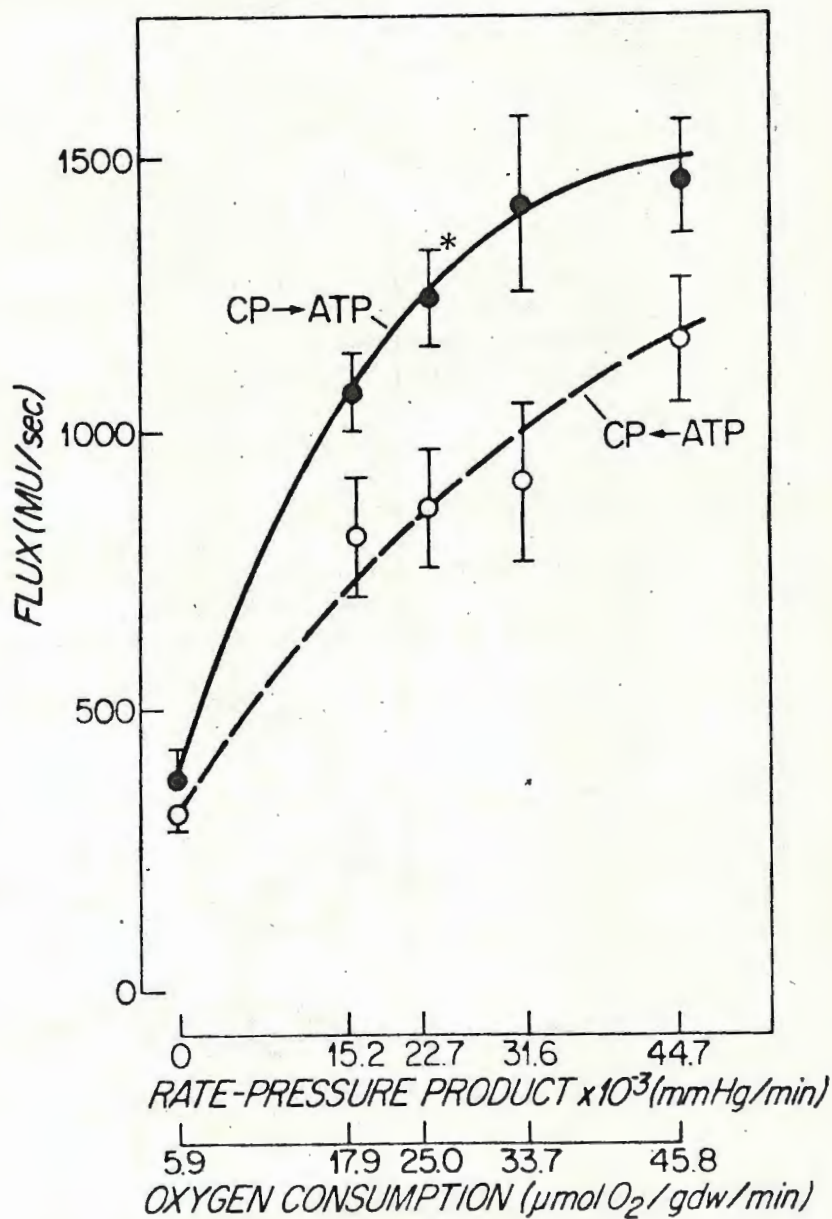


Figure 2: Relationship between creatine kinase flux and cardiac performance in the isolated heart.



The University of Arizona

College of Arts & Sciences
Faculty of Natural Sciences
Department of Chemistry
Tucson, Arizona 85721

1885

1985

A Proud Beginning

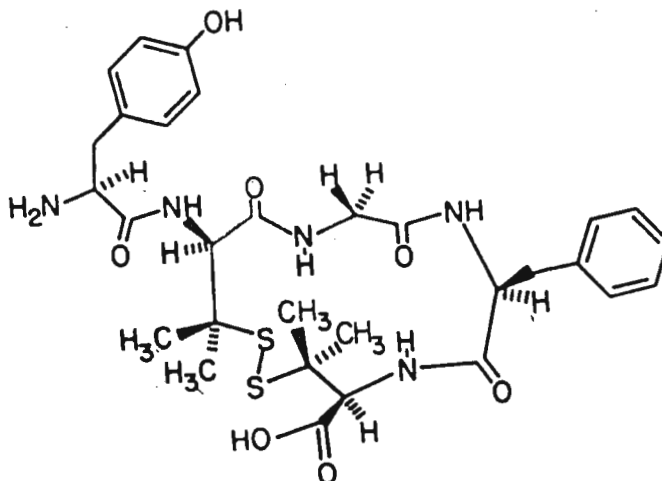
January 4, 1985

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

Re: 2D NMR Studies of a δ -Selective Cyclic Enkephalin

Dear Professor Shapiro:

The cyclic pentapeptide tyr-D-pen-gly-phe-D-pen (DPDPE) has been found to be the most δ -selective enkephalin. A knowledge of the solution conformation will be most important in understanding the binding. The proton chemical



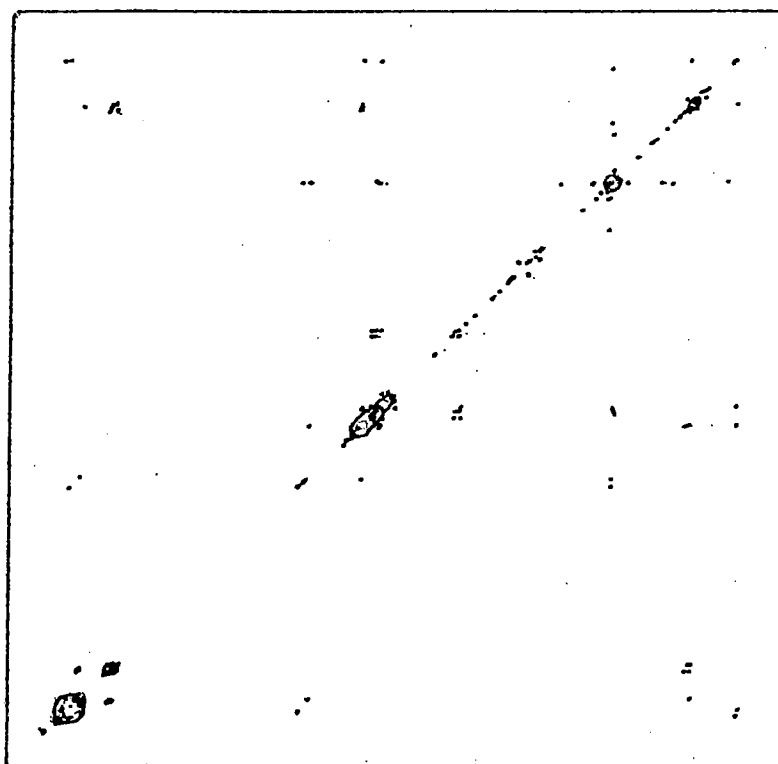
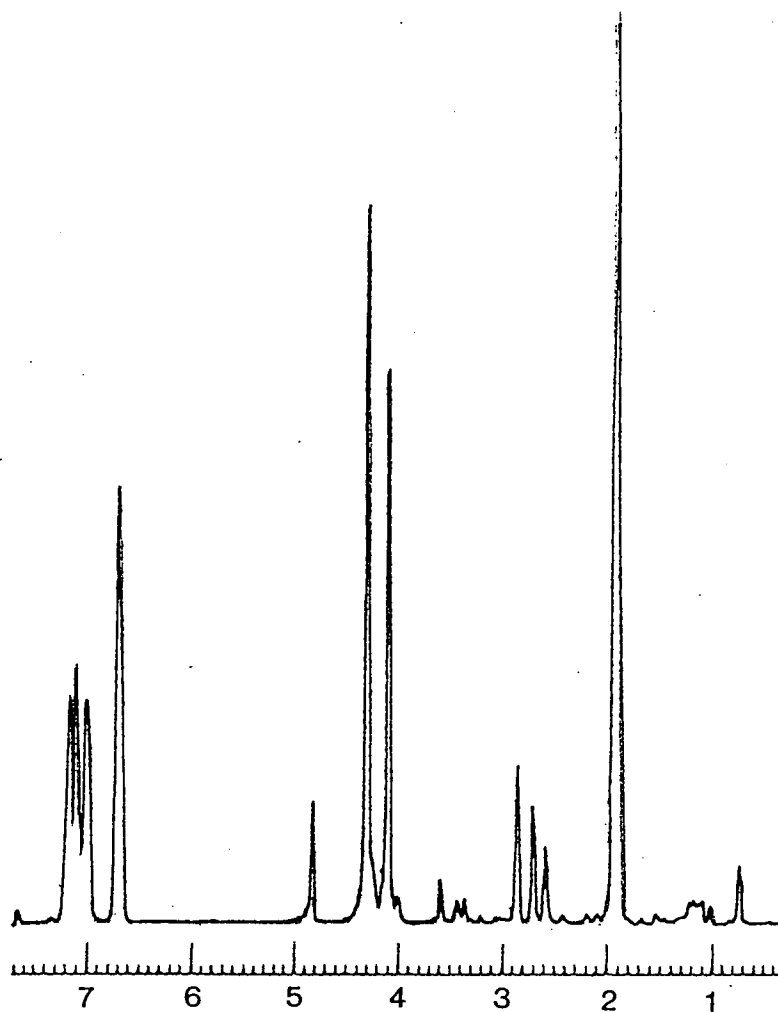
shift assignments were based on the COSY technique (D_2O solvent; WM-250 NMR). To remove the ambiguities in the assignments of the H_α and CH_3 groups of the D-pen² and D-pen⁵, the 2D NOE spectrum (which is reproduced here) was also obtained. The decoupler was set for selective irradiation of the H_2O resonance and the mixing time was set to 0.96 sec. The results of these experiments and the distance constraints are being used to obtain an energy minimized conformation.

Please credit this contribution to Mike Barfield's subscription.

Sincerely yours,

Lung-fa Kao
Lung-Fa Kao

Victor J. Hruby
Victor J. Hruby





University of Delaware

DEPARTMENT OF CHEMISTRY
NEWARK, DELAWARE 19716

January 23, 1985

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

Line Narrowing of Polymer Composites

Dear Barry:

Enclosed is the ^{19}F NMR spectrum of a polymer composite of poly(tetrafluoroethylene) (PTFE) and an inorganic filler. It was obtained by Larry Kasuboski, a graduate student in my laboratory, using the eight-pulse cycle of Rhim, Elleman and Vaughan to suppress dipole-dipole interactions among the fluorine nuclei. The spectrum shows a classic axially symmetric powder pattern, which is quite similar to spectra of highly crystalline PTFE reported in the literature. Most samples of PTFE available tend to be semicrystalline because they have been melted at some time. During recrystallization an amorphous portion is almost inevitably produced. From the NMR point of view the presence of an amorphous region is easily detectable as a rather prominent feature superimposed on the spectrum of the crystalline regions. Thus, it was a surprise to us to see such a spectrum indicative of a highly crystalline material when we examined the composite. It does not appear to be a physical mixture when examined visually, however it may be extremely finely divided. If it is not a physical mixture of so-called "virgin" PTFE with the second component, the fact that NMR shows it to be highly crystalline is indicative of an interesting effect of the preparation process under which this commercial material was made. This is, of course, a first result, and we are proceeding with further investigation of composites.

Best regards with the journal under its new name.

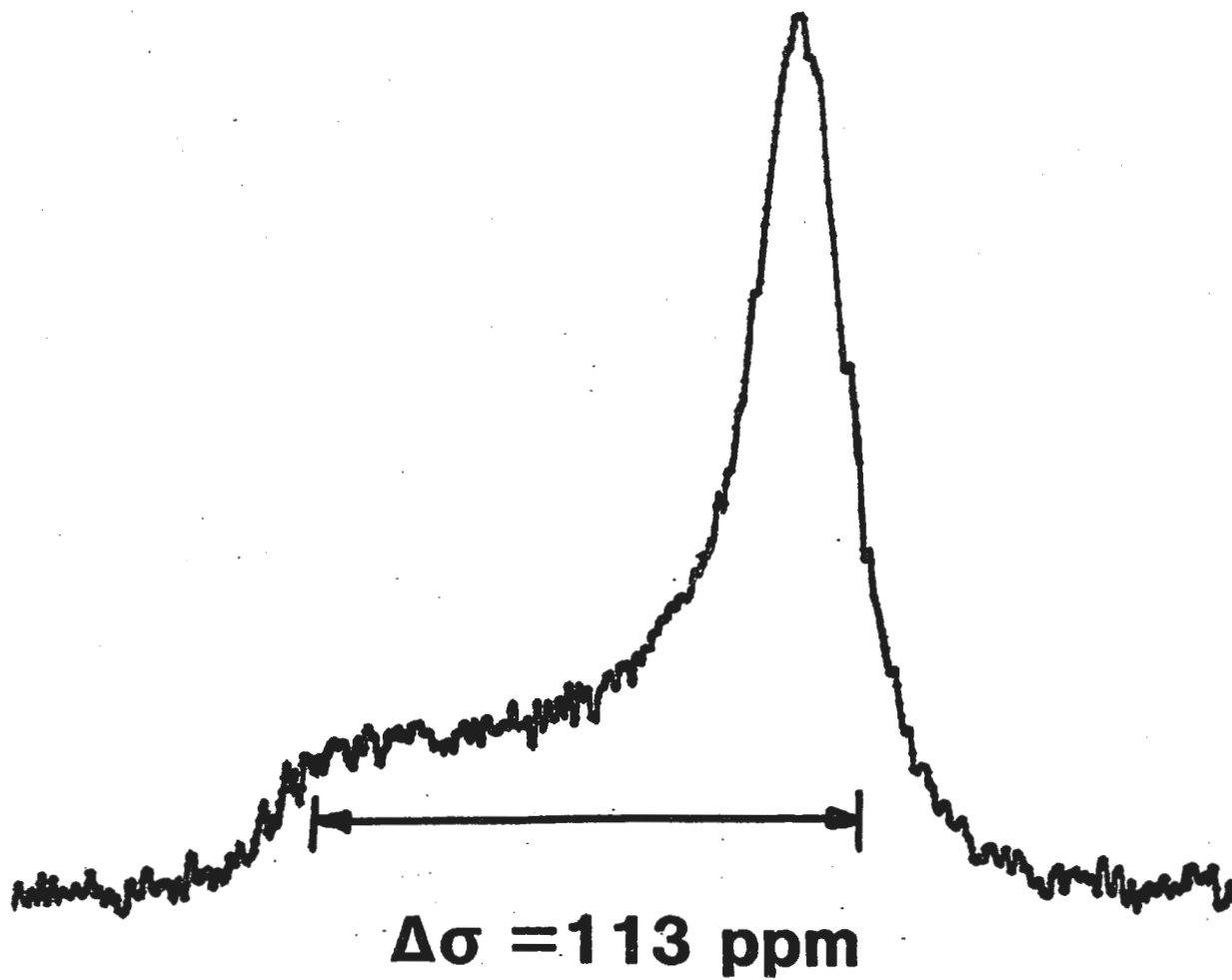
Yours truly,

Cecil

Cecil Dybowski
Associate Professor of Chemistry

sr

EIGHT-PULSE SPECTRUM OF PTFE COMPOSITE





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FACULTEIT DER WISKUNDE
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Prof. B.L. Shapiro
Texas A & M University
College of Science
COLLEGE STATION, Texas 77843
U.S.A.

Uw kenmerk

Uw brief van

Ons kenmerk

U9137/WV,AK,EdB/DvdW Datum

Onderwerp

January 16, 1985

Dear Prof. Shapiro,

Re: Two-dimensional exchange NMR in rotating solids:
A technique to study slow molecular reorientations

With 2D-exchange NMR one can correlate the frequency ω_1 of a certain spin packet during the evolution time t_1 to the frequency ω_2 of the same spins during acquisition. If $\omega_1 = \omega_2$ the spins give rise to a diagonal peak at (ω_1, ω_2) , if $\omega_1 \neq \omega_2$ then a cross-peak can be found at (ω_1, ω_2) . Molecular reorientations in a solid can cause a change in frequency if during the exchange delay the chemical shift tensor has changed its position relative to the magnetic field. Fast magic angle spinning, however, eliminates the orientational dependence of the resonance frequency, at least if we have a less abundant spin, proton decoupled experiment in mind. On the other hand, magic angle spinning is desirable from the viewpoint of resolution and sensitivity. Fortunately, with slow MAS the orientational dependence of the resonance frequency is manifest in the spinning sidebands. Straightforward application of the 2D-exchange technique to a slowly rotating solid, however, yields a two-dimensional spinning side band pattern with spinning sidebands everywhere (top left of figure) because due to the spinning the frequency of a spin at the beginning of the acquisition time t_2 differs from its frequency at the end of t_1 . The solution is to make the exchange delay time *exactly* an integral number of spinner revolutions.

For the technical details we refer to the reference 1, the result is shown in top right of the figure: in the absence of slow molecular reorientations only



FACULTEIT DER WISKUNDE
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KATHOLIEKE UNIVERSITEIT
NIJMEGEN

LABORATORIUM VOOR FYSISCHE CHEMIE

Toernooiveld, Nijmegen
Telefoon (080) 55 88 33

Geadresseerde
Prof. B.L. Shapiro

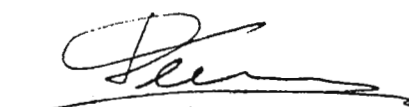
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diagonal peaks. Reference 1 shows the first successful application of this technique to the molecular rotation of dimethylsulfone.

Here we want to report preliminary results on polyoxymethylene (a commercial product from Hoechst)[2]. The lower half of the figure shows the appearance of cross-peaks in POM with exchange delay times of 2-3 seconds. The temperature dependence suggests that the cause is indeed a slow, large amplitude molecular reorientation and not $^{13}\text{C} - ^{13}\text{C}$ spin diffusion. We believe that the molecular reorientation detected here has to be associated with the α -relaxation in polyoxymethylene. From dielectric loss data one infers for this relaxation a frequency of motion of ~ 0.1 Hz at 50°C .


-W.S. Veeman

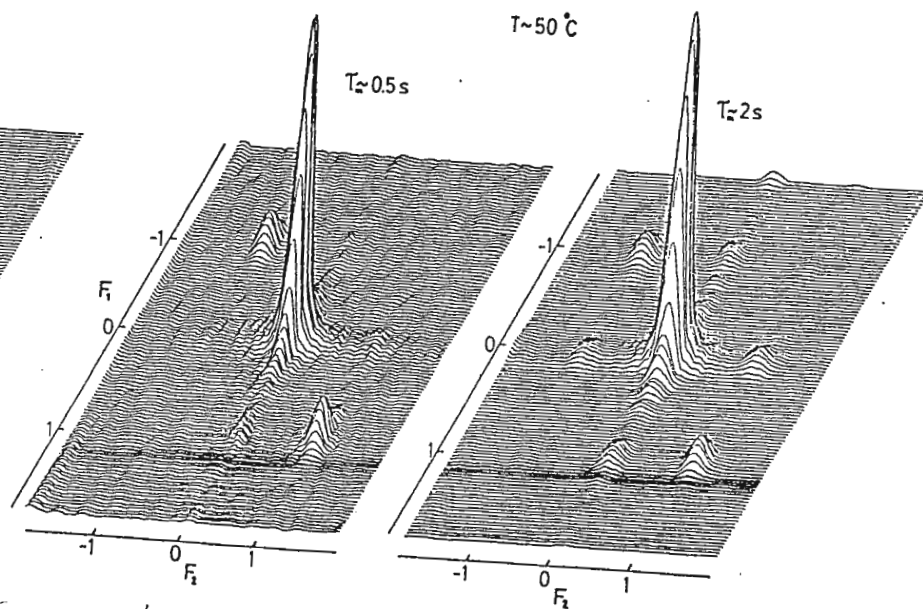
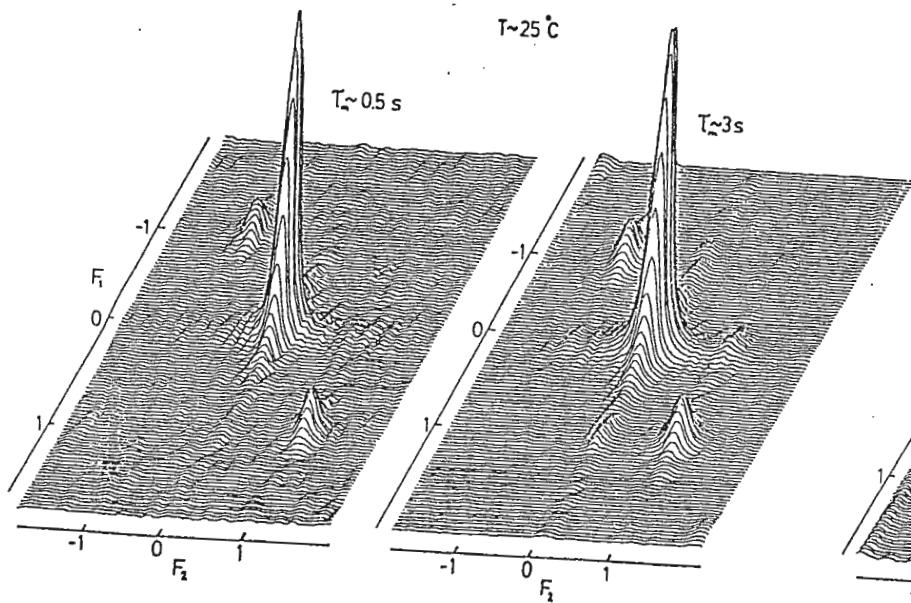
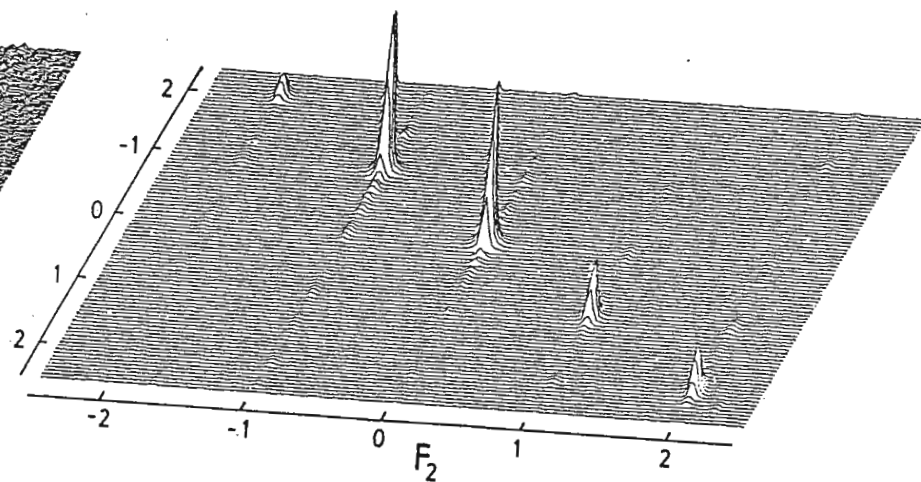
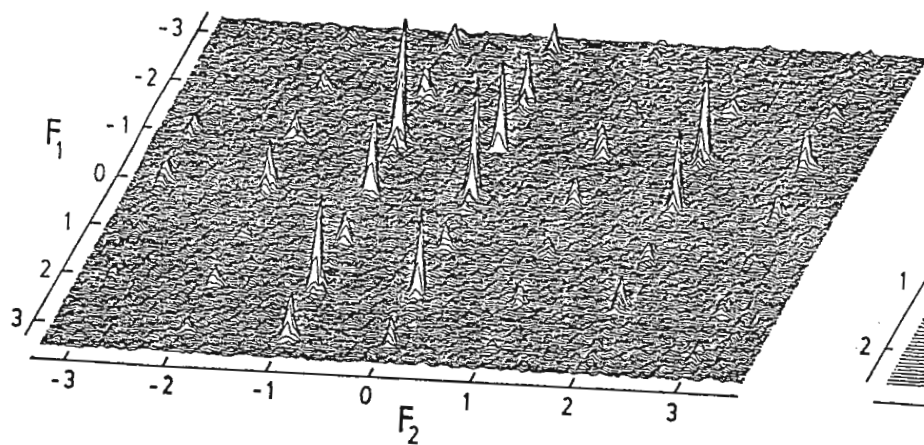

A.P.M. Kentgens


E. de Boer

- [1] A.F. de Jong, A.P.M. Kentgens, W.S. Veeman, Chem. Phys. Lett. 109 (1984) 337.
[2] A.P.M. Kentgens, A.F. de Jong, E. de Boer, W.S. Veeman, to be published.

Figure Caption

top left: ^{13}C 2D spinning side band pattern for hexamethylbenzene, exchange delay equals non-integral number of spinner revolutions.
top right: spectrum when exchange delay is 8 spinner periods [1].
bottom: ^{13}C spectra of bulk polyoxymethylene at two temperatures and two delays, the delays are an integral number of spinner revolutions.
Each spectrum took 2 days of acquisition.





DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service

National Institutes of Health
National Cancer Institute
Bethesda, Maryland 20205

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

January 8, 1985

Dear Barry:

With this contribution, we hope you will remove Otto Gansow's subscription to the TAMU NMR newsletter from your "pink list".

Subject: ^{57}Fe NMR: Biological Incursions

Rolf Tschudin has produced for us a new low frequency probe for the Nicolet 500 MHz spectrometer. That, in conjunction with addition of tuned filter boxes to the receiver console have markedly improved the ^{57}Fe NMR sensitivity. Before and After spectra for t-butylferrocene are shown below.

The new probe, tuneable between 14.5-22 MHz, features a deuterium lock, temperature control, and a horizontal, 10 mm solenoidal coil. Overall, signal-to-noise improved from 4:1, $\Delta\nu_{1/2}=2\text{Hz}$, to 20:1, $\Delta\nu_{1/2}=4\text{Hz}$. In our current work, line widths have been seen to be large for heme proteins.

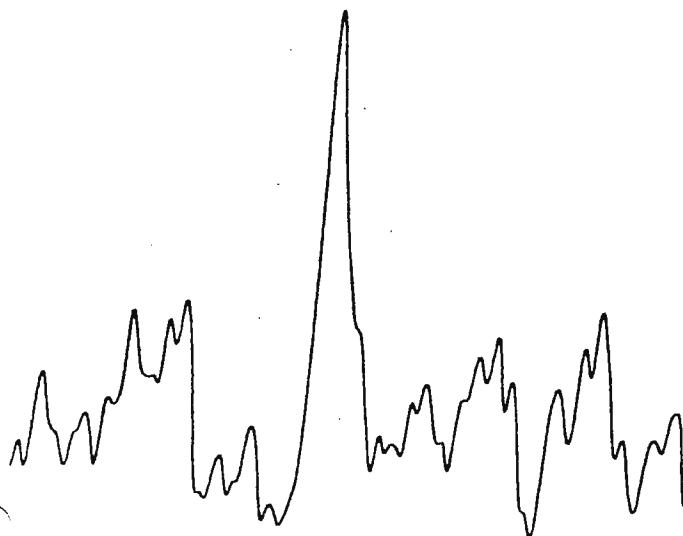
The chemical shift for myoglobin-CO appeared at 8234 ppm vs. $\text{Fe}(\text{CO})_5$. Temperature dependence of chemical shift is substantial for all Fe-57 resonances measured to date, 10-50 Hz per $^{\circ}\text{C}$.

Otto Gansow

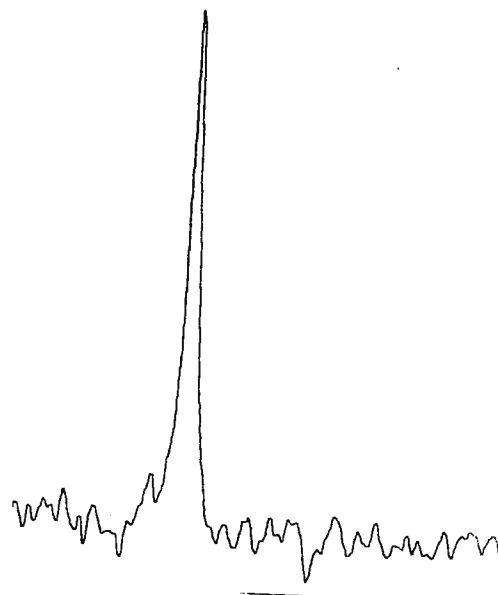
Lars Böttcher

Ted Becker

Rolf Tschudin

*Otto**Lars**Ted**Rolf*

200 Scans



Texas A&M University NMR Newsletter - Book Reviews

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

"Solid State NMR for Chemists"

by

Colin A. Fyfe

University of Guelph, Guelph, Ontario, Canada

C.F.C. Press, P.O. Box 1720, Guelph, Ontario, Canada N1H 6Z9.
1983; 593 pages; CDN \$65, US \$55, plus \$5 postage and handling.

Professor Fyfe, one of the world's leading researchers in the field of solid state NMR, has written this text to describe to a chemical audience the various experiments and techniques available in this field. This is particularly appropriate since the more recently developed solid state NMR techniques have considerable potential in different areas of chemistry. Although many chemically oriented publications have appeared in recent years, these techniques have not been fully exploited and new techniques are continually appearing in the literature. Other books which contain rigorous theoretical descriptions of solid state NMR appear to be written for a physical audience and may not be appealing to a general chemical audience. This book should be of great interest to the chemist with some knowledge of liquid state NMR who desires to explore the various solid state NMR experiments. It should help this person to determine the different types of information which may be obtained in applications to areas of chemical interest.

The field of solid state NMR covers wide ranges of atomic nuclei, physical phenomena, NMR techniques, and classes of samples. Since these topics are intimately interwoven, the organization of this volume may, of necessity, not seem straightforward. Nevertheless, Fyfe has authored an excellent text which is a gold-mine of information on applications as well as a convenient source for solid state NMR techniques.

The book is divided into nine chapters, each being an admixture of the above topics in a progression of advancing modernity and increasing technical complexity. The first chapter classifies solid systems in terms of molecular ordering and motions (crystalline solids, amorphous solids, etc.) and briefly describes the different nuclear spin interactions which affect the width of the NMR signal. The second chapter is concerned with abundant spin-(1/2) nuclei (such as ^1H and ^{19}F) in solids yielding broad NMR lines. The effects of motion on the magnetic dipole-dipole interaction are discussed in terms of the second moment of the NMR line and relaxation times.

The third chapter deals with NMR spectra from quadrupolar nuclei (such as ^2H and ^{11}B). The fourth chapter treats line narrowing experiments on solids containing abundant spin-(1/2) nuclei. These techniques include magic angle spinning and pulse sequences (as WAHUHA). Chapter five treats "dilute" nuclear spin-(1/2) systems (mainly ^{13}C), where homonuclear magnetic dipolar interactions are unimportant, studied with proton decoupling and cross polarization.

The sixth chapter basically extends this topic by including magic angle spinning in addition to cross polarization and proton decoupling (i.e., CP/MAS). High resolution spectra are obtained on powder samples since the magic angle spinning removes the effect of chemical shift anisotropy. This is a techniques chapter, concentrating on descriptions of the various sample spinning systems.

The next chapter describes many specific applications of CP/MAS measurements, mainly on dilute nuclei such as ^{13}C and ^{29}Si . It is, by far, the longest chapter in this book. Chapter eight extends the simple CP/MAS experiment of chapter six to include non-protonated carbon selection, spinning sideband suppression, relaxation time measurements, dynamic nuclear polarization, etc. The last chapter gives an introduction to the relatively new topic of line-narrowing magic angle spinning experiments on quadrupolar nuclei such as ^2H , ^{27}Al , ^{11}B , ^{23}Na , ^{17}O , etc. Except for ^2H , these measurements are applicable mainly to inorganic and geologic samples.

This book describes the solid state NMR techniques, both theoretically and experimentally, to the chemist. Each chapter contains many references and describes many applications of these techniques. It is a first-class exposition of solid state NMR in chemistry. As such, it belongs on the bookshelf of chemists interested in nuclear magnetic resonance.

D.E. Woessner
Mobil Research and Development Corporation
Dallas, Texas

January 1985

Department of Chemistry
University of Denver
Denver, CO 80208
303-871-2980

January 22, 1985

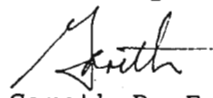
Professor Barry L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

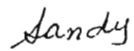
RE: Position Available

Dear Barry:

We have available immediately a postdoctoral position for NMR and EPR studies of metal-radical interactions in biochemical systems. Experience with biological separations is desirable. We have a Chem-magnetics A200 NMR, Varian E9 and IBM ER200 X-band EPR, and homebuilt Q-band and pulsed EPR instruments. If you know of someone who is qualified and interested in such a position, please ask them to contact us.

Sincerely,


Gareth R. Eaton
Professor


Sandra S. Eaton
Visiting Professor

UMEÅ UNIVERSITET

Avdelningen för organisk kemi

Telefon
090 - 16 50 00



UNIVERSITY OF UMEÅ

Department of Organic Chemistry

Telephone
46 - 90 - 16 50 00

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

Jan 24

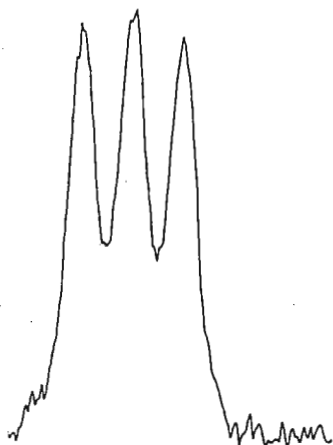
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Dear Barry,

Si-Li Scalar Coupling In Phenyl-substituted Silyl Lithiums;
Quotations to "TAMU".

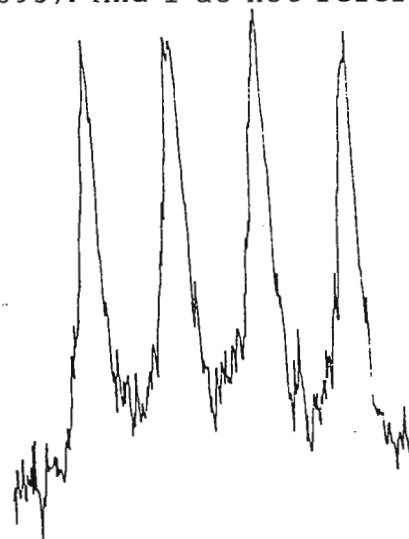
We have recently been performing some variable temperature NMR studies of group IV metal lithiums. Not only has the weather been perfect this winter for handling reactive anions and tuning cold probes, but we have also managed to get a full-proof evidence that phenyl-substituted silyl lithiums exist as monomers. A nice Si-⁷Li quartet is obtained at low temperature (<193 K) indicating a covalent contribution to the bonding. The Si-⁶Li triplet is shown as a comparison. The coupling averages out at increasing temperatures depending on the ethereal solvent and the degree of phenyl-substitution. Interestingly, ⁷Li quadrupolar relaxation is insufficient to average the coupling using these conditions.

It is also very nice to get experimental data published in JACS, especially if you are one of the authors. It is not equally nice to find your own original data published without your permission and cited as "Edlung, U., disclosed in a letter to Prof. B.L. Shapiro Sept. 27, 1979" (JACS 1983, 105, 6895). And I do not refer to that my name was spelt incorrectly.



Best regards

Ulf Edlund



Postal address
S-901 87 UMEÅ
Sweden

Post giro account
156 13 - 3

Ulf - Please see p. 46. B.L.S.

NSF Initiative in Supercomputers

With Irwin Kunz and Larry Crooks I recently attended an NSF workshop on the use of supercomputers in the biological sciences. The workshop was attended by about 50 scientists and the purposes were to advise the biological science divisions of NSF concerning application of funds mandated by Congress for supercomputers; and to inform the scientific community on what is available. It is for the latter reason that I write; while this workshop was oriented toward the life sciences I assume that the situation may be similar for chemistry and physics.

At this moment it is relatively easy for U.S. scientists to get several hours of time on supercomputers at any of three centers (University of Minnesota; Purdue; Boeing), either in some cases administratively, for some NSF grantees, or by peer review proposals. Time is relatively plentiful because it has already been purchased by NSF, but hard cash for such things as local computers or programmers within your group is as scarce as ever. These centers are oriented towards Fortran 77 programs which should run on supercomputers without modification, and they can probably give you some help in increasing efficiency of such programs which generally run at from a few, to more than one hundred, times faster than on a VAX. You do not have to be an expert in supercomputers to get started. For information contact the Office of Advanced Scientific Computing of NSF and the NSF division in your area of research (don't call me!).

Unfortunately communication currently is by mail or 1200 baud telephone though connection to 56 Kbaud Arpanet lines is expected. The Workshop recommended, among other things, that 56kbaud networking be implemented rapidly and felt that this would be suitable for most usage, though >1 Mbaud would be desirable; that this Initiative should not result in seriously decreased support for needed local facilities; and that access be available to foreign researchers. Shortly the NSF will set up two to four new centers devoted to this program.

Alfred Redfield
Graduate Department of Biochemistry
Brandeis University
Waltham, Massachusetts 02254

 Quotation of Results Appearing in the TAMU NMR Newsletter. 

Newsletter readers are once again directed to the policy regarding quotations of results which appear in the TAMU NMR Newsletter, as outlined on the bottom of the front cover of each month's issue. It is a matter of concern that this policy be scrupulously maintained, and a fairly pointed letter has been sent to the individual guilty of breaching this matter of policy in the instance referred to in Dr. Ulf Edlund's which appears on page 45. Fortunately, these instances of illicit quotation of Newsletter contents are very rare.

B.L.S.





January 21, 1985

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

Improvement of NT-200 NMR Lock Unit and Removal of Low Band
Observed Spikes

Dear Professor Shapiro:

Recently when we tried to observe platinum or tellurium NMR signals, we found that our spectra contained many spurious additional spikes.

The observed spikes, which obliterated platinum and tellurium signals, were generated at 10.7 MHz intervals by the lock mixer printed circuit board. These harmonics generated by the Class C transistor amplifier could not be filtered out because they were traveling on the power supplies and grounds. The spike problem was solved by replacing the Class C amplifier with a Class A amplifier powered by the +15 volt supply (Figure 1). This change with the addition of .022 μ f capacitors directly across the integrated circuit chip's power supply and ground pins eliminated the harmonics and improved the power supply and ground isolation.

Another improvement was made on the lock transmitter pulse shape and stability by adding .022 μ f capacitors across the integrated circuits on the lock transmitter printed circuit board. The board's transistors Q1 and Q2 (2N3904's) were replaced by higher gain and higher frequency transistors (MPS6515's) to improve pulse shape. Also, resistor R1 was increased from 1K ohms to 2.2K ohms to center the input waveform about the I.C.'s trigger point (1.5 volts) so the output would have greater drive at the fundamental frequency. This greatly reduced the losses in the lock receiver.

These changes to the lock transmitter and lock mixer boards increased signal levels at the frequency of interest while reducing spurious frequencies when tuned for maximum clean signals.

Sincerely yours,

Kenneth R. Keymel

Kenneth R. Keymel
Industrial Laboratory, Building 339
Kodak Park

KRK:bac



The University of Western Ontario

Department of Chemistry
Chemistry Building
London, Canada
N6A 5B7

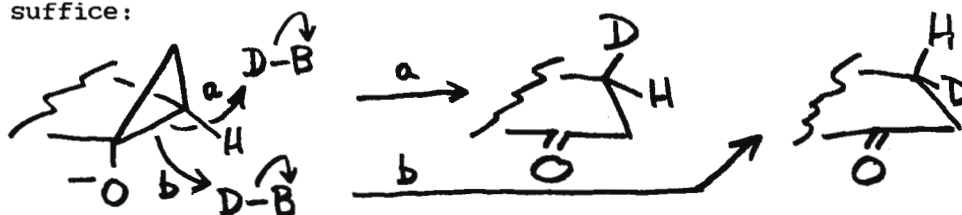
January 21, 1985

Dear Barry:

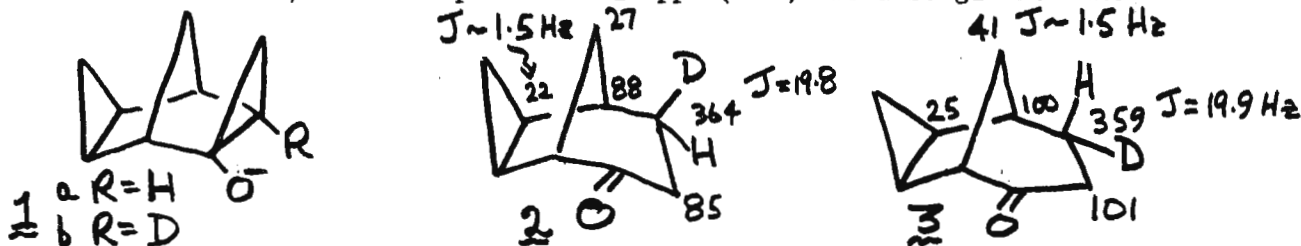
Stereochemistry of Homoketonization revealed by vicinal J_{CD}

Herewith my response to the barrage of colored letters.

In my previous submission passing reference was made to vicinal antiperiplanar ^{13}C - ^2H coupling and this feature has been helpful in some recent work. To determine the stereochemistry of cyclopropoxide cleavage (homoketonization) in various polycyclic systems, we have utilized the observed vicinal ^{13}C - ^2H coupling which is known to be dependent on the dihedral angle in the usual fashion. To illustrate the matter the following should suffice:



Alternatively, one can employ the deuterated analog of the cyclopropoxide with protio base to obtain the corresponding products with the H and D interchanged in each. In this way inversion (path a) and retention (path b) of configuration upon cleavage can be distinguished provided the orientation of the H or D can be determined unequivocally. In the systems with which we have been concerned, the ^{13}C -D vicinal coupling affords the requisite information. As an example, **1a** upon cleavage with KOD/*t*-BuOD gave **2** while **1b** with NaOH/MeOH gave **3**. One resolvable vicinal coupling was observed in each case as indicated; the isotope shifts in ppb (± 5) are also given. The



resolved couplings reveal the anti periplanar ^{13}C and ^2H nuclei showing that the cleavage of **1** proceeds with inversion of configuration at C-4. This method has been employed in several related systems to establish the stereochemistry of ketonization. A neat feature is the fact that it can be done in two ways to strengthen the evidence.

I trust that this will reinstate my subscription.

Sincerely,

J.B. Stothers
J.B. Stothers.

Monsanto

CENTRAL RESEARCH LABORATORIES

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63167
Phone: (314) 694-1000

January 21, 1985

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

Dipolar Rotational Spin-Echo ^{13}C NMR

Dear Barry:

We continue to characterize molecular motions in solids by measuring carbon dipolar tensors at natural abundance using dipolar rotational spin-echo ^{13}C nmr at 15.1 MHz. This is a two-dimensional experiment in which, during the additional time dimension, carbon magnetization is allowed to evolve under the influence of C-H coupling while H-H coupling is suppressed by homonuclear multiple-pulse decoupling. Recently we have switched from WAHUHA decoupling of the protons to a semi-windowless MREV-8 version, and have observed a substantial improvement in refocusing. We now detect dipolar echos with 60-70% refocusing after 16 MREV-8 cycles, even for systems with tightly coupled protons (figure, left). This is a 50% improvement over refocusing using WAHUHA decoupling on the same systems. The improvement makes feasible collection of data over several echo periods. For rigid systems with no slow motions, the C-H Pake doublet is the same whether characterized by the first or second echo (figure, right).

Sincerely,

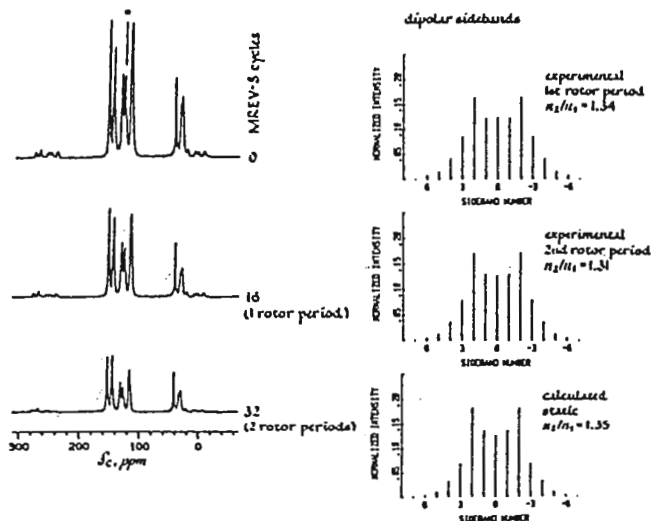
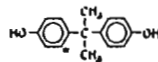
Jake

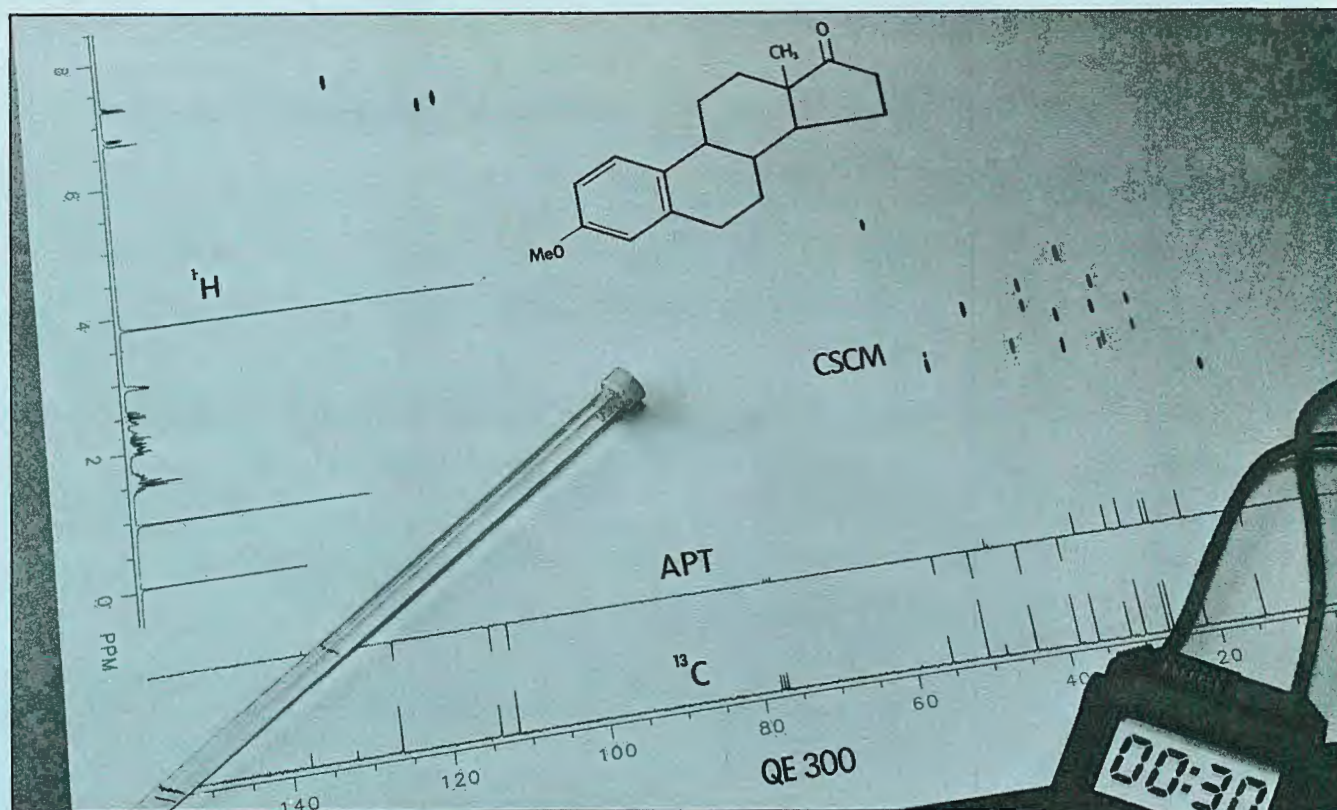
Jacob Schaefer

Joel

Joel R. Garbow

Dipolar Rotational Spin-Echo ^{13}C NMR of
Bisphenol-A (crystalline)
(MAS = 1859 Hz)





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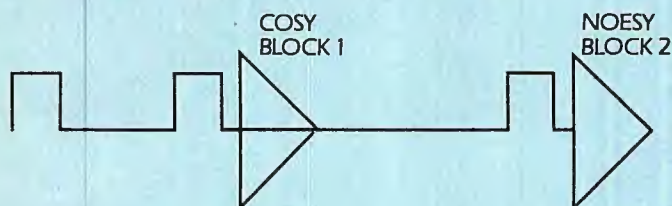
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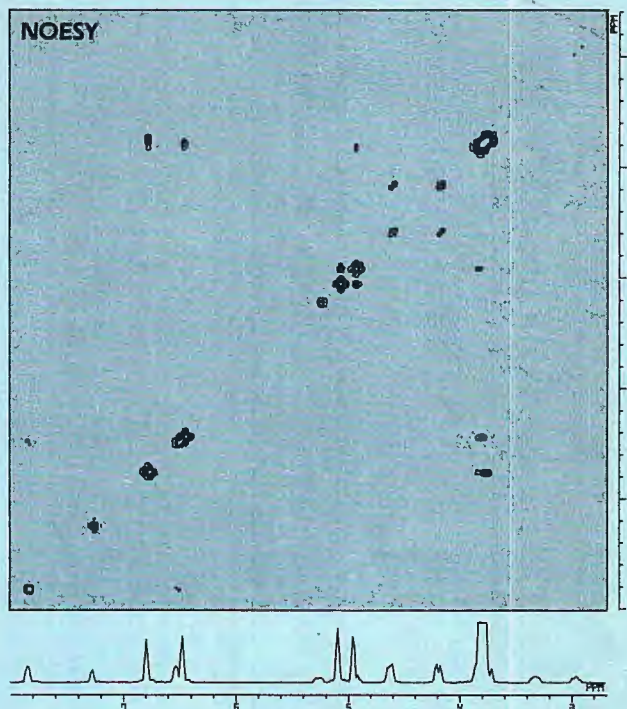
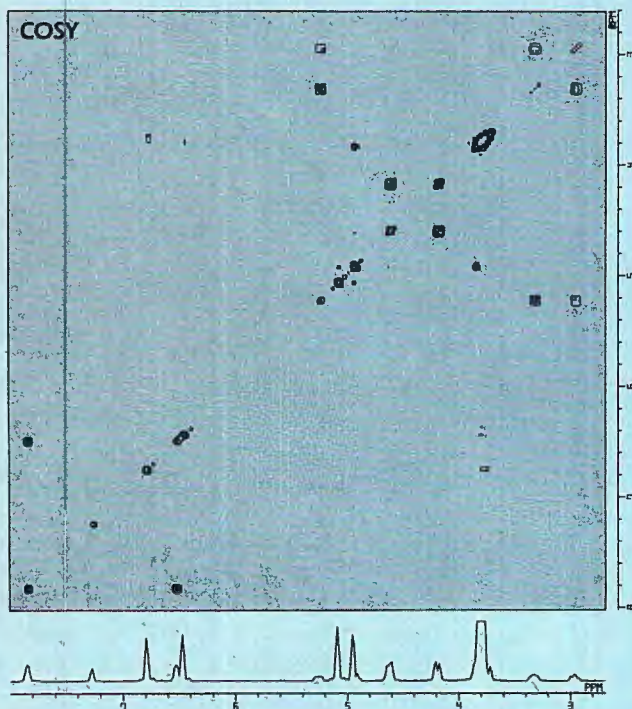
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