TEXAS A&M UNIVERSITY
NMR
NEWSLETTER

No. 410

November 1992



*Continued on Inside Back Cover*

TABLE 1 DEUTERATED SOLVENTS

| Cat. No. | Description | Formula | Min. Isotopic Purity (% D) | Density (g/cc) | MP (°C) | BP (°C) | $-\chi_v \times 10^6$ @ (°C) |
|---|---|---|---|---|---|---|---|
| D-11 | Acetone-d6 | $CD_3OD$ | 99.5% | 1.1[illegible] | [illegible] | [illegible] | 0.551 (32) |
| D-120 | Acetone-d6 + 1% TMS | [illegible] | [illegible] | | | | |
| D-13 | Acetone-d6 | $CH_3COCD_3$ | 99.9% | 0.8[illegible] | 94 | [illegible] | 0.460 (20) |
| D-121 | Aceonte-d6 + 1% TMS | | 99.8% | | | | |
| D-129 | | | | | | | |
| D-14 | | | | | | | 543 (20) |
| D-21 | | | | | | | 0.611 |
| D-122 | | | | | | | |
| D-130 | | | | | | | |
| D-28 | Choloroform-d | $CDCl_3$ | 99.8% | 1.50 | -64 | 62 | 0.740 (20) |
| D-31 | Chloroform-d + 1% TMS | | 99.8% | | | | |

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|---|---|---|---|
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| WCV-60 ([illegible]) | [illegible] | [illegible] | Gridded-Two Color |
| WCV-XL ([illegible]) | [illegible] | [illegible] | Gridded-Two Color |
| WCV-XLFT-[illegible] | [illegible] | [illegible] FT | Gridded-Two Color |
| WCV-XL-200 | 11" X 26" | XL-200, XL-300, XL-400 | Gridded-Two Color |
| [illegible] | [illegible] | [illegible] | [illegible] |
| WCV-20 (CFT-20) | 11" X 16 3/4" X 17" | CFT-20, FT-80, FT-80A All Model [illegible] 16 1/2" or 16 | Gridded-Two Color Blank |

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## FORTHCOMING NMR MEETINGS

PITTCON'93, Atlanta, Georgia, **March 8-12, 1993**; Contact: Dept. 60, Suite 332, Penn Center Blvd., Pittsburgh, PA 15235-5503; Phone: (412) 825-3220, Toll-free: 1-800-825-3221; Fax: (412) 825-3224.

1993 Keystone Symposia on Molecular & Cellular Biology, Taos, New Mexico: **March 8-14, 1993**, *Frontiers of NMR in Molecular Biology - III*; Organizers: T. L. James, S. W. Fesik, and P. E. Wright; Information: Keystone Symposia, Drawer 1630, Silverthorne, CO 80498; Telephone: (303) 262-1230.

34th ENC (Experimental NMR Conference), St. Louis, Missouri, **March 14-18, 1993**; Contact: ENC, 815 Don Gaspar, Santa Fe, New Mexico 87501; Phone: (505) 989-4573; Fax: (505) 989-5073. See TAMU NMR Newsletter 408, 45.

High Resolution NMR Spectroscopy (a residential school), University of Sheffield, England, **April 1993**; Organizer: Dr. B. E. Mann (Sheffield); For information, contact Ms. L. Hart, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, England; Tel.: 071-437-8656.

35th Rocky Mountain Conference on Analytical Chemistry, Denver, Colorado: **July 25-29, 1993**; Contact: Patricia L. Sulik, RML, Inc., 456 S. Link Ln., Ft. Collins, CO 80524; Phone:: (303) 530-1169.

Additional listings of meetings, etc., are invited.

HARVARD MEDICAL SCHOOL
DEPARTMENT OF BIOLOGICAL CHEMISTRY
AND MOLECULAR PHARMACOLOGY
Professor Gerhard Wagner

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4366

Fax: (617) 432 4383

240 Longwood Avenue
Boston, Massachusetts 02115

September 20, 1992 (received 9/28/92)

**Experience with a Heteronuclear Cross-Polarization HCCH TOCSY**

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto, CA 94303

Dear Barry:

In order to keep our supply of newsletters active we should write what we are currently up to. The other day we played with heteronuclear proton-carbon cross polarization and obtained quite good results. We followed essentially the routes described by E. Zuiderweg (J. Magn. Reson., 89, 533, 1990). The purpose was to obtain better HCCH TOCSY spectra. The pulse sequence is shown in Fig. 1. We used a DIPSY-3 spin lock for the heteronuclear $^{1}H$-$^{13}C$ and for the homonuclear $^{13}C$-$^{13}C$ transfers. The experiments were carried out on a Bruker AMX600 using an AMT amplifier to boost $^{13}C$ pulses.

The experiment was applied to the uniformely $^{15}N$ and $^{13}C$ labeled 10 kDalton N-terminal domain of the ada protein, a DNA repair protein from E.coli. The experiment was carried out in $H_2O$ at a sample concentration of 1.5 mM. Fig. 2 shows a cross plane from the 3D spectrum. Although this protein is rather small, the $^{1}H$-$^{1}H$ correlations seem to be more complete than in homonuclear TOCSY experiments or in INEPT HCCH TOCSYs, although we have not done a quantitative comparison.

With best regards

Chandrasekhar Kasibhatla  Larry Myers  Gerhard Wagner

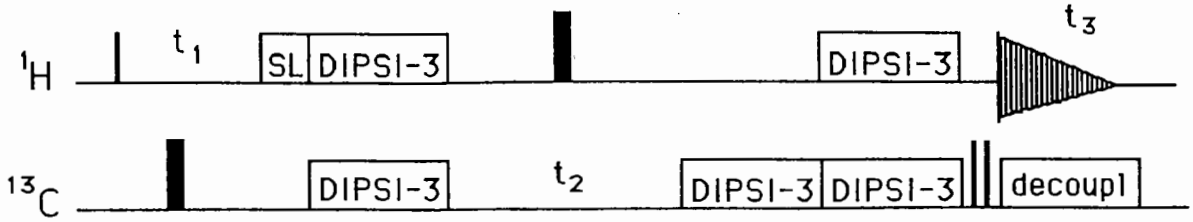



Fig. 1: Pulse sequence for the CP HCCH TOCSY. The heights of the bars and the boxes indicate the relative rf field strength.

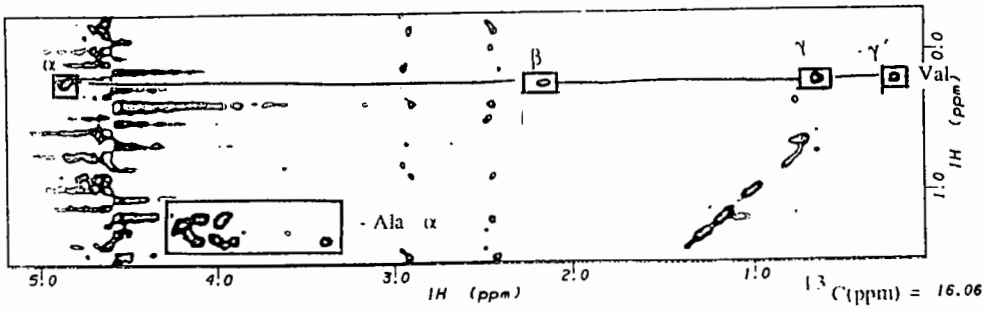



Fig. 2: Cross plane of a 3D spectrum recorded with the experiment of Fig. 1 on a 1.5 mM sample in $H_2O$ of the N-terminal domain of the ada protein. A valine and some alanine cross peaks are labeled.

Continued from page 4:

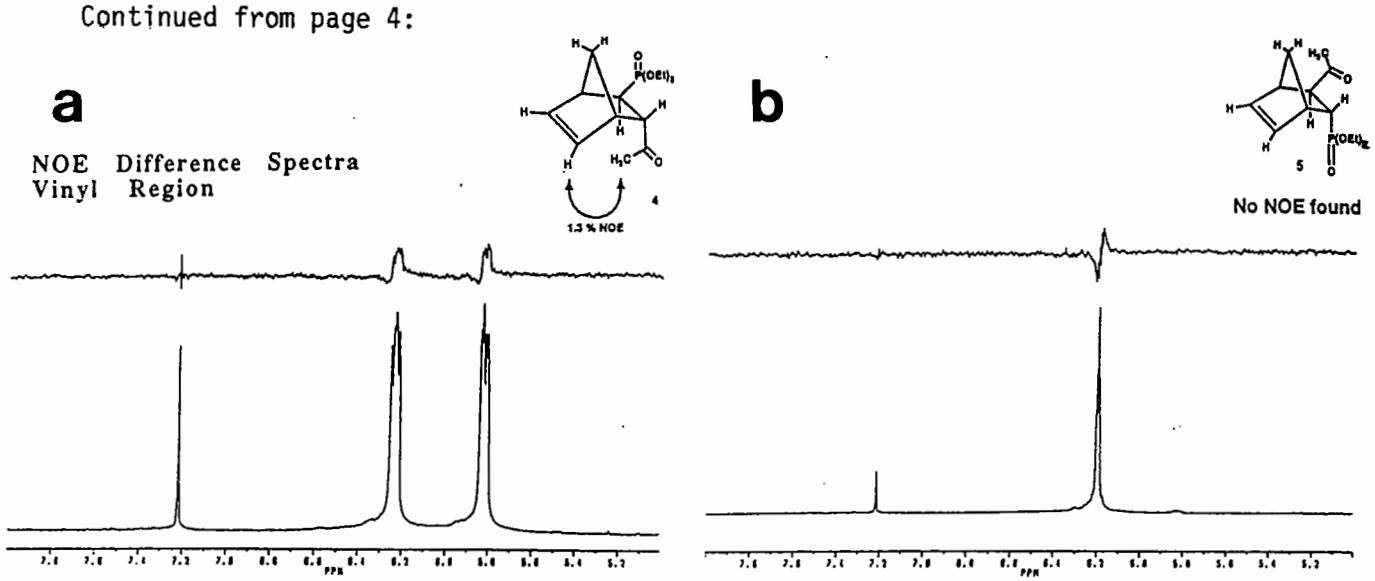



**Figure 1: Downfield region of the 1D proton and NOE difference spectra for a) the endo isomer and b) the exo isomer.**

Sincerely,

Karl Hansen, Martha Bruch, and Cynthia McClure

Please credit this to the account of Dr. Cecil Dybowski.

University of Delaware

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
NEWARK, DELAWARE 19716

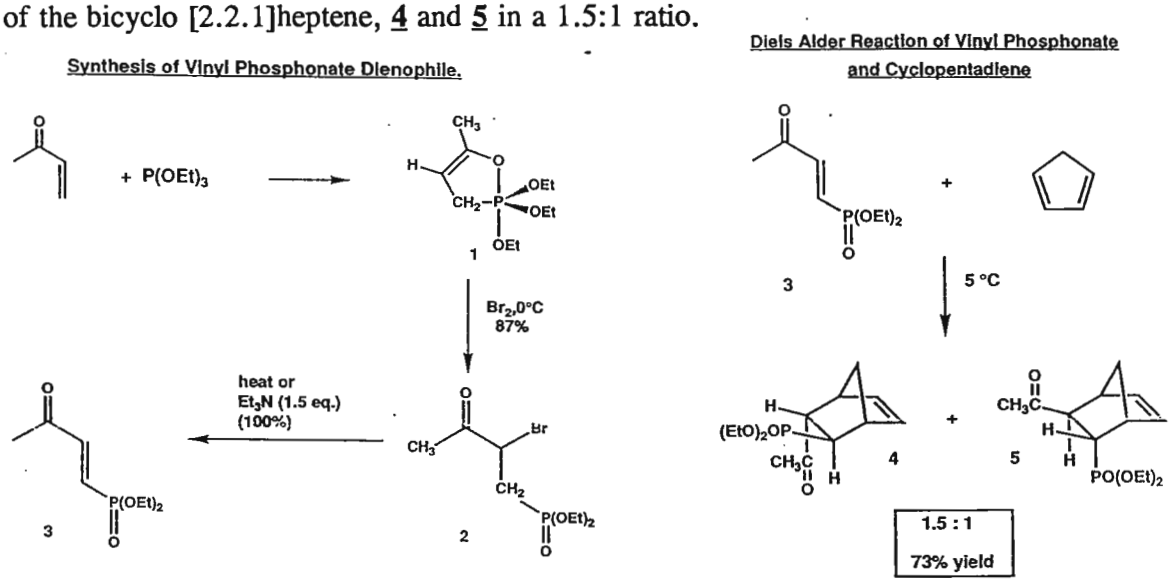
(received 9/29/92)
September 21,1992

**Conformational Analysis of Flexible Organic Molecules From NOE Studies**

Dear Dr. Shapiro:

The nuclear Overhauser effect (NOE) is a powerful tool for conformational analysis of a rigid molecule in solution. However, a common misconception is that this method is not useful for a very flexible molecule. Recently, we were able to distinguish two isomers of an organic compound through the use of NOE interactions involving a highly flexible part of the molecule.

We are interested in the synthesis of analogs of phosphate sugars; these compounds will be used for enzyme mechanistic studies. The synthetic scheme for two of these compounds is shown below. In the first step, methyl vinyl ketone is condensed with triethylphosphite to form a pentacovalent oxaphospholene 1, which is then condensed with bromine to form 2. This compound is treated with triethylamine to form the vinyl phosphonate 3. The Diels Alder reaction between vinyl phosphonate 3 and cyclopentadiene produced two isomers of the bicyclo [2.2.1]heptene, 4 and 5 in a 1.5:1 ratio.




To determine whether the preferred product has the acetyl group endo or exo, we performed NOE experiments on both compounds. The relative orientation of the ring protons is nearly identical in the two isomers, so NOE interactions involving protons in the rigid part of the molecule cannot be used to distinguish between the two. Although the acetyl group is highly flexible, the region of space which can be sampled by the acetyl group is quite different in the two isomers. If the acetyl group is endo, then the methyl group can spend some time in close proximity to the alkene protons on the other side of the ring. However, the methyl group can never get close to the alkene protons if the acetyl group is exo. Indeed, a NOE difference experiment showed a small enhancement (ca. 1%) of both vinyl protons upon irradiation of the methyl group of the endo isomer, whereas no measurable NOE was observed in the exo isomer (Figure 1). Therefore, we were able to assign each of the two compounds to a specific isomer despite the flexibility of the molecule.

Continued on page 3.

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Prof. B. L. SHAPIRO
Editor
TAMU NMR Newsletter
966 Elsinor Court
Palo Alto, CA 94303

U. S. A.

N./Réf.
V./Réf.

Wissembourg, le 09.09.92
(received 9/24/92)

Dear Barry,

The use of $B_0$ field gradients in high resolution NMR spectroscopy has been described a long time ago[1], but it is not until recently, with the introduction of actively shielded gradient coils, that this method really proved to be of great interest[2]. The appearance in the litterature of methods to acquire phase sensitive experiments with gradient pulses will without any doubt lead to a wide field of applications[3].

Based on the method which allows to record phase sensitive HSQC experiments[3b], we recently recorded a phase sensitive 3D HSQC-TOCSY in water. The experiment turned out to work very efficiently and gave a good result. The pulse sequence represented in Fig1. was used with gradient pulses of ratio 80:8:20.3. This experiment was recorded on an AMX 600 equipped with a Bruker Gradient Unit with an amplifier of 10 Amps connected to gradient wave form memories which allowed us to use sine shaped gradient pulses. The probehead was an inverse broadband probe with an actively shielded Z-gradient coil. The sample was 2 mmol Ribonuclease T1 in 90% H2O which was provided by the group of Prof. Rüterjans[4]. The experiment was recorded with 128*128*1024 points and 4 scans. The efficiency of the water suppression can be seen on the 2 planes which are represented below the 3D cube.

Best regards.

A. BELGUISE W. BERMEL C. BREVARD

1: a) A. A. Maudsley, A. Wokaun and R. R. Ernst, *Chem. Phys. Letters*, **55**, 9 (1978).
b) A. Bax, P. G. De Jong, A. F. Mehlkopf, and J.Smidt, *Chem. Phys. Letters*, **69**, 567 (1980).

2: Non exhaustive list of references:
a) R. E. Hurd, *J. Magn. Reson.*, **87**, 422 (1990).
b) R. E. Hurd, and B. K. John, *J. Magn. Reson.*, **91**, 648 (1991).
c) B. K. John, D. Plant, S. L. Heard, and R. E. Hurd, *J. Magn. Reson.*, **94**, 664 (1991).
d) J. -M. Tyburn, I. M. Brereton, and D. M. Doddrell, *J. Magn. Reson.*, **97**, 305 (1992).

3: a) A. L. Davis, E. D. Laue, and J. Keeler, *J. Magn. Reson.* , **94**, 637 (1991).
b) R.Kerssebaum, W. Bermel, and J. A. B. Lohman ; submitted.

4: a)E. Hoffmann, and H. Rüterjans, *Eur. J. Biochem.* , **177**, 539 (1988)
b)J. M. Schmidt, H. Thüring, A. Werner, H. Rüterjans, R. Quaas, and U. Hahn, *Eur. J. Biochem.* , **197**, 643 (1991)

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Fig1: Pulse sequence of Gradient Accelarated phase sensitive HSQC-TOCSY.

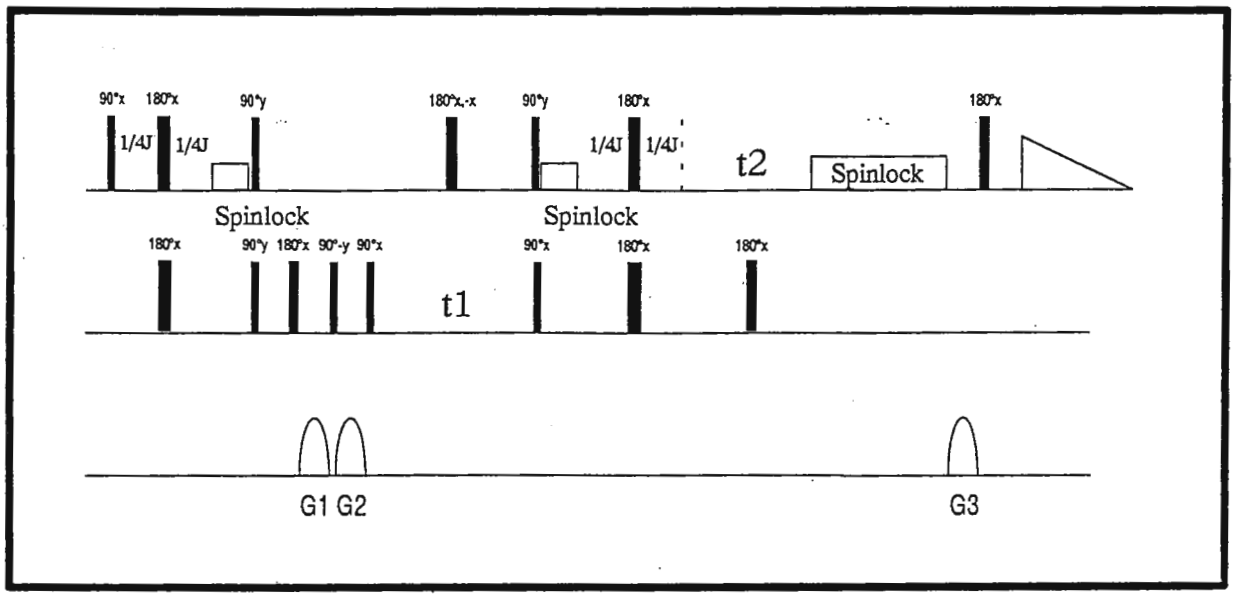
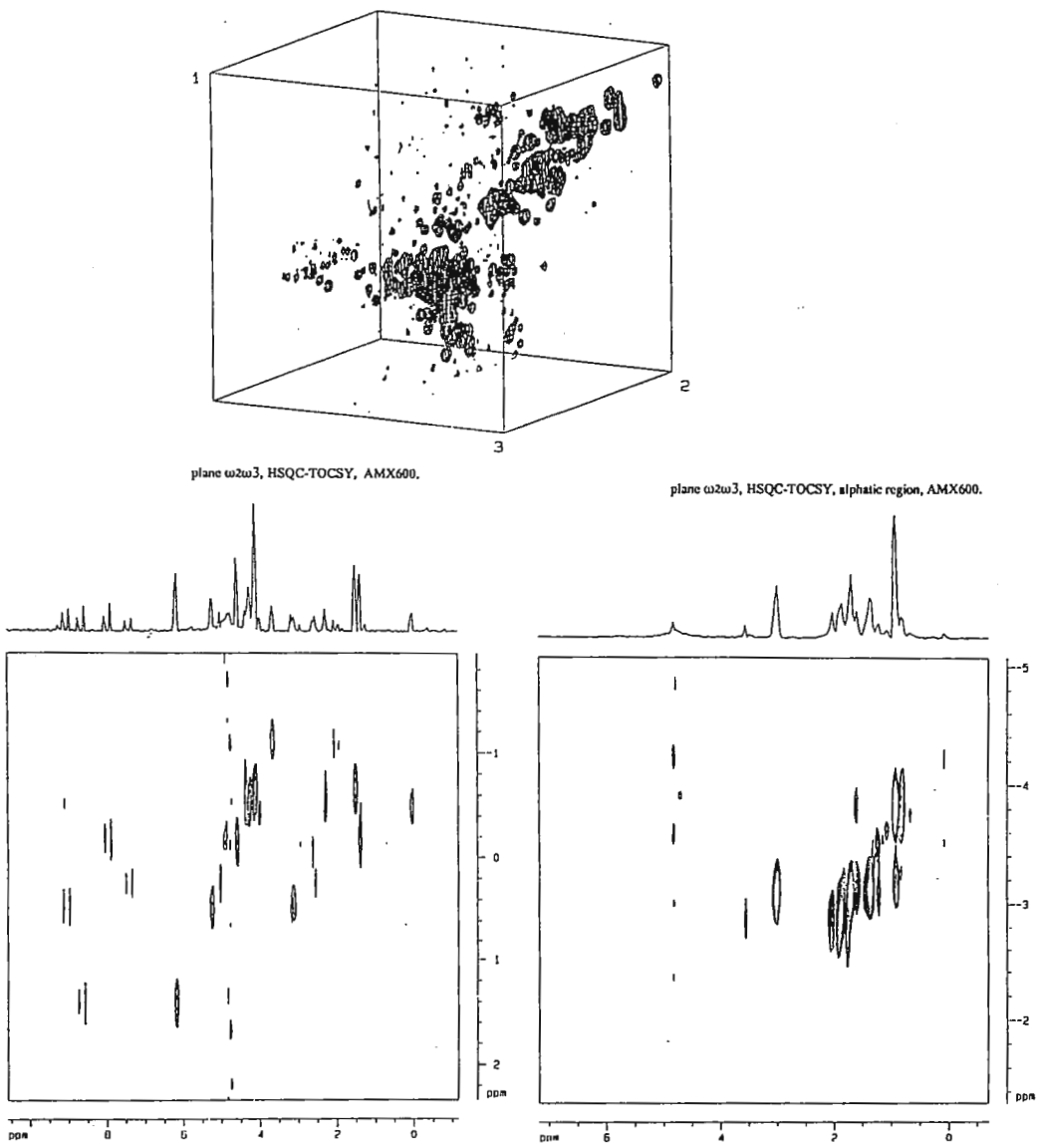
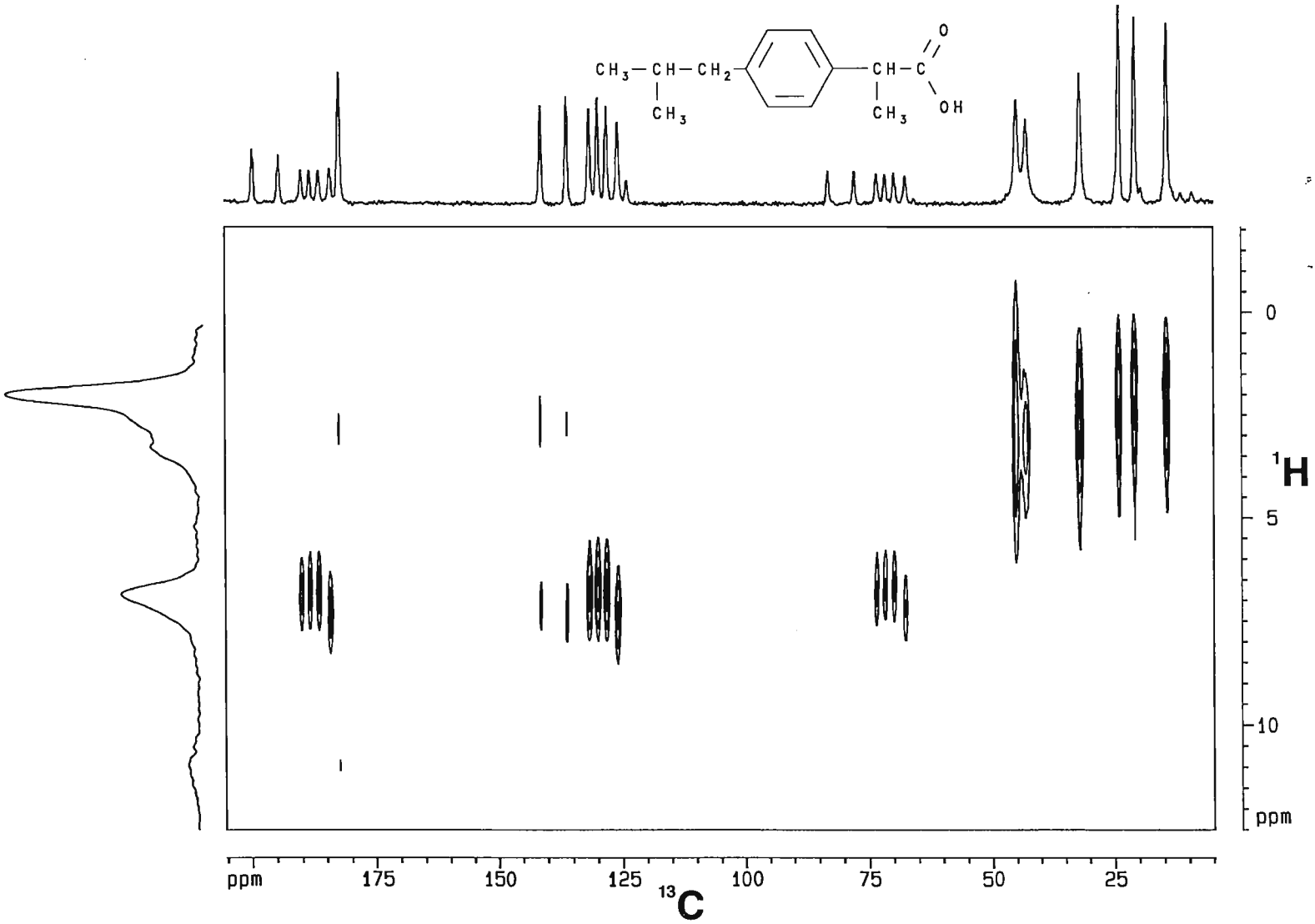



Fig2: Gradient enhanced HSQC-TOCSY on Ribonuclease T1, 2mmol in 90% H2O.



# ASX-Advanced Solids Excellence




## Solid State 2D HETCOR of Ibuprofen

In this spectrum the solid state 2D HETCOR experiment, developed in the Bruker applications laboratory, has been applied to the pharmaceutical compound ibuprofen. For comparison, 1D $^{13}C$ CPMAS and BR-24 $^{1}H$ CRAMPS spectra are displayed along the axes in place of the usual 2D projections. Strong cross peaks are visible for all of the directly bonded proton-carbon groups, as well as first order sidebands for the four aromatics. In addition, each of the three non-protonated carbons is shown to correlate to at least two long range protons. Note that minute differences in proton chemical shift, impossible to resolve in the 1D CRAMPS spectrum, are clearly visible in the 2D spectrum. 2D HETCOR requires simultaneous, fully windowless pulse sequences to be applied to both protons and carbons during the evolution and mixing periods. All the data shown here was obtained and processed on a Bruker ASX-300.

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October 2, 1992 (receiced 10/6/92)

Prof. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA
94303 USA

Dear Professor Shapiro:

re: Tickling $^{19}F$ on a $^{1}H$ coil

We recently had occasion to perform a triple resonance experiment which involved tickling of $^{19}F$, broadband decoupling of $^{1}H$ and observation of $^{13}C$. Because the actual field strength required at the fluorine frequency was very small ($\gamma B_2/2\pi < 1$ Hz), it was decided to try coupling the fluorine signal into the proton decoupling coil of the standard 5 mm C/H probe of our AM 300. The frequency was generated by a PTS160 synthesizer, doubled with an MCL SRA1 mixer configured as a doubler, filtered, and added to the proton decoupler signal with a Bruker directional coupler temporarily borrowed from our AMX 500. A Texscan 1 dB step attenuator was used to control the actual tickling field strength. A diagram of the complete set-up is included as Figure 1, and typical results on a test sample of ortho-difluorobenzene are shown in Figure 2.

We did notice, however, that the actual power required varied considerably (ca 25 dB) from sample to sample. Since the fluorine frequency is well down on the slope of the tuning response curve, it is likely that differences in sample dielectric constant are responsible for these effects.

The apparatus was then used to determine the signs of some "through-space" F-F couplings, and complete results will be published in conjunction with Prof. Ludger Ernst of the Technische Universität in Braunschweig.

Please credit this letter to Ted Schaefer's account.

Sincerely,

Kirk Marat

Encl.

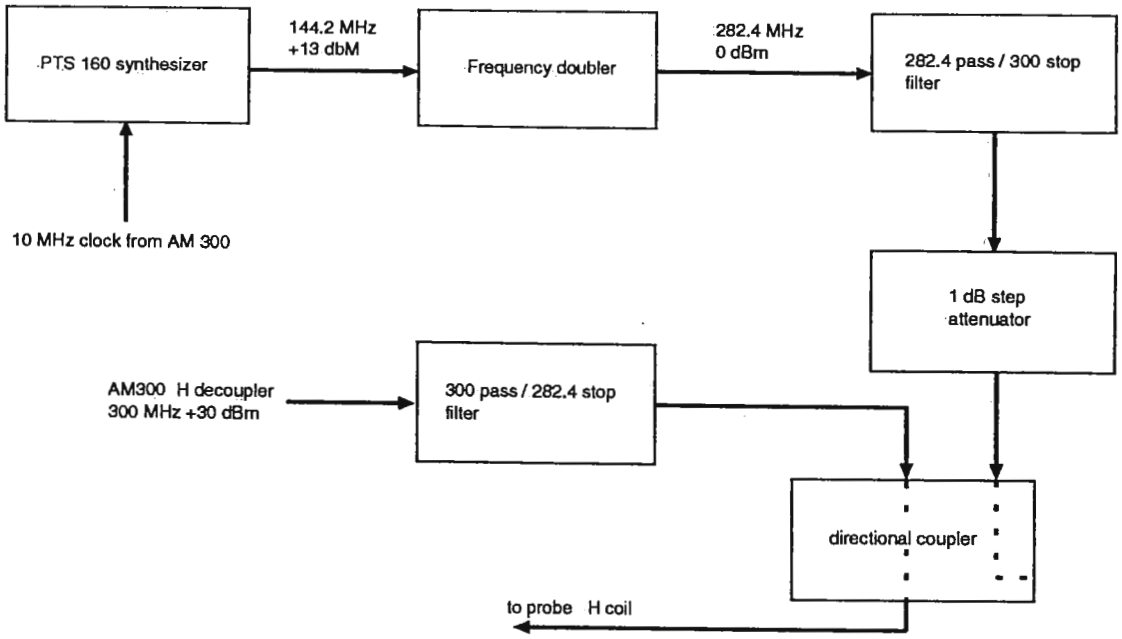



Figure 1. Circuit for coupling a low level fluorine signal into a proton decoupling coil

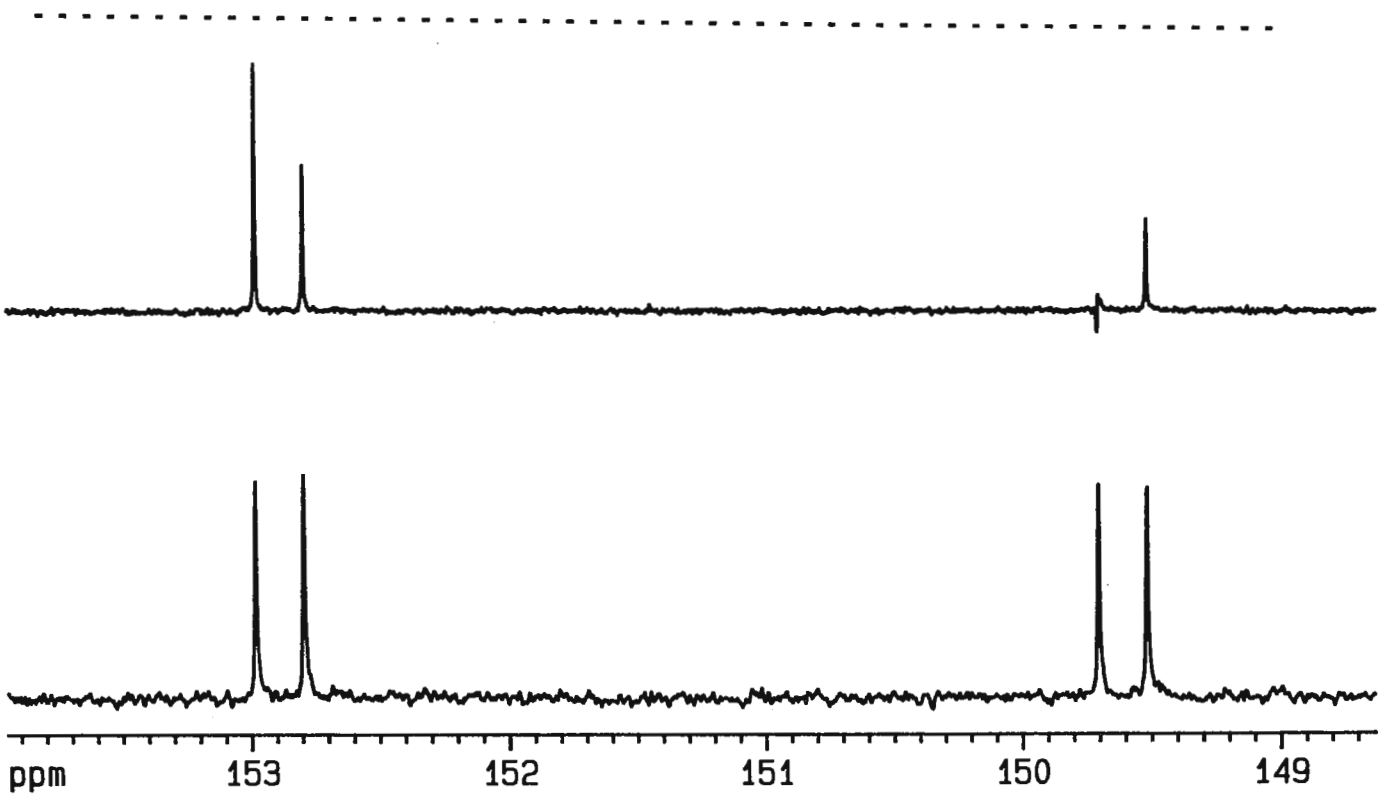



Figure 2. bottom: Normal spectrum of the C-1 carbon on ortho-difluorobenzene.

top: The effect of irradiating the lowest frequency carbon satellite peak in the fluorine spectrum. 25 db of attenuation.

University of Turku
Department of Chemistry
SF-20500 Turku, Finland

Kalevi Pihlaja
*Professor, Dr.*



Professor Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

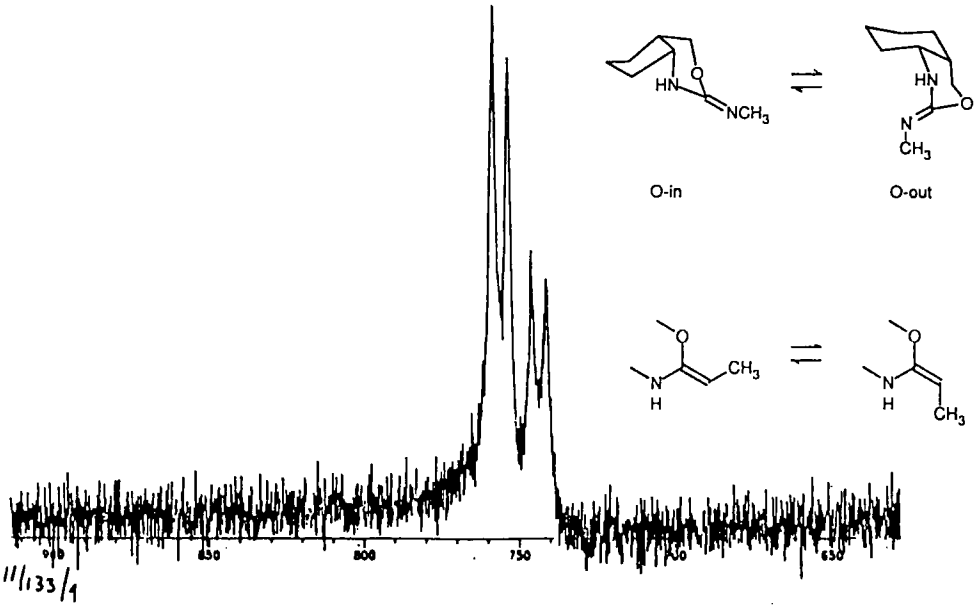
Turku, September 19, 1992
(received 9/30/92)

Dear Dr. Shapiro,

**DYNAMIC NMR ON cis-2-N-METHYLIMINO-5,6-TETRAMETHYLENE-TETRAHYDRO-1,3-OXAZINE**

When studying the low temperature $^1$H NMR spectra of some fused skeleton heterocycles we found an interesting dynamic process in the title compound. At going down to 178 K the ring inversion was frozen out and separate signals were obtained for the O-in (68%) and O-out (32%) conformations (see below). However, another process froze out simultaneously as shown by the fact that the N-methyl signals of both forms split further into doublets (Figure). This is due to freezing out the exchange between the **E** and **Z** orientations of the imino methyl both of which are nearly equally populated.

Similar behaviour could also be found in the thiazine analogue. In the continuation of our study we try to clarify what kind of effect is introduced by substitution of the ring nitrogen atom.




Sincerely

Jorma Mattinen
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Dr. B. L. Shapiro
TAMU-NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303
U. S. A.

Sep. 30, 1992
(received 10/3/92)

Dear Dr. Shapiro:

The NMR center at the Institute of Biomedical Sciences (IBMS), Academia Sinica in Taiwan, is devoted to the studies of structural biology and magnetic resonance imaging and spectroscopy. We now have 600 MHz Bruker AMX600 and 400 MHz Bruker AMX400WB equipped with solid state and microimaging capabilities. An animal imaging system (Biospec BMT 4.7T/40cm) will be installed in next June. In addition, a well-equipped wet chemistry laboratory and excellent in-house molecular modeling and computational facilities are available.

We now have several Permanent and Postdoctoral Positions available. Rank commensurates with qualification. Excellent research support is available. We are also looking for a Laboratory Manager. Qualification for this position is an earned M.S. degree or above and should have strong computer and electronic background, some knowledge and great interest in NMR. Interested applicants, please send CV and research interest to either of the two persons below::

(1) NMR Study of Structural Biology

Dr. Tai-huang Huang
Tel: 011-866-2-789-9039, FAX: 011-886-2-785-3569
E.mail: BMTHH@TWNAS886.BITNET or BMTHH@ccvax.as.edu.tw

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Nankang, Taipei 11529
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Sincerely,

Tai-huang Huang

Chen Chang

LOVELACE MEDICAL FOUNDATION

PRACTICAL USE OF NMR: VOLUME MEASUREMENT OF FLOWING WATER MIXED WITH AIR

(received 10/14/92)

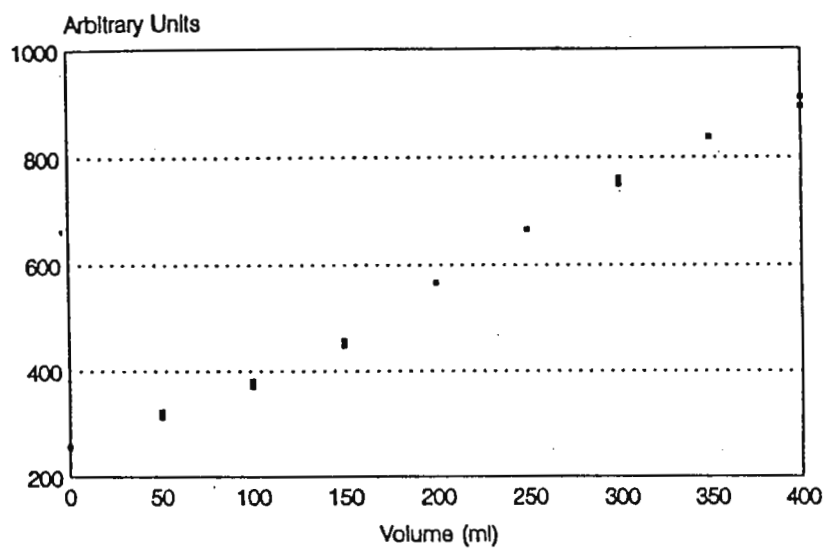
Dear Professor Shapiro,

Following in the footsteps of others, including Southwest Research Institute's efforts such as tractor driven NMR for soil water measurement, dynamite detector for checked airline baggage, etc., we applied NMR to another practical problem, i.e., the determination of total volume of water that flows for a well defined event. This was prompted by NASA's need to make such a measurement in a gravity-less spacecraft. There, the flow is characterized by variable mixture of air and water and the water will have a time dependent velocity distribution. The total volume of flow will be in the range of 100 to 1000 ml over times of the order of 15 to 30 seconds. We called this study "Project-P."

Our idea was to use proton NMR and accumulate signals from prepolarized protons passing through a measurement "window" in such a way that all protons are counted only once. We applied a train of $\pi/2$ pulses with separation $\tau$ where $v_{max}\tau < L$ for window width L and maximum velocity $v_{max}$. In these experiments, $\tau$=20 ms and L=9 cm. The FID was sampled once after each rf pulse and the signals accumulated in the computer. In order to avoid echoes from the successive $\pi/2$ pulses, we applied pseudorandom crusher gradient pulses, i.e., uniform duration but variable strength intensity values of a single gradient component, between the $\pi/2$ pulses. The effectiveness of the crushers was checked by applying the pulse sequence to a static sample in the window and minimizing the FID amplitudes after the first FID. The small residual signal will be the upper limit to the signal from the slowest moving spins in the flow experiment.

We performed the study in a 1.9T/31 Oxford horizontal bore magnet with a Nalorac Quest 4300 NMR imager/spectrometer. The flow system consisted of a 1/4 inch i.d. plastic tubing connected to house vacuum through a phase separator made out of a 2 liter flask. Measured volumes of tap water was poured into a funnel at the input end and any amount of air could be included in the flow by adjusting the way the water was poured. Approximately 12 feet of tubing was coiled inside the bore, upstream of the test section, to provide sufficient nuclear polarization. The test section was defined by two copper foils wrapped around the tubing.

The figure at right shows the total signal as a function of volume of water passed through the system. There are two points at each flow volume representing results of two independent runs where no efforts were made to pour the measured volume of water in the same way. The repeatability ranged from ± 1.7% at small flows to ±0.7% at the fastest flows so that, despite the slight nonlinearity of the data, this plot can be used as calibration to extract accurate flow volumes.

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For an actual airborne device, a suitable single-purpose instrument would have to be designed to minimize weight and power consumption. A combination of narrow band rf electronics and special purpose permanent magnets (of around 0.5 T field) made of neodymium-iron-boron could keep the weight down around 60 pounds. The heaviest component is the prepolarization magnet which probably should be a separate unit because of its lack of strigent field homogeneity specifications. The NMR magnet could be a tubular dipole magnet in which N segmented magnets are arranged so the magnetization direction is rotated by $4\pi/N$ from one segment to the next [K. Halbach, Nucl. Instrm. Methods 169, 1 (1980)]. No iron is needed because the return path of the field will be inside the magnet.

There is a perception out in the real world that most of NMR is imaging as used in clinical medicine. This example demonstrates the versatility of non-imaging NMR for "lowbrow" practical uses. This work was carried out for NASA, in collaboration with Lovelace Scientific Resources, by Steve Altobelli, Arvind Caprihan, Jerry Davis, Eiichi Fukushima, Jasper Jackson, and Hans Petersen.

Sincerely,

---

## Position Available

Eli Lilly and Company, a $5+ billion leader in the development, manufacture and marketing of pharmaceuticals, medical devices and diagnostics, and animal health products, is seeking a Ph.D. level NMR spectroscopist who will collaborate with established groups from several disciplines involved in structure-based drug design.

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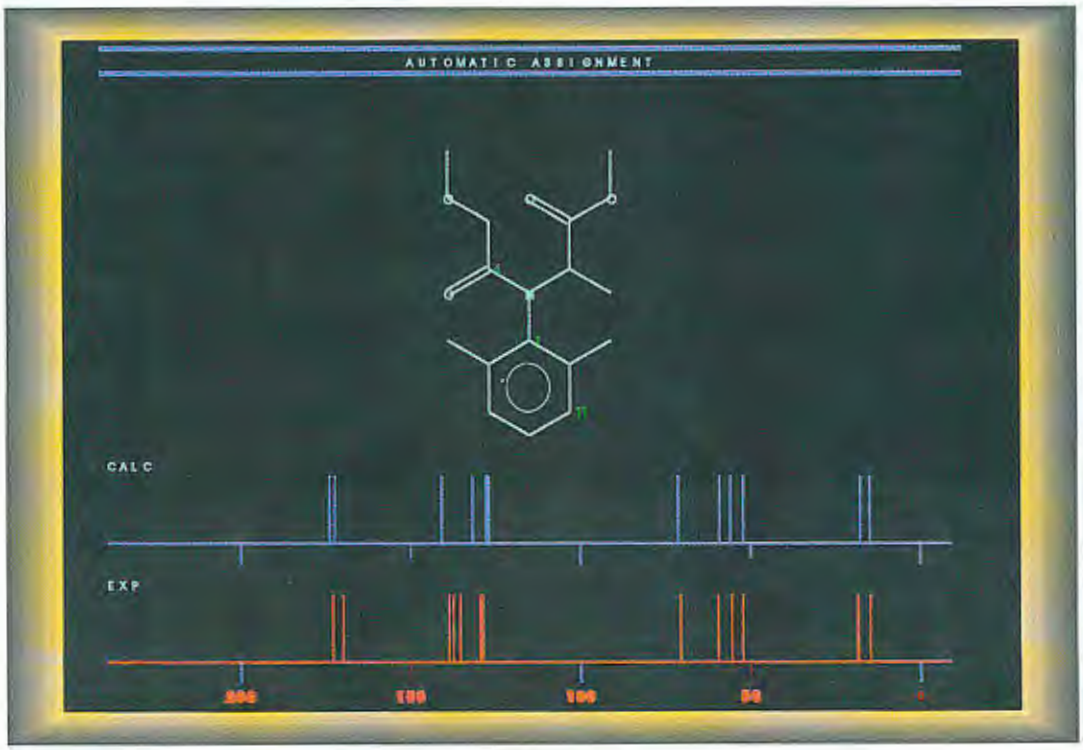


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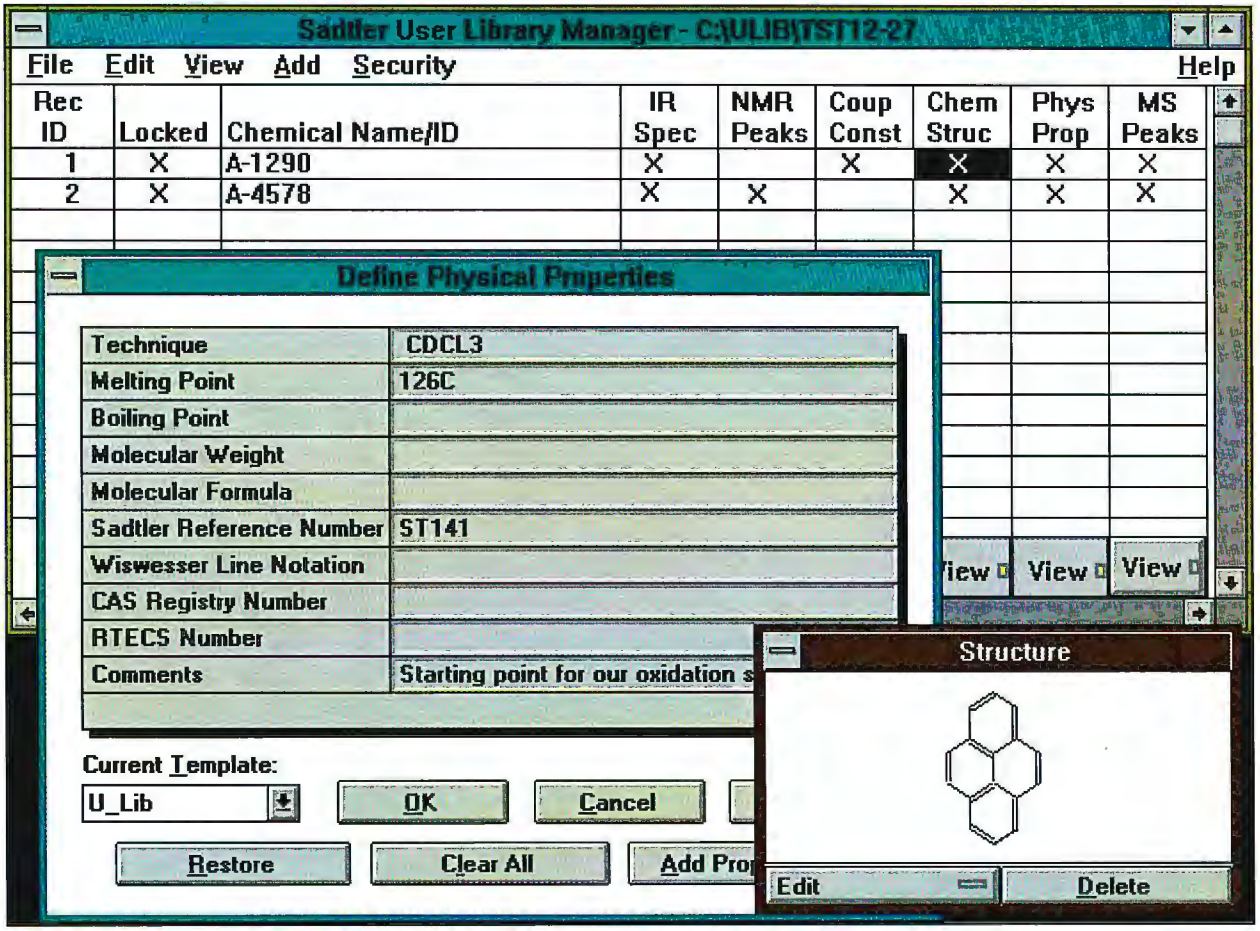


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Professor M. Barfield
Department of Chemistry

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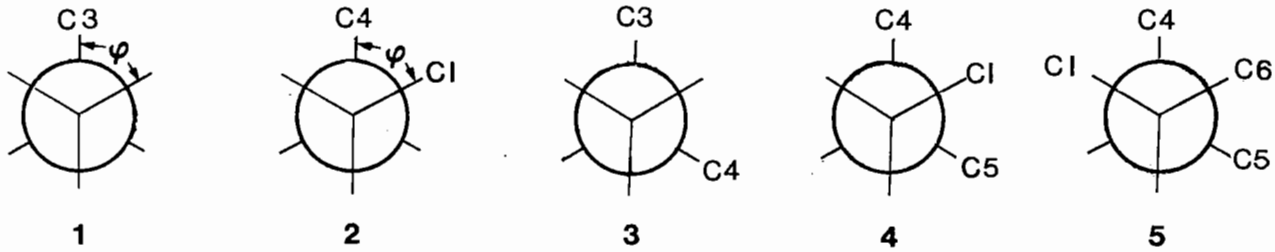
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 9403

(received 10/3/92)

Dear Barry: RE: TOWARDS A QUANTITATIVE $\gamma$-EFFECT IN $^{13}C$ NMR

The ab initio IGLO method for chemical shielding was used in a previous study [1] to describe the $^{13}C$ chemical shift conformational dependencies at the $\alpha$-, $\beta$-, and $\gamma$-positions of aliphatic and alicyclic hydrocarbons. The results for the angularly dependent $\gamma$-effect were in accord with the general experimental observations [2,3] and but did not include a detailed comparison with the experimental data as a function of dihedral angle. More recent shielding calculations, where were described at a recent NATO Workshop on Chemical Shielding, will eventually appear in print[4]. Results were based on the IGLO (individual gauge for localized orbitals) formulation of Kutzelnigg and Schindler [5] for energy optimized structures at the HF/3-21G* level. Carbon-13 shielding calculations were performed as a function of dihedral angle for the series of molecules propane **1**, *n*-butane **2**, *i*-butane **3**, 2-methylbutane **4**, and 2,3-dimethylbutane **5**. Three $\gamma$-effect models arise




in taking the molecules in pairs.

Depicted in Figure 1 are the calculated $\gamma$-effects $\Delta\delta$ inferred from the n-butane/propane model plotted as a function of the dihedral angle $\varphi$ (absolute values) measured about the C2-C3 bond. The solid curve is the best fit to the calculated

Figure 1

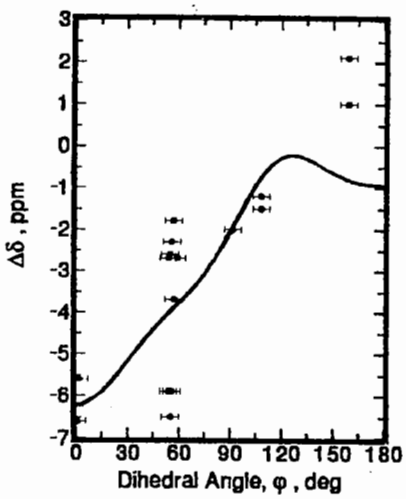



Figure 2

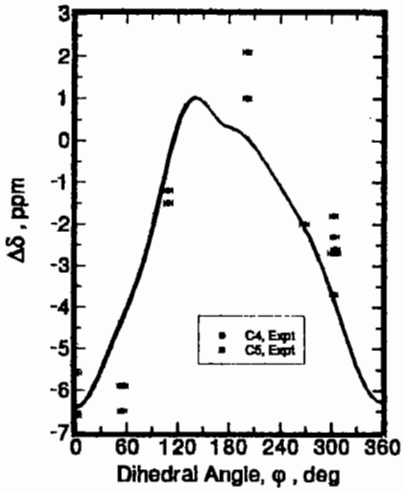
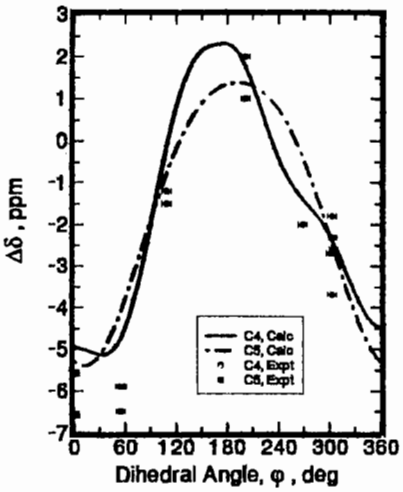



Figure 3



results (Basis Set II' in the notation of the Bochum group [5]). Experimental data for comparison in Fig. 1 are those for a series of relatively rigid molecules [4,6] such as the methyl-substituted bicyclo[2.2.1]heptanes, bicyclo[2.2.2]octanes, and *trans*-decalins. These are all examples of methyl-disubstituted molecules containing the $CH_3$-CH-CH-$CH_3$ moiety (from which $\gamma$-effects are deduced by taking the differences in chemical shift with those molecules having one less methyl group). Uncertainties in dihedral angles based on molecular mechanics procedures are arbitrarily taken to be 5°. Note the large spread of data for the gauche arrangement - about the best that can be said is that any monotonically increasing function is consistent with the experimental data. The pattern of these empirical data in Figure 1 are reminiscent of those in plots given by Lambert and Vagenas [3].

Depicted in Figure 2 are the $\gamma$-effects results for a model based on **3** and **4**. The 180° periodicity is lost. The asymmetry of the curve corresponds to better conformity with large range of gauche $\gamma$-effects. The C4 and C5 carbons in **4** exhibit equivalent $\gamma$-effects, but in anticipation of the next model, the experimental data are conform to two different physical situations.

In Figure 3 are plotted the results of the $\gamma$-effect model which is based on model compounds **4** and **5**. The $\gamma$-effects for the C4 and C5 methyl groups now exhibit different dependencies on dihedral angle, and these are identified with *threo* and *erythro* arrangements, respectively. The experimental data for C4 (filled circles) and C5 (filled squares), which are also plotted in Figure 3, are in much better conformity with the calculated results.

In a related context Kutzelnigg, Fleischer, and Schindler noted [5] a chemical shift difference in the calculated and experimental $^{13}C$ chemical shifts of the two isomeric forms of 3,4-dimethylhexane.

[1] Barfield, M. and Yamamura, S. *J. Am. Chem. Soc.*, **112**, 4747-4758 (1990).
[2] Grant, D. M., Paul, E. G. *J. Am. Chem. Soc.*, **86**, 2984-2990 (1964).
[3] Lambert, J. B. and Vagenas, A. R. *Org. Magn. Reson.*, **17**, 265-270 (1981).
[4] M. Barfield, "Ab Initio IGLO Study of the Conformational Dependence of the $\gamma$-Effect in the $^{13}C$ NMR Spectra of Cyclic Hydrocarbons," in "The Calculation of NMR Shielding Constants and their Use in the Determination of the Geometric and Electronic Structures of Molecules and Solids," J. A. Tossell, ed., Kluwer, Academic Publishers, Dordrecht, in press.
[5] Kutzelnigg, W., Fleischer, U., and Schindler, M. *in* P. Diehl, E. Fluck, and R. Kosfeld, eds., NMR Basic Principles and Progress, Springer, Berlin, Vol. 23, p 165, 1990.
[6] Whitesell, J. K. and Minton, M. A. "Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy," Chapman Hall, New York, 1987.

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12-Oct-92 (received 10/14/92)

*Department of Nuclear Magnetic Resonance*
*and Medical Spectroscopy*

*7701 Burholme Avenue*
*Philadelphia, Pennsylvania 19111*
*215 728 3049*
*FAX 215 728 2822*

Simultaneous and interleaved $^{1}H$—$^{31}P$ Chemical Shift Imaging. (3D—CSI)

Dear Dr. Shapiro,

*In vivo* localized spectroscopy is a diagnostic tool correlating the anatomy from the MRI image with underlying physiology and metabolism, obtained from the distribution of observable metabolites of a particular nucleus. If more than one nucleus is to be observed, the examinations must now be carried out serially, one nucleus at a time, taking considerably longer, since spectroscopy examinations usually require 30—60 minutes each.

We have developed a method to eliminate the need for serial measurements, performing 3D-CSI simultaneously on several hetero-nuclei, (e.g., $^{1}H$, $^{31}P$). The different nuclei are observed at the same field of view (FOV) by exciting each higher $\gamma$ nucleus, at later times, during the same phase encoding gradient waveform as shown in Fig. 1. We adjust the timing of each rf excitation such that the integral of the remaining gradient waveform ($S_{1,2}$ in Fig. 1) times the $\gamma$ of that nucleus, yields an identical number, the FOV, for all nuclei. Since CSI inherently employs only broad-band, short duration rf pulses, it is possible to halt the gradient waveform briefly for the rf pulse and resume them immediately, as shown. Additionally, since protons have a shorter $T_1$ and much higher sensitivity than in vivo phosphorus, it is possible to interleave additional $^{1}H$-only acquisitions between the simultaneous dual observations for a higher spatial resolution proton CSI image.

We use a Siemens Magnetom, equipped with an experimental second rf channel, and our custom-built, dual tuned, head size birdcage coils. We acquired 3D 16×16×16 $^{1}H$ and 8×8×8 $^{31}P$ simultaneous and interleaved spectra of a phantom shown in Fig. 2. The localized spectroscopic $^{1}H$ and $^{31}P$ data have the same spatial distribution and overlap well with the MR images in the Fig. The procedure requires about an hour, indicating that clinical, multinuclear 3D-CSI examinations can be performed in the duration of a currently single nucleus measurement.

Sincerely,

Oded Gonen Joseph Murphy-Boesch Jiani Hu Truman R. Brown

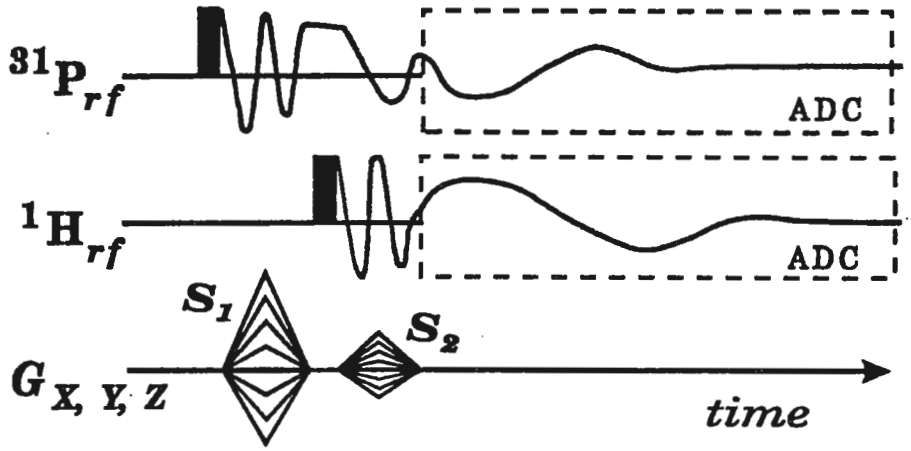



**Fig. 1** Gradient ($G_X$, $G_Y$, $G_Z$) and rf ($^{31}P_{rf}$, $^{1}H_{rf}$), waveforms for simultaneous 3D-CSI experiment. CSI allows gradient splitting, into lobes (due to short, nonselective rf pulse) $S_1$, $S_2$ yielding equal FOV for both nuclei.

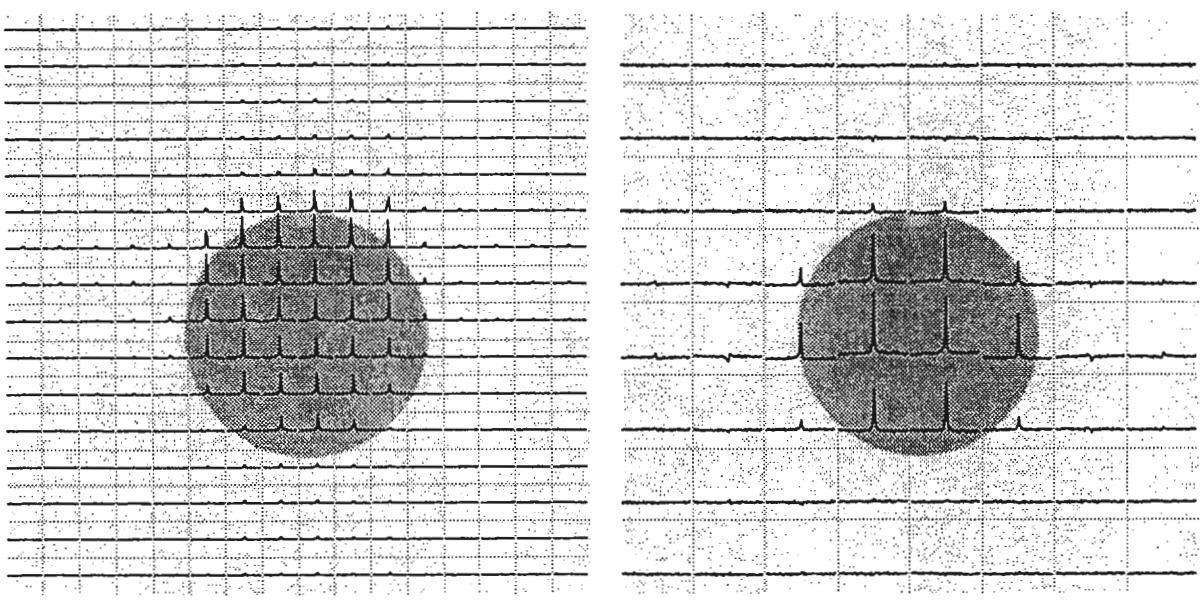


**Fig. 2** Phantom spectra from a single slice: 16×16 $^{1}H$ (left) and 8×8 $^{31}P$ (right) from a 16×16×16 / 8×8×8 $^{1}H/^{31}P$ 3D-CSI set, measured simultaneously. The spectra are superimposed on an MRI image of the phantom slice (in gray) for spatial reference .

GEORGETOWN UNIVERSITY

*Department of Chemistry*

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

September 24, 1992
(received 10/2/92)

**DYNAMIC CONFORMATIONAL ISOMERISM IN CYCLOHEXANE-$d_{12}$**

Dear Dr. Shapiro:

Recently we have been interested in observing phase transitions and dynamical behavior in cyclohexane using a variety of solid state NMR techniques including $^{13}C$ CP/MAS, $^{2}H$ quadrupole echo, and static wideline $^{1}H$. Neat cyclohexane is known to exist at atmospheric pressure in at least two different thermodynamically stable solid phases. Upon heating, a solid to plastic crystalline phase transition occurs at 186.2 K which extends to the isotropic transition (melting point) at 279.8 K. Of particular interest to us was the gradual changeover in the static wideline $^{1}H$ NMR spectra from a Lorentzian lineshape at 240 K to a Gaussian lineshape at 205 K. Since there are no phase transitions in this temperature range (a number of very useful conversations with Prof. Mark Conradi convinced us of this), we decided to investigate cyclohexane in this temperature region using a deuterium Bloch decay combined with magic angle spinning.

The attached $^{2}H$ NMR spectra were obtained on cyclohexane-$d_{12}$ using a single 9$\mu$s $\pi/2$ RF pulse combined with a MAS spin rate of 3 KHz in a static field of 7.04 T (Larmor frequency 46.1 MHz). The two distinct resonances separated by 23 Hz. at 193 K correspond to the axial and equatorial deuterons of cyclohexane which are not exchanging (via ring inversion) on the NMR timescale. As the temperature is raised, the two peaks are observed to coalesce at approximately 222 K, and at higher temperatures the single resonance becomes progressively narrower accompanied by a slight upfield shift. The exchange rate at the coalescence point was calculated to be 51 $s^{-1}$ with a $\Delta G^{\ddagger}$ corresponding to 45.3 kJ $mol^{-1}$.

The rate of ring inversion in cyclohexane has been extensively reported in the liquid and gas phases, recently in a thiourea inclusion complex [1], and in *perfluorinated* cyclohexane [2]. However, we believe that this is the first reported observation of ring inversion in neat cyclohexane in the plastic crystalline phase. We are currently investigating various systems where this technique may be useful as a probe of molecular dynamics, free volume, etc.

We would like to thank the Naval Research Laboratory for use of NMR instrumentation for this work. Please credit this to the Naval Research Laboratory subscription.

Sincerely,

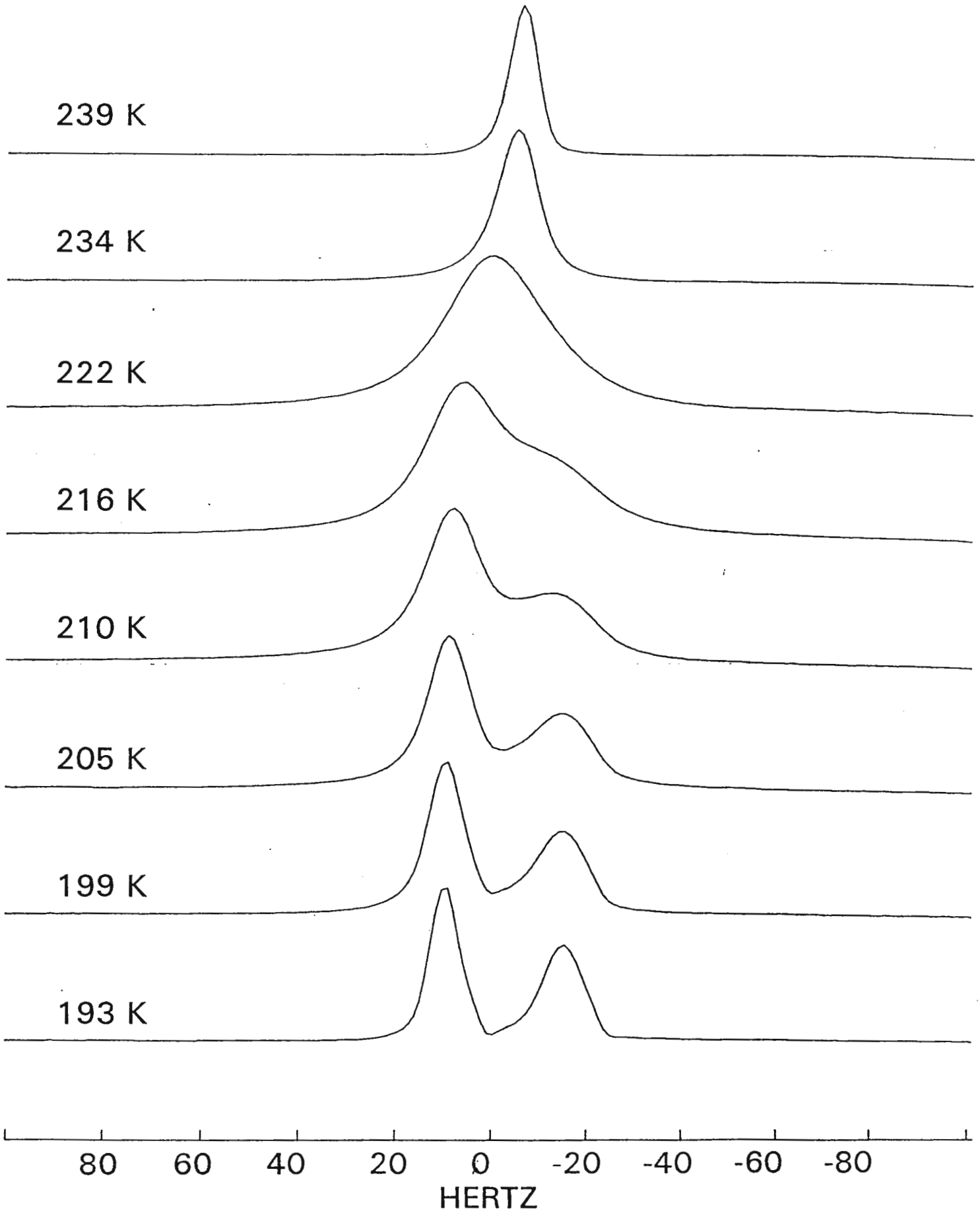
Ken McGrath
Chemistry Division
Naval Research Laboratory

Dick Weiss
Dept. of Chemistry
Georgetown University

[1]. R. Poupko, E. Furman, K. Muller, and Z. Luz, J. Phys. Chem. **95**, 407 (1991).
[2]. J.D. Ellett, R.G. Griffin, and J.S. Waugh, J. Am. Chem. Soc. **96**, 345, (1974).

*Washington DC 20057-2222*
*202-687-6073 FAX: 202-687-6209*

**Deuterium NMR Bloch Decay with 3 KHz MAS on Cyclohexane-$d_{12}$**



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These spectra of AlPO-11 below illustrate these effects. The top spectrum shows single resonance DOR at 625 Hz spinning. The bottom trace shows significant improvement at 980 Hz; note especially the appearance of the octahedral peak at 30 ppm. The middle trace shows 625 Hz DOR with proton decoupling; the peaks are narrower than at 980 Hz, especially the octahedral signal.

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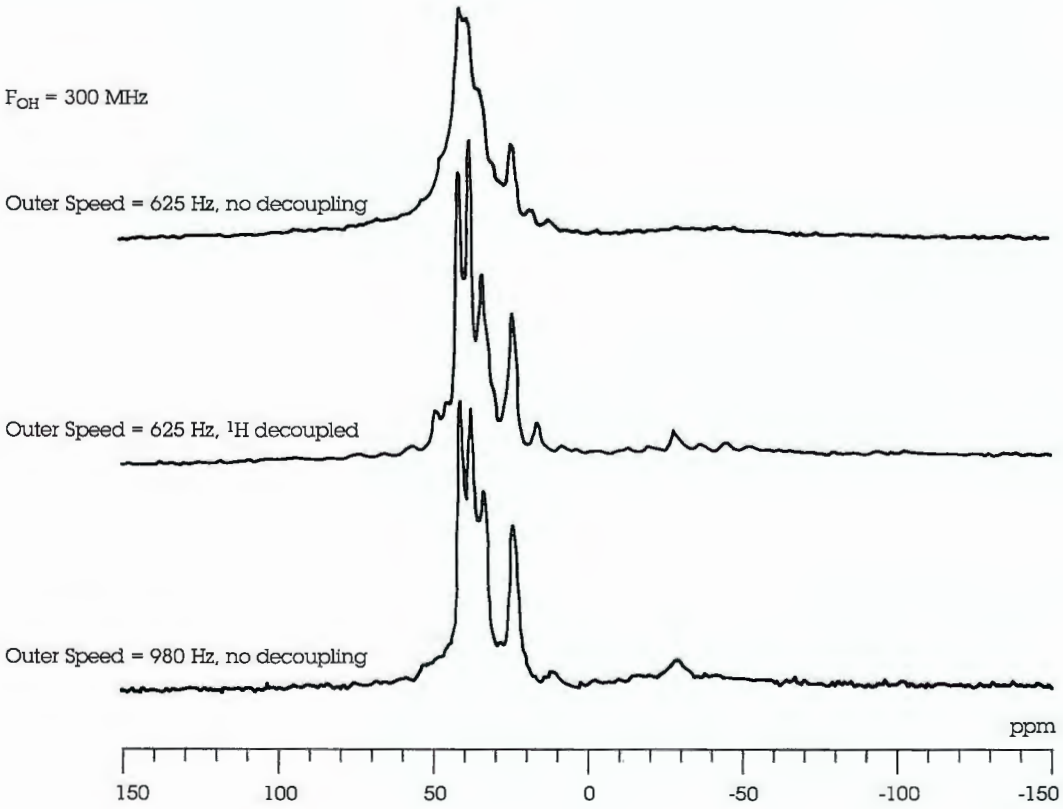


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### Two Channels

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| | ▪ Rotational Resonance | ▪ HCCH-TOCSY | ▪ $^{1}H$, $^{19}F$, Gradient Field Spectroscopy |
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### Three Channels

| Solids | Liquids | Liquids+Imaging |
|---|---|---|
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| | ▪ $^{1}H$, $^{13}C$, $^{15}N$, HMQC-TOCSY | |

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Bernard Shapiro, Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

October 6, 1992
(received 10/10/92)

The Absolute Value of Signs in NMR

Dear Dr. Shapiro,

Cavalier attention to sign (e.g., + or -) in NMR is common, almost a tradition. The choice of sign is inconsequential if one is self-consistent and if one doesn't compare a derivations based on different conventions. This usually applies to the sign of the gyromagnetic ratio and the sign of the J coupling. Variation in sign convention is often a nuisance in chemical shift scales. The variability of sign is also evident in the precession of a magnetic dipole in a magnetic field. Some use the convention $\omega = -\gamma B$ and others use $\omega = +\gamma B$. But once a convention is chosen, the precession of the vector is fixed by the definition that "angular velocity ...(is) a vector whose direction and sense are such that the motion appears clockwise to one looking in the direction of the vector." Given that $\tau = \mu \times \mathbf{B}$ using the right-hand rule, then (for $\gamma > 0$) $\omega = -\gamma B$. That is, a field in the +z direction causes a clockwise precession when viewed in the -z direction. Furthermore, a 90° pulse with +x phase will rotate magnetization from the +z axis to the +y axis. And because $\omega = d\theta/dt$, the pulse angle is formally $\theta = -\gamma B_1 t_p$. I offer a survey of the conventions used in some texts.

| Ref | $\omega =$ | Rotation caused by +z field as viewed from above (along -z axis) is | A 90° pulse with +x phase rotates dipole from the +z axis to the | $\theta =$ |
|---|---|---|---|---|
| 1. | $+\gamma B$ (p.167) | counterclockwise (p.256) | +y axis (p.50,199,241) | $+\gamma B_1 t_p$ (p.242) |
| 2. | $-\gamma B$ (p.21) | counterclockwise (p.xxx) | +y axis (p.26,39) | $+\gamma B_1 t_p$ (p.25) |
| 3. | $+\gamma H$ (p.13,37) | clockwise (p.9) | +y axis (p.18,38,54) | $+\gamma H_1 t_p$ (p.17) |
| 4. | $-\gamma B$ (p.2,7) | counterclockwise (p.7) | +y axis (p.24) | $+\gamma B_1 t_p$ (p.23) |
| 5. | $-\gamma H$ (p.2,17,107) | counterclockwise (p.108) | +y axis (p.114) | $-\gamma H_1 t_p$ (p.4 and 7) |
| 6. | $-\gamma B$ (p. xxii) | | −y axis (p.118) | $-\gamma B_1 t_p$ (p.118) |
| 7. | $-\gamma B$ (p.12) | clockwise (p.16) | +y axis (p.36) | $-\gamma B_1 t_p$ (p.34) |
| 8. | $\lvert\gamma\rvert B$ (p.8), $+\gamma B$ (p.69) | clockwise (p.9) | +y axis (p.xx) | $+\gamma B_1 t_p$ (p.74) |

Sincerely,

E. Rhetentiv

Eanole Rhetentiv

(1) S. W. Homans, A Dictionary of Concepts in NMR, (New York, Oxford, 1989); (2) T. C. Farrar, Pulse Nuclear Magnetic Resonance Spectroscopy: Introduction to the Theory and Applications, (Farragut Press, Chicago, 1987); (3) R. T. Schumacher, *Introduction to Magnetic Resonance: Principles and Applications*, (New York, Benjamin, 1970); (4) B. C. Gerstein, and C. R. Dybowski, *Transient Techniques in NMR of Solids: An Introduction to Theory and Practice*, (New York, Academic, 1985); (5) M. Goldman, *Quantum Description of High-Resolution NMR in Liquids*, (New York, Oxford, 1988); (6) R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, (New York, Oxford, 1987); (7) N. Chandrakumar, and S. Subramanian, *Modern Techniques in High Resolution FT-NMR*, (New York, Springer-Verlag, 1987); (8) R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*, (New York, Wiley, 1986).

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30 Years of Activity

ETTORE MAJORANA CENTRE FOR SCIENTIFIC CULTURE

# Advanced School on Magnetic Resonance and Protein Dynamics

## Erice, Trapani, Sicily, Italy
## 15-21 March 1993

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### Program and Lecturers

**Basic Methods for the Study of Macromolecular Dynamics**

| | |
|---|---|
| Modern NMR Spectroscopy | Richard R. Ernst, ETH Zentrum, Zurich |
| 3D and Multidimensional NMR | Hartmut Oschkinat, EMBL Heidelberg |
| Molecular Dynamics Studies of Protein-Nucleic Acid Complexes | Michael Levitt, Cell Biology, Stanford |
| NMR and Optical Fluorescence in the Study of Macromolecular Dynamics | Rudolf Rigler, Karolinska Inst., Stockholm |
| The Definition of Motional Processes in Proteins | Gerhard Wagner, Harvard Medical School |

**Combinations of Biological and Physical Methods and the Implications of Dynamics**

| | |
|---|---|
| Protein Dynamics and their Implications for Protein Structure Determination by NMR | Oleg Jardetzky, SMRL, Stanford |
| NMR Studies of Protein Folding | Christopher M. Dobson, Oxford |
| Studies of Flexible Proteins: NMR and other Physical Methods | Michael Weiss, Harvard Medical School |
| Isotopic Spectral Editing in NMR Studies of Protein Structure and Dynamics | John L. Markley, University of Wisconsin |
| The Use of Site-Directed Mutagenesis in NMR Structural Studies | Sture Forsén, University of Lund, Sweden |
| Structure and Flexibility of Biological Active Peptides Determined by NMR | Jean-François Lefèvre, IBMC, Strasbourg |

**Studies of Specific Systems**

| | |
|---|---|
| NMR Studies of the Structure and Dynamics of Large Proteins: the Antibody System | Yoji Arata, University of Tokyo |
| Structure and Dynamics of Metalloproteins | Ivano Bertini, University of Florence |
| Muscle Proteins | Brian D. Sykes, University of Alberta |
| Structure and Dynamics of Nucleic Acids | Cornelius W. Hilbers, NSR Centre, Nijmegen |
| Mechanisms of Intermembrane Lipid Transport | Fritz Paltauf, Technische Universität Graz |
| NMR Studies of Macromolecular Interactions | Gordon C. K. Roberts, NMR Centre, Leicester |
| Dynamics of Polysaccharides | Robert G. Shulman, Yale Medical School |

### PURPOSE OF THE SCHOOL

The purpose of the School is to present the different methods for analyzing molecular dynamics, illustrated by the most advanced studies ranging from the determination of very fast internal motion in macromolecules to the observation of the slow process of protein folding. These analyses also consider the biological activity of the protein. The implication of the dynamics for the determination of three-dimensional structure will also be developed. The subjects which will be covered during the school fall into three broad categories:

1. Basic Methods for the Study of Macromolecular Dynamics
2. Combinations of Biological and Physical Methods and the Implications of Dynamics
3. Studies of Specific Systems

NMR has reached the stage where both three-dimensional structure and dynamics can be studied quite accurately. An integrated approach between these two aspects should be utilized more and more in future research. The proposed course should bring together the interesting features of such an integrated approach.

### VENUE

The Ettore Majorana Centre for Scientific Culture was founded in 1963 in the pre-medieval mountain town of Erice near Palermo as a Conference Centre, taking its inspiration from the Italian Physicist, Ettore Majorana. The Centre's lecture halls are located in two restored monasteries and the ancient Plazzo Ventimiglia. School participants are housed in the Centre Institutes or local hotels.

### GENERAL INFORMATION

*Prospective participants should apply to either:*

Prof. Oleg Jardetzky or
Stanford Magnetic Resonance Laboratory
Stanford University
Stanford, CA 94305-5055
USA
fax: +415/723-2253
telex: 348402 STANFRD STNU A

Prof. Jean-François Lefèvre
Institut de Biology Moleculaire et Cellulaire
15 rue Descartes
67084 Strasbourg Cedex
France
fax: +33/88 61 06 80

*stating:* (1) date and place of birth, nationality, qualifications and present position; (2) address, fax and phone numbers; and (3) list of publications.

Young researchers with little experience should enclose a letter of recommendation from the head of their research group or from a senior scientist active in the field.

Applicants interested in submitting unpublished results should send the title and an outline in about 200 words. Selected papers will be presented and discussed in special sessions.

The total fee, including full board and lodging (arranged by the School) is US $700. Limited financial aid available. Participants should arrive by 5 p.m. on the 15th.

THE CLOSING DATE FOR RECEIPT OF APPLICATIONS IS JANUARY 15, 1993. NO APPLICATION FORM IS REQUIRED.

*Attendance will be limited to ~50 students, to be selected by the Co-Directors. Further details will be mailed with the acceptance letter.*

Oleg Jardetzky
Co-Director of the School

A. Zichichi
Director of the Centre

Jean-François Lefèvre
Co-Director of the School

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October 12, 1992
(received 10/19/92)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro:

Computer Program for Shift Prediction and Spectral Simulation

In the use of $^{13}C$ NMR for organic structure determinatiuon, a major task is to predict the $^{13}C$ chemical shifts of suspected structures and to match the expected spectrum with the experimental spectrum. Two of the more common methods entail: (1) structure search using a spectral library (or a computer database); (2) use of empirical shift additivity rules. Computer approaches have been devised, including an earlier effort by this author[1] (program CSHIFT).

In view of the continuing need for quick estimates of $^{13}C$ shifts, a new PC-based program (called CSPEC) has been written, applicable to aliphatic carbons. The major features are given below:

1. Easy input and editing of structures,
2. Detailed shift additivity rules to improve shift prediction,
3. Provision for saving and retrieving structures,
4. A "parent structure" option whereby the shifts of a compound (say, methylcyclohexane) can be calculated from the known shifts of a "parent structure" (viz., cyclohexane).
5. Provision to plot the simulated spectrum (with optional "noise").

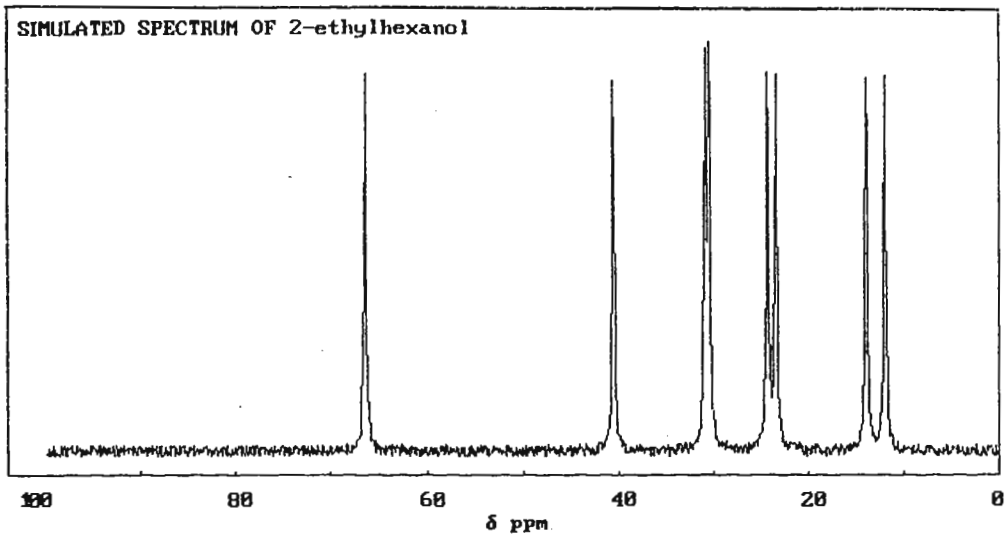
The shift rules are transparent to the user. The user simply types in the structure as he/she would draw on paper. All operations are carried out with the F1-F10 keys (e.g., erase structure, calculate shifts, fix known shifts, parent structure option, output, and others).

An example of shift estimation for 2-ethylhexanol and the simulated spectrum are given below:

```
CSPEC        1         2         3
   123456789012345678901234567890 12
  1
  2
  3
  4
  5      C*C*C*C*C*C*OH
  6                *
  7                C
  8                *
  9                C
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
```

```
Shift of carbon at: 5 , 6  =  14
Shift of carbon at: 5 , 8  =  23.4
Shift of carbon at: 5 , 10  =  30.5
Shift of carbon at: 5 , 12  =  30.9
Shift of carbon at: 5 , 14  =  40.6
Shift of carbon at: 5 , 16  =  66.4
Shift of carbon at: 7 , 14  =  24.3
Shift of carbon at: 9 , 14  =  12
```

```
curr file :
9 , 14   shift c : 12
1-ERASE  2-CALC  3-FIX  4-PCALC  5-XPAND  6-OUT  7-LOAD  8-SAVE  9-CLR  10-QUIT
```




Some of the features of the program have been previously described in ref. 2. The program has been submitted to Quantum Chemistry Program Exchange, Creative Arts Building, Indiana Univ., Bloomington, IN 47405 (E-Mail: QCPE @UCS.Indiana.EDU). Anyone interested may write to QCPE and ask for QCMP Number 122. I understand that the total cost (including processing and handling) is $60.00.

Yours very truly,

H. N. Cheng
Research Associate

References:

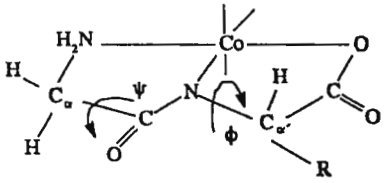
1. H. N. Cheng, S. J. Ellingsen, *J. Chem. Inf. Computer Sci.*, 23, 197 (1983).
2. H. N. Cheng, M. A. Bennett, *Anal. Chim. Acta*, 242, 43 (1991).

(received 9/24/92) September 10, 1992

Mayo Foundation Rochester, Minnesota 55905 Telephone 507 284-2511

Mayo Clinic Mayo Medical School
Mayo Graduate School of Medicine

*Department of Biochemistry and Molecular Biology*




HH COUPLING ACROSS *trans* PEPTIDE BOND

Dear Professor Shapiro:

We were able to observe and study interproton coupling $^5J_{\alpha\alpha'}$ across *trans* peptide bond in dipeptides chelated to cobalt(III). As it is known, a rigid backbone of a dipeptide is established upon formation of two five-membered chelate rings (Scheme). Peptide backbone dihedral angles ψ and ϕ are then found in the regions $0^0 \pm 20^0$ and $180^0 \pm 20^0$ degrees, respectively. The well defined and rather rigid structure of chelated dipeptides thus provided an excellent reference conformation for calibration of the coupling constant across the *trans* peptide bond.

Positive coupling constants, 1-2 Hz, have been observed (Fig.1). The most attractive aspect, however, is in probing of $^5J_{\alpha\alpha'}$ coupling sensitivity on changes in electronic character of the peptide bond. Namely, peptide oxygen is the most favorable proton aceptor of the chelated dipeptide and may be fully protonated (Fig.2), without affecting peptide conformation. We expect this study to resolve dispute on applicability of $^5J_{\alpha\alpha'}$ coupling constant for elucidation of peptide conformation in solution.[1,2]

1. Davies, D.B., and Khaled, Md. A., *J. Chem. Soc., Perkin Trans. 2* **1976**, 187-196; 1238-1244; 1327-1334.
2. Barfield, M., Al-Obeidi, F.A., Hruby, V.J., and Walter, S.R., *J. A. Chem. Soc.*, **1982**, *104*, 3302-3306.

Sincerely yours,

Nenad Juranić
INTERNET: juranić@mayo.edu

Slobodan Macura
INTERNET: macura@mayo.edu

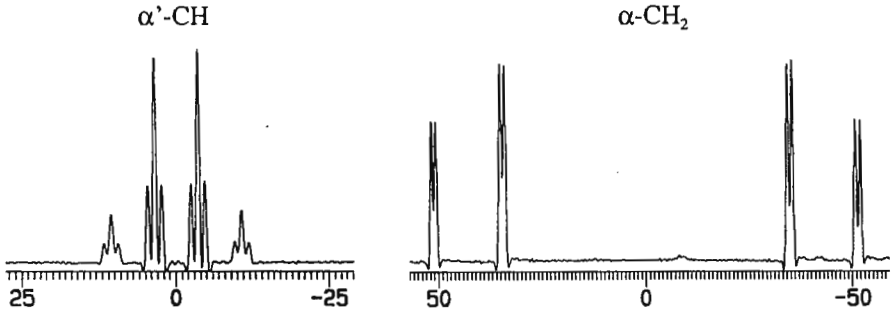



FIG.1. Partial $^1H$ NMR Spectrum (Hz) of $[Co(Gly\text{-}L\text{-}Ala)(NH_3)_3]Cl$ in $D_2O$ (AMX-500).

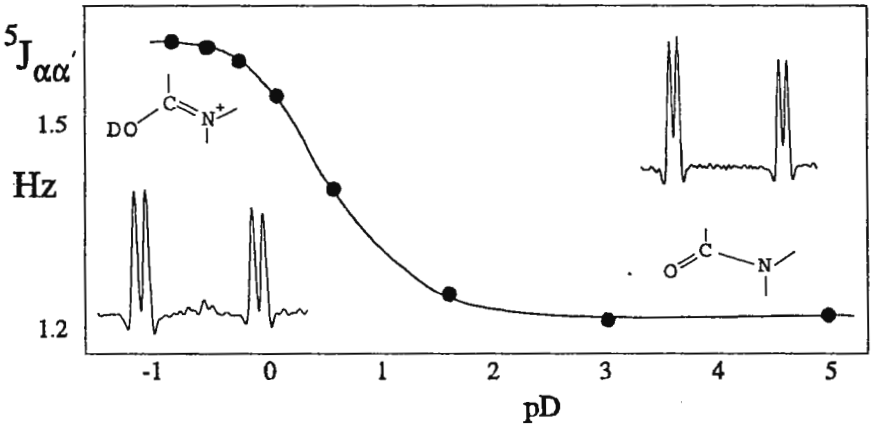



FIG.2. pD dependence of chelated Gly-L-Alanine interproton coupling across *trans* peptide bond ($^5J_{\alpha\alpha'}$).

HUNTER COLLEGE
of The City University of New York
Department of Physics and Astronomy • 695 Park Avenue, New York, N.Y. 10021 • (212) 772-5248

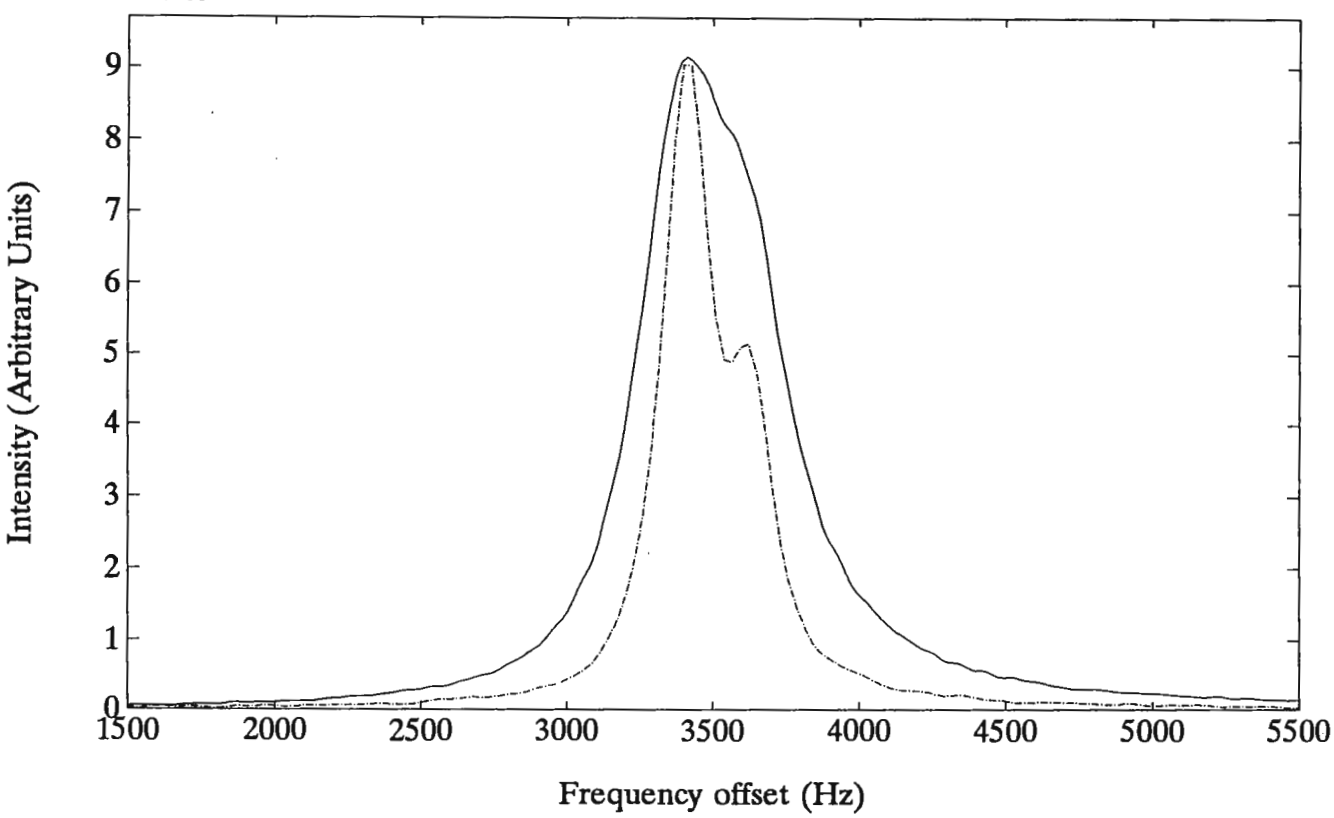
Dear Dr. Shapiro: (received 10/17/92) October 15, 1992

**Re: NARROWING OF NQR LINES BY NON-RESONANT IRRADIATION**
A contribution to the Texas A & M NMR Newsletter

The actual lineshapes of Nuclear Quadrupole Resonance (NQR) signals is due to a variety of interactions which reflect molecular and crystal structure and dynamics. Often this lineshape structure is obscured by a diffuse broadening due to dipole-dipole interactions with neighboring spins, typically protons, and it might sometimes be desirable to reduce this spin-spin coupling. In this letter we would like to present results on a non-resonant method to accomplish "spin-spin decoupling" in NQR.

In the figure below, the solid line is the $^{14}N$ NQR spectrum of Triethylenediamine, $C_6H_{12}N_2$, at 77 K, in the earth's magnetic field. The resonance frequency is close to 3693.5 kHz. The site has spin I=1 and an axially symmetric electric field gradient. The dashed line shows the same spectrum obtained when a second irradiation is present with frequency 11 kHz, magnitude of 20 Gauss peak, and circularly polarized along the rf coil axis. A narrowing of around a factor of two is evident. This effect can be understood in terms of the "dressed atom" theory of S. Haroche [Ann. Phys. (France) **6**, 189 (1971)]. The structure resolved by this line-narrowing scheme cannot be due to the protons, and remains a mystery to me at this time.

Sincerely,
Robert A. Marino
Robert A. Marino
Professor



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- ***1987*** ***1000 G/cm Pulsed Field Gradient***
- ***1987*** ***7 mm MAS at 9 kHz***
- ***1988*** ***650°C MAS***
- ***1989*** ***Precision Temperature Controller***
- ***1990*** ***Dynamic Angle Spinning***
- ***1991*** ***14 mm MAS at 7 kHz***
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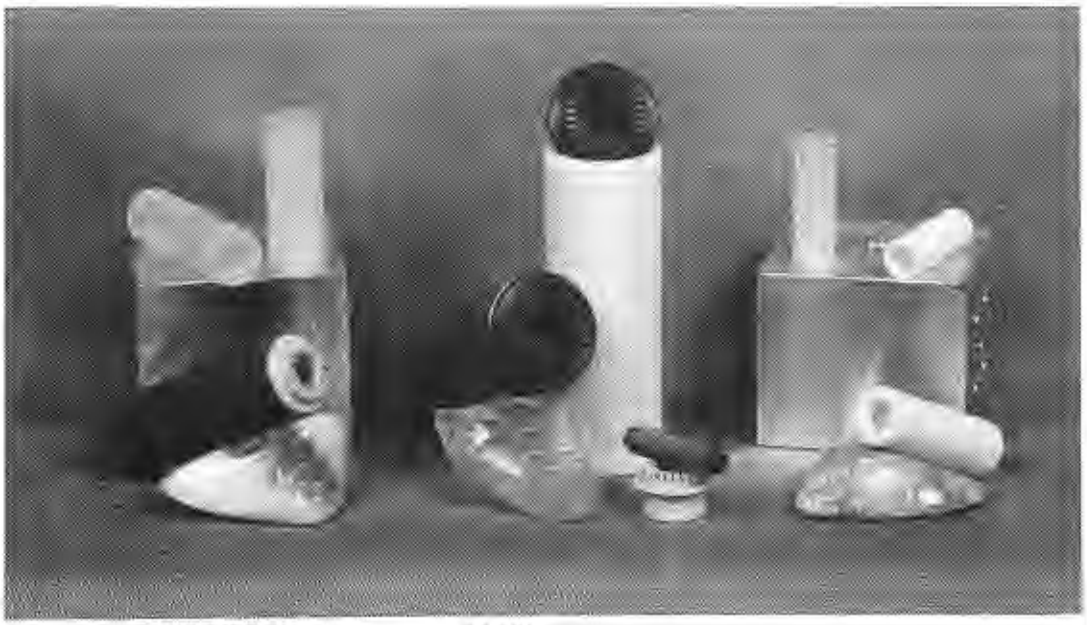

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Edmonton

Department of Biochemistry

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474 Medical Sciences Building, Telephone (403) 492-5460
Fax (403) 492-0886

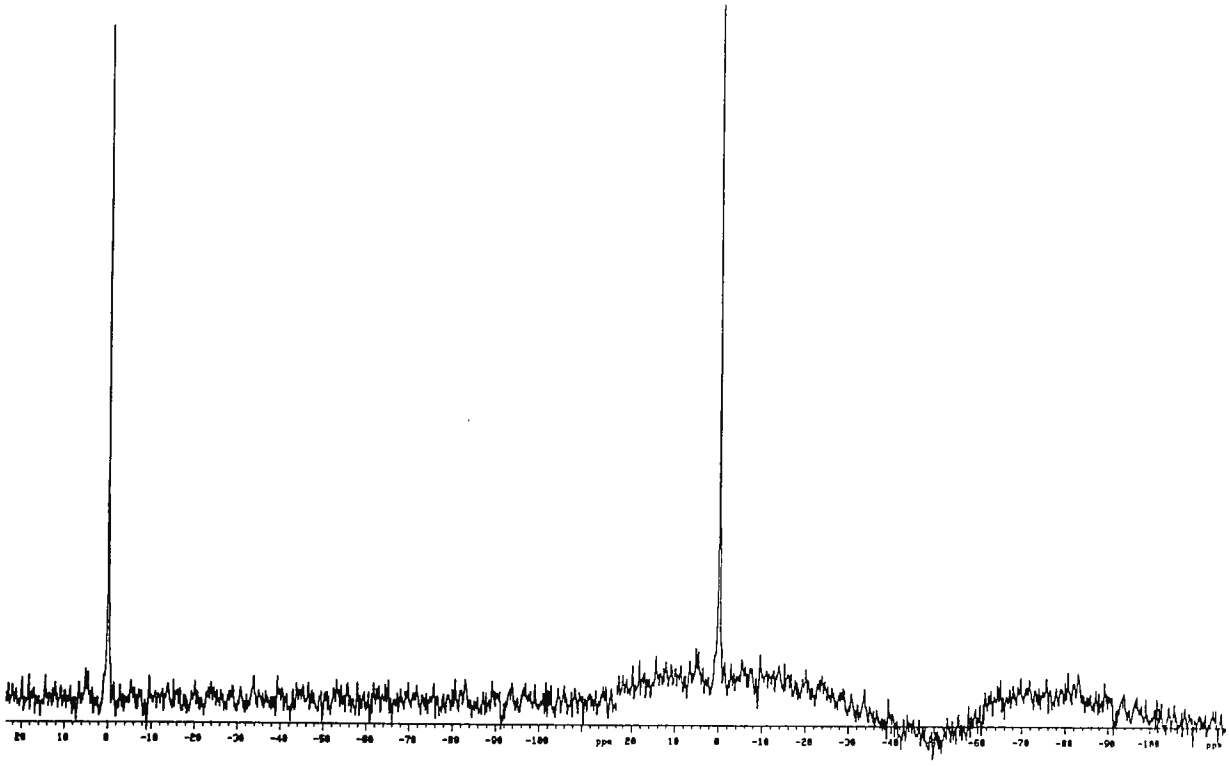
September 23rd, 1992
(received 9/29/92)

TAMU NMR Newsletter
c/o Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303
U.S.A.

**Title: 'Removal' of $^{19}F$ Background**

Dear Barry:

In these days of 2D, 3D and 4D triple resonance, $^{1}H$, $^{13}C$, and $^{15}N$ NMR we still keep an active interest in $^{19}F$ NMR which can be a very useful nucleus for studying biological reactions, especially in large proteins. Recently we have been studying the complex of smooth muscle myosin subfragment-1 (MW ~110,000) with ADP and either $AlF_4^-$ or $BeF_3^-$ using $^{19}F$ NMR on our Unity 300. These studies are in collaboration with M. Ikebe at Case Western and his former colleague S. Maruta who is at Soka University in Tokyo. One problem that continues to plague these studies is $^{19}F$ background from the probe, shielded cable, etc. especially when studying relative broad lines (≈100 Hz) at low concentrations (~0.1 mM) with wide sweep widths (≈200 ppm). Figure 1A shows a spectrum of TFA with the 'baseline' roll that results from the $^{19}F$ background. We have found that backwards linear predication (using the standard Varian software) is a very effective way of removing this baseline roll. Figure 1B shows the resulting spectrum after the first 8 points have been corrected by this procedure.



Best regards,

Brian

Brian D. Sykes, Ph.D.
Professor of Biochemistry

Gillian D. Henry
Research Associate

**THE UNIVERSITY OF MELBOURNE**
School of Chemistry

Professor B. L. Shapiro,
966 Elsinore Court,
Palo Alto, Ca 94303.

22 September, 1992
(received 9/26/92)

**NMR OF PARAMAGNETIC TUNGSTEN COMPLEXES**

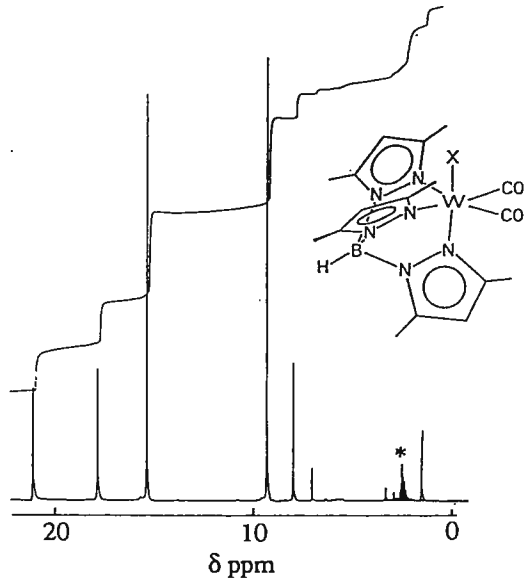
Dear Professor Shapiro,

As models for tungsten enzymes and as a means of stabilizing unusual combinations of π-base and π-acid ligands, we are exploring the chemistry of hydrotris(3,5-dimethylpyrazolyl)borate (L) complexes of tungsten. Typically NMR is employed for the characterization of diamagnetic complexes and EPR is employed in the case of paramagnetic W(V) complexes. However, we have discovered that paramagnetic W(II) and non-oxo-W(IV) complexes such as $LW^{II}(CO)_2X$ and $LW^{IV}X_3$ (X = halide) exhibit paramagnetically shifted spectra which provide the same valuable structural information typically obtained by NMR studies of diamagnetic compounds. In the spectra of the above complexes the respective molecular $C_{3v}$ and $C_s$ symmetry is clearly revealed by the resonance patterns (Table). The spectrum of $LW(CO)_2Br$, which is oxidized to the unusual oxo-(carbonyl) complex LWO(CO)Br, is shown in the Figure. Thus, when disappointing results attend the recording of $^1H$ NMR spectra in the 0-10 ppm region, it is our current practice to explore a greater spectral width for paramagnetic species. This has in many cases proved a valuable protocol.

Table: Chemical Shifts (vs $CHCl_3$ = 7.23 ppm)

| Compound | δ ppm (*n* H) | | | Symmetry |
|---|---|---|---|---|
| $LW(CO)_2Br$ | 1.5 (1) | 8.2 (2) | 9.6 (6) | $C_s$ |
| | 15.8 (6) | 18.4 (3) | 21.6 (3) | |
| $LWCl_3$ | 16.3 (3) | 20.7 (9) | 21.8 (9) | $C_{3v}$ |

Figure: $^1H$ NMR spectrum of $LW(CO)_2Br$ in $CDCl_3$




Charles G Young.

Please credit to Dr. D. P. Kelly's subscription.

**Charles G. Young, Aston A. Eagle, Les J. Laughlin, Simon Thomas**

The University of Melbourne, Parkville, Victoria 3052, AUSTRALIA
Tel: (61 3) 344 6515/6473 Fax : (61 3) 347 5180
email: charles_young.chemistry@muwayf.unimelb.edu.au

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of Yeshiva University
Jack and Pearl Resnick Campus
1300 Morris Park Avenue, Bronx, NY 10461

Phone: (212) 430-2729
FAX: (212) 828-1377

*Department of Physiology and Biophysics*

October 1, 1992
(received 10/5/92)

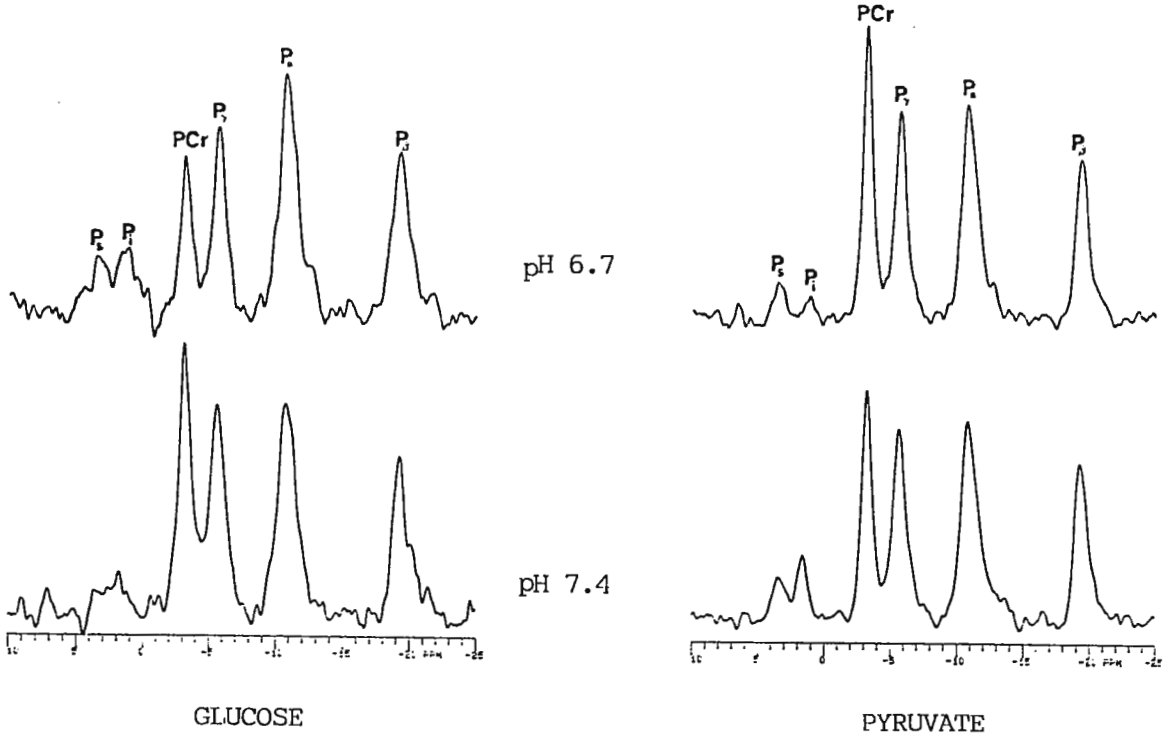
Dr. B. L. Shapiro
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry,

**SUBSTRATE-DEPENDENT EFFECTS OF METABOLIC ACIDOSIS ON CARDIAC $^{31}$P NMR SPECTRA**

High energy phosphates in Langendorff perfused rat hearts were evaluated by $^{31}$P NMR during metabolic acidosis. During acidosis, cardiac $pH_i$ approached that of the perfusing solution (pH~6.7). In hearts perfused with glucose as the sole carbon source, the ratio [phosphocreatine]/[ATP] decreased during acidosis (see Figure). In contrast, in hearts supplemented with pyruvate (2.8 mM) this ratio increased during acidosis. Oxygen consumption decreased in both glucose only and pyruvate-glucose perfused hearts. Using the creatine kinase equilibrium constant and the intracellular free [$Mg^{2+}$] (measured from the $^{31}$P NMR spectra), [MgADP] was found to be significantly decreased in pyruvate-perfused hearts but was not significantly altered in glucose-perfused hearts during metabolic acidosis. These data indicate that [MgADP] may be the regulator of cardiac oxidative phosphorylation in the presence of excess pyruvate; however, during metabolic acidosis in hearts perfused with glucose only, ATP synthesis appears limited by the availability of pyruvate via glycolysis.

Linda A. Jelicks  Raj K. Gupta




$^{31}$P NMR spectra of rat heart perfused with glucose (left traces) or pyruvate-glucose (right traces) before (lower traces) and during (upper traces) metabolic acidosis.

# PURDUE UNIVERSITY

DEPARTMENT OF CHEMISTRY

Dr. Barry Shapiro
TAMU Newsletter
966 Elsinore Court
Palo Alto, CA 94303

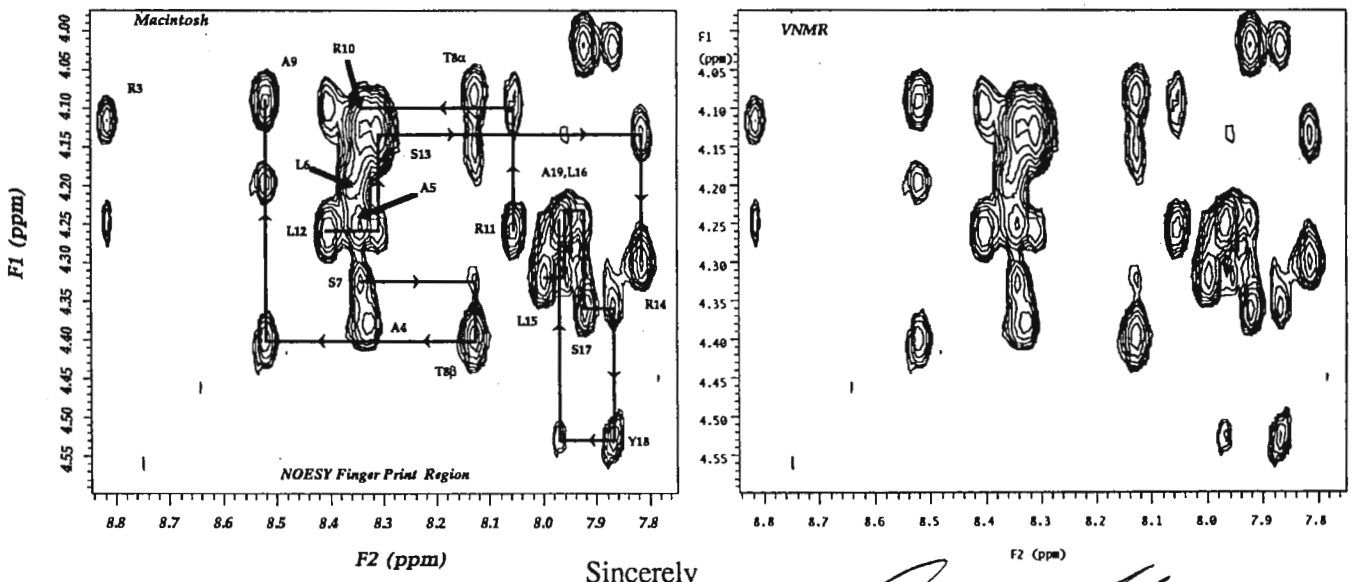
MONDAY, OCTOBER 5, 1992
(received 10/9/92)

Dear Barry:

We have often found that our traditional methods of annotating 1D and 2D NMR spectra to be unsatisfactory. As we have several Macintosh computers in the lab we desired a way to transfer spectra from VNMR (Varian) or FELIX (Hare) into Macintosh drawing programs such as MacDraw or MacPaint. As we were not aware of any commercial software that accomplished this task we chose to write our own software.

We have written a program for the Macintosh, HPGLtoClipboard, that translates an HPGL file generated by VNMR or FELIX into a spectrum drawn in PICT format. This spectrum can then be copied into the Macintosh clipboard and pasted into MacDraw, MacPaint or any other program capable of using PICT format. An example of the type of annotation possible is shown below.

HPGLtoClipboard requires system 7.0 or above and can be obtained by writing us at the address listed below. Please send a 3.5 in. floppy disk and a postage paid, self addressed envelop.




Sincerely

Kevin Thornton

David G. Gorenstein

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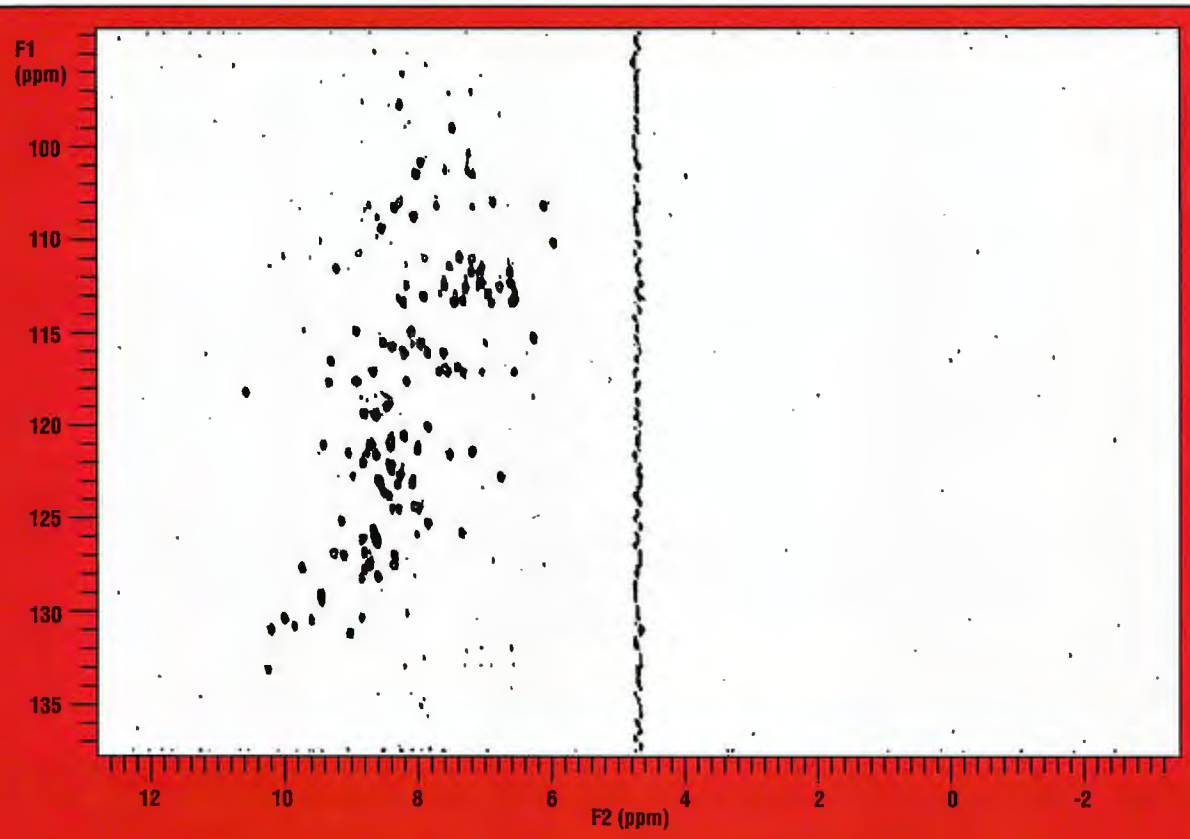


*This phase sensitive $^{15}N$ HSQC spectrum of 1.7 mM uniformly $^{15}N$ enriched 110 amino acid cellulose binding domain fragment of cellulase in 90% $H_2O/D_2O$ was obtained on a UNITY® 500 MHZ spectrometer equipped with Varian's new Pulsed Field Gradient module. The experiment was acquired with 1 transient per increment and no presaturation. Sample provided by Dr. L. Kay (University of Toronto).*

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MARBURG, DEN 07. Oktober 1992

TELEFON (06421) 28-1 (received 10/13/92)

DURCHWAHL: (06421) 28 5520

TELEX 482372

TELEFAX (06421) 285547

Prof. Dr. B. L. Shapiro
TAMU-NMR Newsletter
966 Elsinore Court
Palo Alto, Cal. 94303
USA

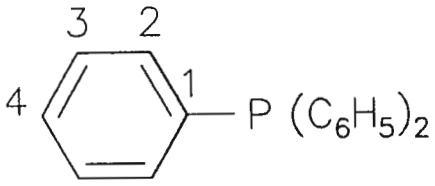
**Contribution #25: 3D H,C,P Correlation**

Dear Barry,

To celebrate my 25th contribution to this wonderful newsletter I thought of an even more important communication than all the 24 before...

After our experience with several 2D $^{13}C,^{nn}X$ correlations[1-3], obtained on a Bruker AMX-500 with an inverse multinuclear probehead, where the proton coil was double tuned to $^{13}C$, Peter Bast and I tried to run our first 3D NMR spectrum. Instead of the popular triple H,N,C we switched to phosphorus, thus our model peptide is triphenylphosphane (**1**).
In **1** all protons show an H,P spin coupling. However, of the proton bearing carbon atoms only the ortho and meta carbon atoms have a C,P spin coupling. Thus, if one detects in a 3D manner with protons all those carbon atoms, which are coupled to phosphorus, one should obtain 2 signals. These are nicely to be seen below. We are currently testing these techniques with more convincing applications.

Sincerely yours

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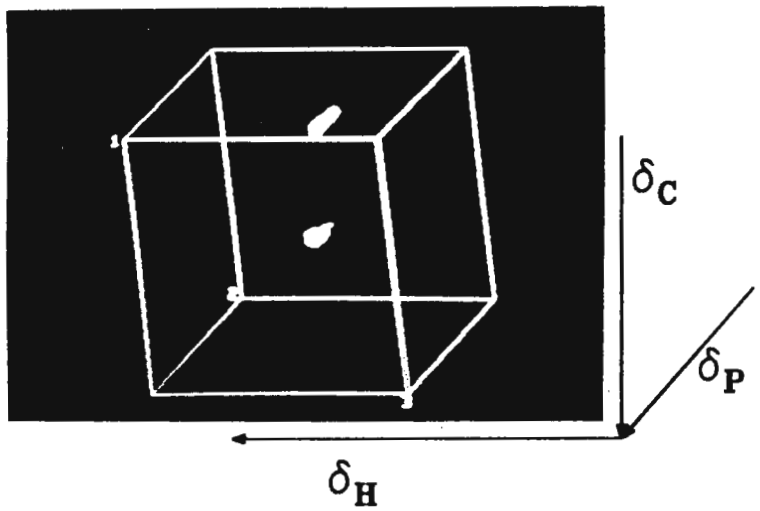


1) $^{13}C,^{31}P$: P. Bast, S. Berger und H. Günther, Magn. Reson. Chem., **30**, 587-594 (1992).
2) $^{13}C,^{29}Si$: S. Berger, J. Magn. Reson., in press.
3) $^{13}C,^{119}Sn$: S. Berger and T. N. Mitchell, Organometallics, in press.

Carleton University
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1942-1992

Dr. B.L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto Cal. 94303 USA

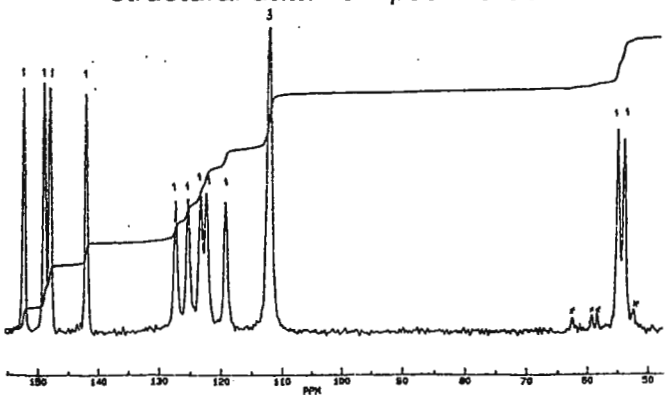
Sept. 16,1992
(received 9/22/92)

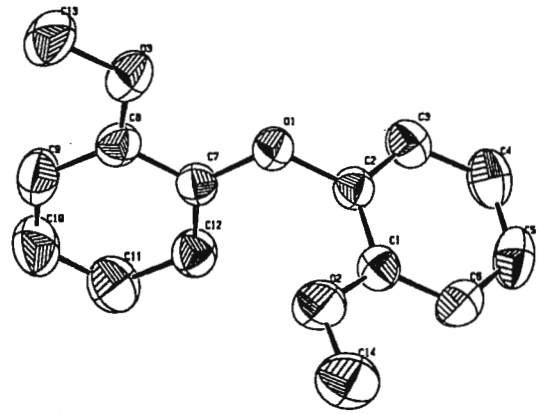
Title: Ortho-dimethoxydiphenyl ether: $^{13}C$ CPMAS NMR and X-ray Structure

As a model for some of our recently synthesized dibenzo-crown ethers, we have obtained the $^{13}C$ CPMAS NMR spectrum of the title material as well as its X-ray crystal structure (below). The NMR spectrum is consistent with the totally asymmetric conformation of this molecule as found in the crystal.

In the aromatic CH region of the spectrum between 110 and 130 ppm are observed 6 resonances of relative intensity 1:1:1:1:1:3, with the triple intensity line at 111.9 being upfield of all others by at least 7.2 ppm. Based on solution spectra, the C6 and C9 sites, which are ortho to the methoxyl groups, are expected to resonate near 112 ppm. The question arises as to whether it is C3 or C12 which gives rise to the third shielded resonance.

Examination of the torsional angles in the X-ray data shows one key difference between C3 and C12. Specifically, for the C2-O1-C7-**C12** network, the angle is $4.4^{o}$, while that for the corresponding C7-O1-C2-**C3** network is $107.9^{o}$. On this basis, it is strongly suggested that **C12** is the third contributing carbon to the triple intensity line at 111.9 ppm. AB Initio LORG calculations of the $^{13}C$ shifts are in progress using the X-ray structural data as input in order to substantiate the argument.

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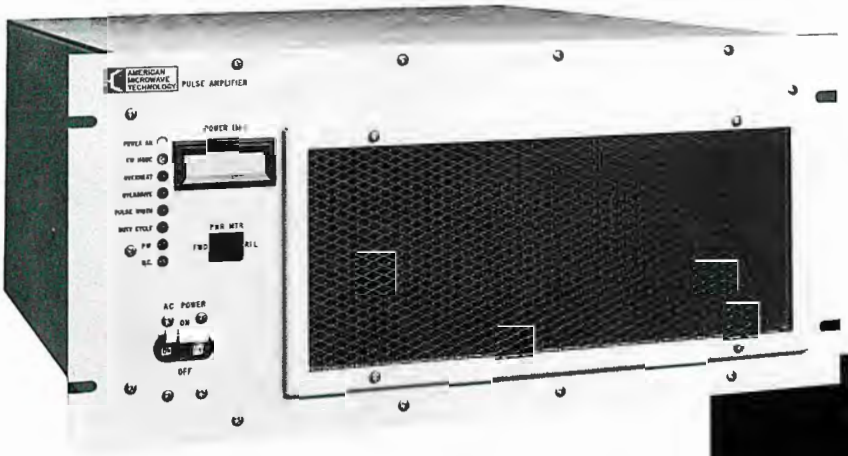


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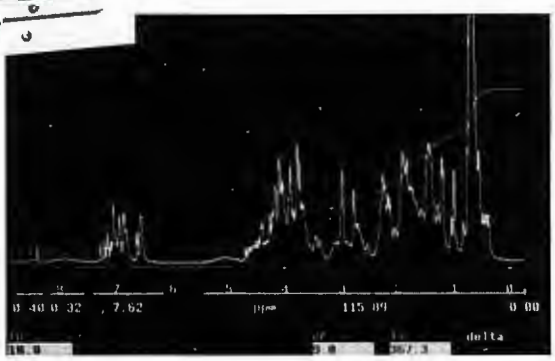

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UNIVERSITY OF CAMBRIDGE
DEPARTMENT OF CHEMISTRY

Professor Barry Shapiro,
Editor, TAMU NMR,
966 Elsinore Court,
Palo Alto,
California 94303,
USA.

7 September 92
(received 10/17/92)

Dear Barry,

**"Binomial Filters"**

Most NMR techniques that have to invoke randomization of some variable usually turn out to be better implemented by a more "deterministic" scheme. This has been vindicated in the case of noise decoupling and the "jiggle" method for suppressing steady-state effects in FT NMR when $T_2$ is comparable with the pulse interval. The "chemical shift filter" appears to be another such candidate, requiring randomization of a delay so that off-resonance signals mutually interfere.

We have been experimenting with filters that pass signals near resonance but suppress signals around some predefined offset ($\Delta f$), using analogs of the binomial pulse sequences. The "1:1 filter" adds a free induction signal to the same signal shifted in time by $\tau = 1/(2\Delta f)$. Alternatively, two separate experiments may be performed with different delays. A wider rejection band can be achieved with the 1:2:1 filter, which adds free induction decays with delays 0, $\tau$ and $2\tau$ with relative intensities 1:2:1. Better still is the corresponding 1:3:3:1 filter. The response curves follow the familiar $\cos\theta$, $\cos^2\theta$ and $\cos^3\theta$ functions respectively. Figure 1 shows experimental tests of the three filters. Consideration of the form of these response curves suggests that a much broader rejection band could be achieved by combining these three filters in the ratio 1:2:1 to give the composite filter 1:4:7:8:7:4:1 which has the response shown in Figure 2. If we wish to have the rejection band at resonance and the acceptance band at the offset $\Delta f$, the alternating phase versions $(1:\bar{1})$, $(1:\bar{2}:1)$ or $(1:\bar{3}:3:\bar{1})$ may be used.

The filters act in a similar manner to the corresponding "solvent suppression" pulse sequences. To the extent that the NMR response is linear, the latter can be considered to superimpose signals that are delayed by multiples of $\tau$ and weighted by the binomial coefficients.

Yours sincerely,

Ray Eriks

Ray Freeman and Ēriks Kupče*

*On leave from the Institute of Organic Synthesis, Riga, Latvia.

Fig. 1

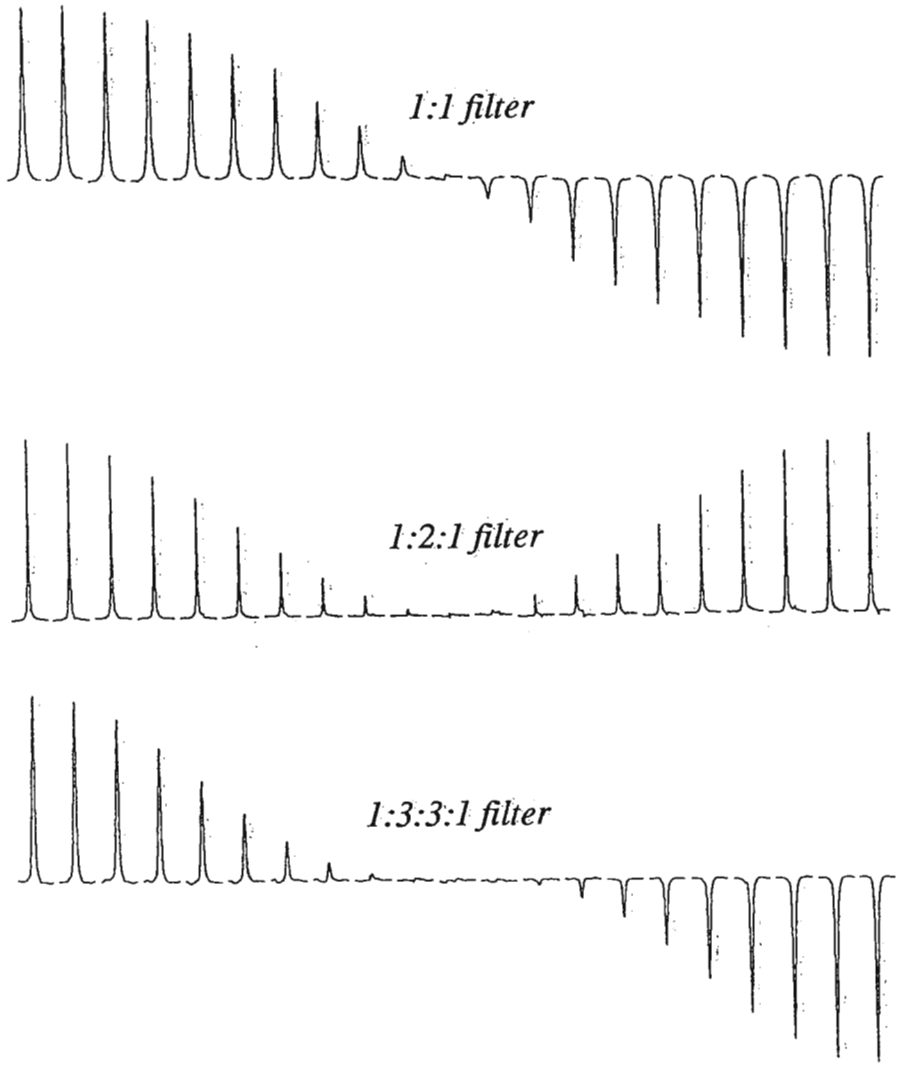
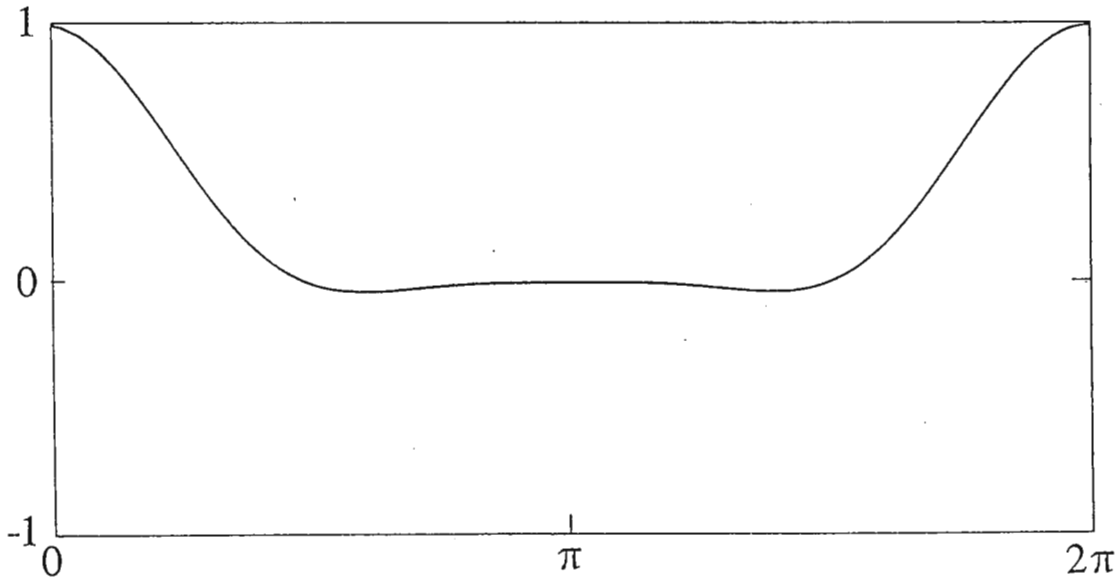



Fig. 2

Response function of composite binomial filter: 1:4:7:8:7:4:1



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All Newsletter Correspondence

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Palo Alto, CA 94303, U.S.A.

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No. 412 (January 1993) - 18 December 1992
No. 413 (February) -------- 22 January 1993
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# α NMR

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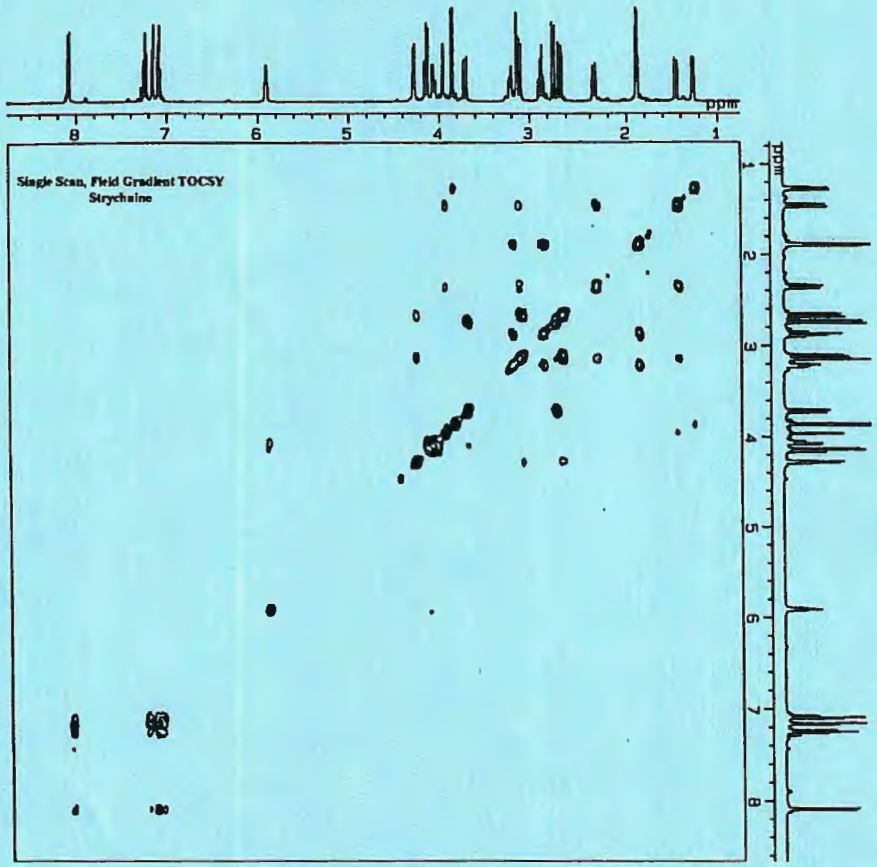


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