

NMR

NEWSLETTER

NO. 321

JUNE 1985

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Forthcoming NMR Meetings (Additional listings are solicited)

Seventh International Meeting on NMR Spectroscopy - July 8-12, 1985; University of Cambridge; Chairman: Dr. Derek Shaw; Details from Dr. John F. Gibson, Secretary (Scientific), The Royal Society of Chemistry, Burlington House, London W1V 0BN England.

The Society of Magnetic Resonance in Medicine - August 19-23, 1985; London; Information from either Renee Sauers, Society of Magnetic Resonance in Medicine, 15 Shattuck Square, Suite 204, Berkeley, CA 94704, or Peter Peregrinus Ltd., P.O. Box 26, Hitchin, Hertfordshire, SG5 1SA, United Kingdom.

Second International Symposium on the Synthesis and Applications of Isotopically Labeled Compounds - September 3-6, 1985; Kansas City, Missouri; Dr. Donald Wittk, Symposium Coordinator, University of Missouri-Kansas City, School of Pharmacy, 5100 Rockhill Road, Kansas City, MO 64110-2499.

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, DE 19898; see TAMU NMR Newsletter 319, 9, (April 1985).

1985 Eastern Analytical Symposium - November 19-22, 1985; Penta Hotel, New York; see pages 17-18.

27th ENC - April 13-17, 1986; Baltimore Hilton; Chairman: R.G. Bryant, Department of Radiology, University of Rochester Medical Center, 601 Elmwood Avenue, Rochester, NY 14642.

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

→ Have you returned the readership survey card which was inserted into issue No. 317 (February)? If not, please let us know promptly how many people routinely read, inspect, or have the opportunity to use your copy of the Newsletter. Your cooperation will be appreciated. ←

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.

Please note revised dates. →

DEADLINE DATES

No. 323 (August) ----- 29 July 1985

No. 324 (September) ---- 26 August 1985



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May 17, 1985

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

Instrumentation Needed

Dear Barry:

On a recent trip to Southern Europe, I was abruptly reminded of how fortunate we are in being able to pursue our research with high quality instrumentation. The chemistry department of the University I was visiting was struggling to teach obviously bright undergraduates, and perform research with almost no equipment, and little chance of obtaining any. The only major piece, a C.W. NMR spectrometer (I suspect the pride and joy of the department) was of a type which disappeared from most U.S. labs fifteen years ago. If any of the Newsletter's readers are planning to surplus, or could permanently loan analytical equipment suitable for a general chemistry department (and, in particular an F.T. NMR instrument) perhaps they could phone me or drop me a line, and I'll put the needy department in touch with them.

Sincerely yours,

David I. Hoult, M.A. D.Phil
Office of the Chief

Biomedical Engineering and
Instrumentation Branch, DRS

TEXAS A&M UNIVERSITY
DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843-3255

Professor Bernard L. Shapiro

31 May 1985

TAMU NMR Newsletter Subscription Notices for 1985-86

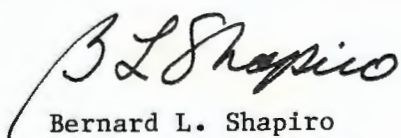
Following our usual practice, subscription notices with invoices for the Newsletter year October 1985 - September 1986 will be sent out to all subscribers on July 1, 1985. Despite a significant increase in postage costs and a very large increase in our local printing costs, we will hold the subscription rate for 1985-86 at the same level as it has been for the last two years. Our ability to keep the Newsletter subscription costs down to their current level is the result of some economies in our operation, but is mainly due to our increased **advertising** revenue. To a small but useful extent, we also have been fortunate in attracting increased financial contributions from our **Sponsors** and **Contributors**.

We are very grateful for the continuing vote of confidence in the Newsletter which the increased advertising and donation funds imply, and we look for continuing modest incrementation of these two important sources of funds. Newsletter subscribers can help the process, of course, by making sure that our Advertisers, Sponsors, and Contributors know that you value the TAMU NMR Newsletter, and appreciate their support of it.

One of the ways in which our Newsletter recipients can help us run an economical operation is to respond promptly to the invoice mailing. Our labor costs are lowered significantly when we do not have to execute reminder letters, etc. Your cooperation will be greatly appreciated.

Further to the response to invoice question: The notices will be going out by first class mail to the U.S. and Canada, and by airmail to our overseas recipients. **If for any reason you have not received an invoice by July 20, please call or write my office so that a duplicate can be sent.** Thanks again.

The ideal response to the invoice mailing is, of course, for you just to send a check - properly identified, made out to "Texas A&M University," and for our foreign subscribers, in net U.S. funds, drawn on a U.S. bank. I realize, however, that in larger organizations, including governmental ones, processing requests for payment simply takes a long time. In such cases, it is helpful to us to receive even a very brief notice from you that payment has been requested and is in progress. This will let us plan our finances, including cash flow, and assure us that the invoice notice in fact reached you.


Bernard L. Shapiro
Editor and Publisher
TAMU NMR Newsletter



Oklahoma State University

Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74078

May 17, 1985

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

Title: ^{77}Se Chemical Shift Measurement on 4-Selenanone

Dear Barry:

We have been working with our XL-300 with a focus on different nuclei and especially ^{77}Se . We have recently developed a synthesis of 4-selenanone (to be published this summer) and have now recorded the ^{77}Se shift which is 176.6 ppm downfield from dimethyl selenide. This shift is reminiscent of that found for di-*n*-butyl selenide¹ (167 ppm) but, to the best of our knowledge, the ^{77}Se shift for selenanone is the first recorded for a six-membered, selenium-containing ketone. We had noted the striking effect that branching has on ^{77}Se shifts such as displayed by diisopropyl selenide¹ (432 ppm) and this suggests that the nucleus may have good diagnostic value for nearby stereochemical considerations. This remains to be evaluated. We would not like our data quoted until our publication appears. Your recent citation to unauthorized quotes is certainly not in the spirit of the NMR Letter. I am glad you caught the problem. I trust this suffices for our contribution. Dr. Ford sent in the last as I recall.

Sincerely yours,

K. Darrell Berlin
Regents Professor

¹J. D. Odom, W. H. Dawson, and P. D. Ellis, J. Am. Chem. Soc. 1979, 101, 5815.

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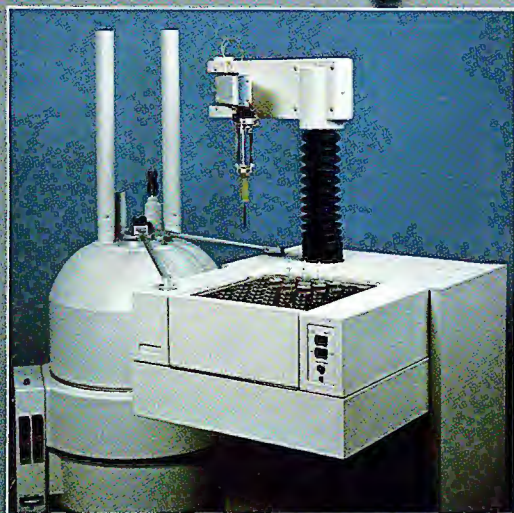


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May 3, 1985

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

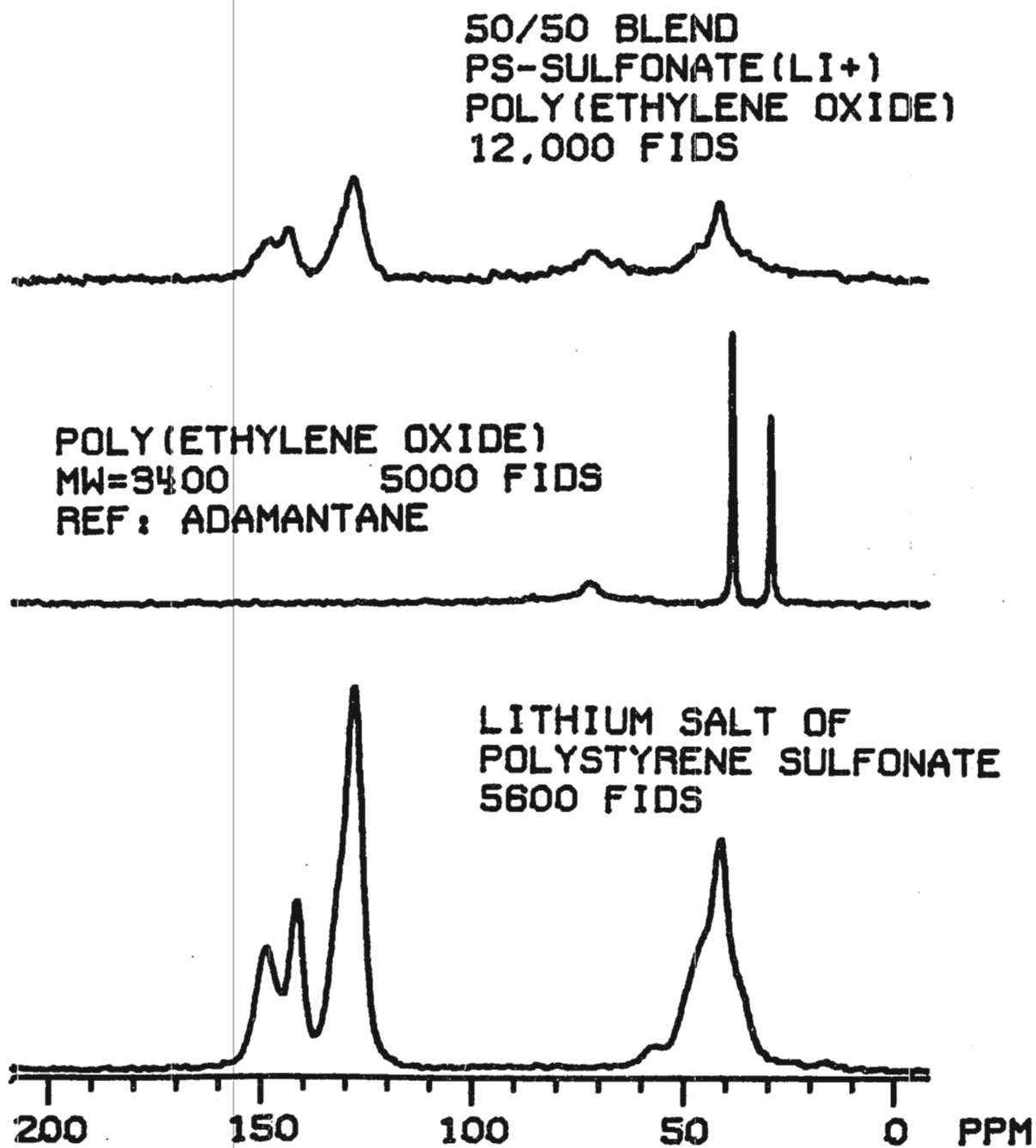
SUBJECT: Miscibility in Polymer-Polymer Blends via Proton Spin
Diffusion

Dear Professor Shapiro:

This is my first contribution to the Texas A&M NMR Newsletter. The research program that I have initiated at Colorado State University is a relatively new one. Fortunately, the expertise and instrumentation available at the Regional NMR Center in the Department of Chemistry have provided an excellent foundation for future NMR research of macromolecules. We are investigating miscibility and phase separation in a variety of multicomponent polymers which carry an industrially important tag. These include short segmented block copolymers (DuPont's Hytrels), tri-block copolymers (Shell's Kratons), ion-containing polymers, polyurethanes, and polymer-polymer blends. One example of miscibility detection in a polymer blend via high-resolution solid state carbon-13 NMR is illustrated herein. We have exploited the existence of ion-dipole interactions between the lithium salt of polystyrene sulfonate and poly(ethylene oxide). The enhanced miscibility in this system has been documented by Hara and Eisenberg [1]. Factors affecting miscibility are (i) type and concentration of the neutralizing cation, (ii) molecular weight of poly(ethylene oxide) and (iii) overall composition of the blend.

As Lyster, Yannoni and co-workers [2] have demonstrated, the cross polarization (CP) carbon-13 NMR spectrum of poly(ethylene oxide), (PEO), exhibits poor signal-to-noise at ambient temperature. This is attributed to the occurrence of the proton $T_{1\rho}$ minimum in the vicinity of 25°C and subsequent difficulty encountered in the CP process. In fact, the IBM researchers deliberately lowered the temperature to -140°C in order to obtain a reasonable spectrum of PEO. We have blended PEO with the lithium salt of polystyrene sulfonate with hope of enhancing the PEO resonance (at ~70 ppm) via intermolecular cross polarization with the solid polyelectrolyte. Intermolecular CP is possible only when mixing occurs on a molecule-for-molecule basis. The carbon-13 NMR spectrum of the 50/50 blend (on a weight basis) suggests that mixing between these two homopolymers is indeed favorable. However, the efficient proton $T_{1\rho}$ process in PEO becomes a viable

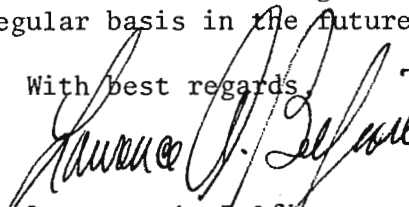
relaxation pathway for the proton reservoir of the rigid polyelectrolyte solid via proton spin diffusion. Consequently, a blend spectrum is obtained with very low carbon-13 signal intensity after twice the number of accumulated transients relative to the spectrum of undiluted polystyrene sulfonate (lithium neutralized).



Future efforts will focus on the use of a carbon-13 analog of the Goldman-Shen experiment in conjunction with multiple-pulse homonuclear proton decoupling to distinguish rigid *versus* mobile domains and to monitor the rate of interdomain polarization transfer in multiphase polymers. This research endeavor is planned in collaboration with Dr. Chuck Bronnimann of the Colorado State University Regional NMR Center.

I look forward with much enthusiasm to receiving the Texas A&M University NMR Newsletter on a regular basis in the future.

With best regards,



Laurence A. Belfiore
Assistant Professor

LAB:shp

- [1] M. Hara and A. Eisenberg, Macromolecules, 17, 1335 (1984).
 - [2] W. W. Fleming, C. A. Fyfe, R. D. Kendrick, J. R. Lyster, H. Vanni, and C. S. Yannoni, in "Polymer Characterization by ESR and NMR," edited by F. A. Bovey and A. E. Woodward, ACS Symposium Series, 142, 193 (1980).
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April 2, 1985

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

Dear Dr. Shapiro:

Re: Frequency accuracy and δ values.

From a letter in the March issue (318-40) of the TAMU newsletter it appears that there is some misunderstanding about the way in which modern nmr spectrometers generate frequencies and how this relates to the measurement of δ values. The δ shift scale is the resonance frequency of the nucleus in question reported as if TMS resonated at exactly 100 MHz. Or,

$$\delta = \frac{F}{F_{\text{TMS}}} \times 100.$$

δ values can therefore be considered to be unitless ratios rather than absolute frequencies. Any proportional error which affects both the numerator and denominator leaves the ratio unchanged.

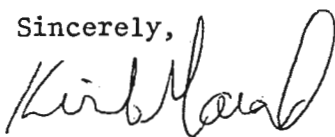
In the Bruker AM series spectrometers all frequencies, including offsets, are derived from a single 10 MHz clock by a combination of digital synthesis, phase-locked loops and frequency multiplication. Other manufactures use similar schemes. This clock is either a thermostated quartz oscillator in the "LO" unit or a temperature compensated quartz oscillator in the PTS 160 synthesizer. While the frequency of this oscillator is not absolutely accurate (in fact, it is as good as many frequency counters!) The error is proportionately the same in all frequencies derived from it; a 1 Hz error at 10 MHz becomes a 10 Hz error at 100 MHz a 30 Hz error at 300 MHz, etc. Frequency ratios, therefore, have absolute accuracy. The software merely simulates the frequency synthesis process to arrive at the final "SF" value which on Bruker spectrometers is the frequency of 0 ppm. The frequency of any line is just the "SF" value plus the shift of the line from 0 ppm. Line frequencies thus determined contain an error due to the error in the 10 MHz clock frequency, but this is a proportional

error which does not affect a ratio such as a E value. No attempt should be made to "calibrate" the software unless all frequencies can be corrected. In any event, there is no need to.

In order to determine a E value all that is necessary is to determine the observed proton frequency of TMS (or possibly a secondary reference) and the observed frequency of the nucleus under study, form the ratio, and multiply by 100. The two measurements should preferably be made on the same sample, an operation which is very easy on spectrometers, such as the AM series, equipped with computer-switchable dual probe/pre-amp systems. If different samples must be used the same solvent and lock signal should be used. For unlocked operation the "FIELD" setting must be the same for all samples. For most purposes a table of TMS frequencies recorded in different solvents is sufficiently accurate.

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Sincerely,



Kirk Marat.

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Laboratoire Associé au C.N.R.S. N° 233

Montpellier, le 25 avril 1985

Professor B.L. SHAPIRO
Department of Chemistry
Texas A and M University
College Station, Texas 77843
USA

^{13}C High Resolution NMR in organic
conductors : Resolved Knight Shifts
and Relaxation Times

Dear Pr. Shapiro

We report here the results of a ^{13}C high resolution NMR study of the organic conductor : $(\text{TMTSF})_2\text{ClO}_4$. This Bechgaard salt is built up of $\text{TMTSF}^{+0.5}$ cations and ClO_4^- anions stacked along an axis which is the direction of strongest overlap between nearest neighbour molecular orbitals (fig.1). The charge carriers are delocalized along this stacking axis, which yields a large anisotropy of conductivity (quasi-one-dimensional conductor).

In our study, we have been able to resolve the individual shifts of the resonance lines (Knight shift) for all of the 10 carbons of the $\text{TMTSF}^{+0.5}$ cation with respect to the resonance lines of the neutral molecule, as well as their individual relaxation times T_1 (except for the very lowest among them) (ref.1). The observed shifts allowed us to calculate the local spin-densities at the carbon nuclei and compare them to those obtained by quantum chemical calculations.

A similar work on $(\text{FA})_2\text{PF}_6$ has been recently published by Mehring et al. (ref.2). Our measurements were carried out on a Bruker CXP200 spectrometer at 50.3 Mhz using magic angle spinning.

While a standard proton enhancement sequence was efficient to provide a good S/N ratio for the carbons with the largest relaxation times, it was unefficient for the observation of the resonance lines of the two center carbons of the $\text{TMTSF}^{+0.5}$ cation. Indeed, the relaxation times for these carbons are expected to be very small. These lines were finally observed using a $\pi/2$ pulse sequence without decoupling. The spectra of the neutral TMTSF in the liquid and solid state are presented at the top of figure 2. The spectrum of $(\text{TMTSF})_2\text{ClO}_4$ is shown at the bottom.

These experiments, with Mehring's one, are the first direct observation of resolved Knight shifts on organic conductors.

Sincerely yours,

P. BERNIER



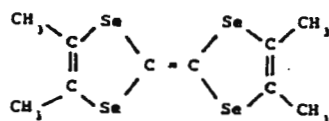
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- 1 - P. BERNIER, M. AUDENAERT, R.J. SCHWEIZER, P.C. STEIN, D. JEROME, K. BECHGAARD, A. MORADPOUR, submitted to Journal de Physique Lettres (Paris)
- 2 - M. MEHRING, J. SPENGLER, Phys. Rev. Lett., 53, 2441 (1984).



TMTSF

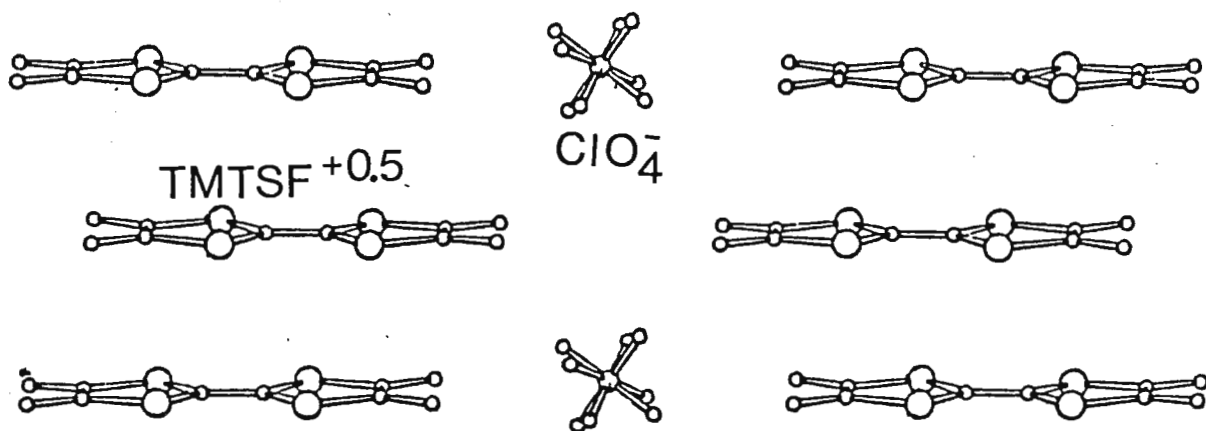
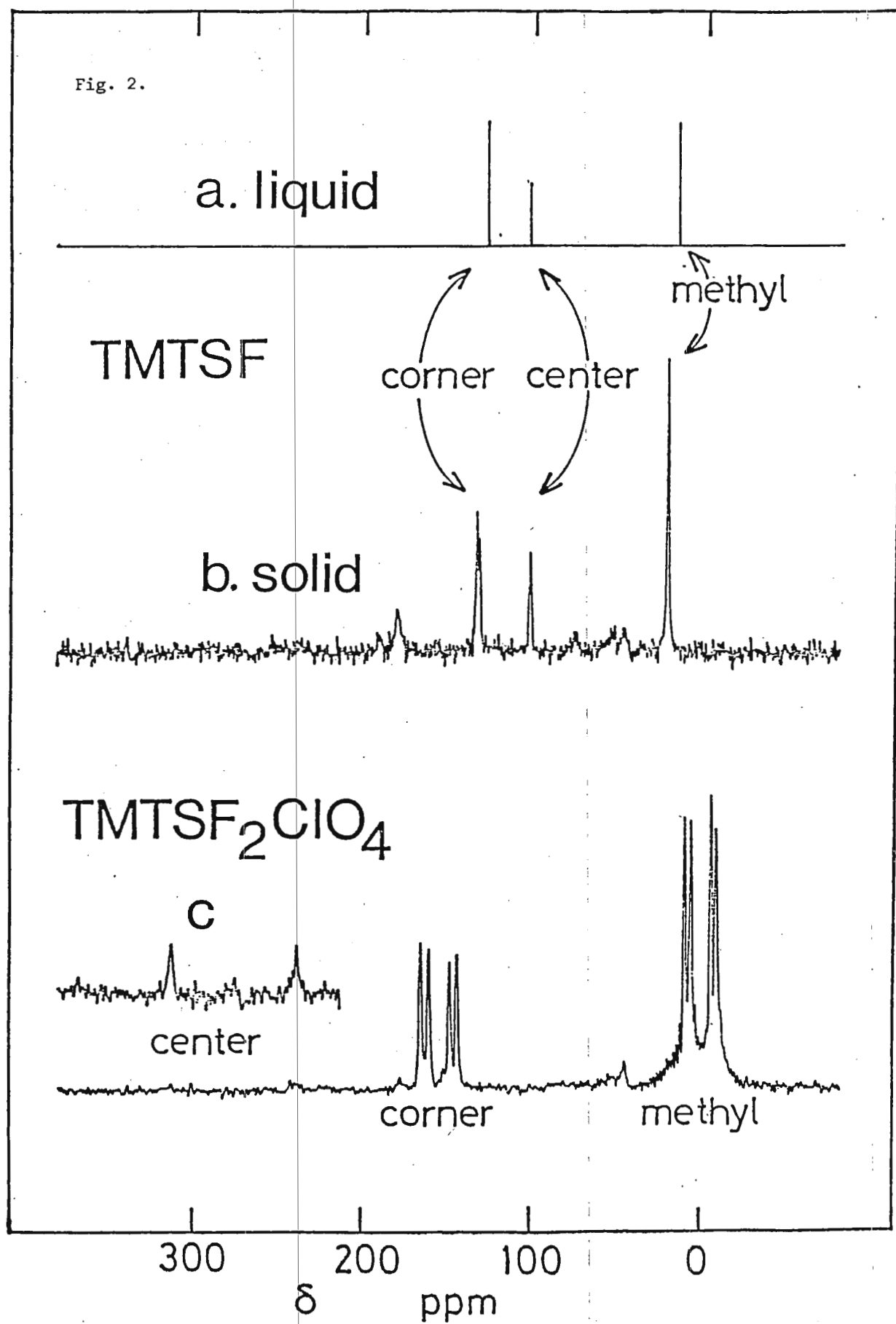


Fig.1. TMTSF molecule and the structure of (TMTSF)₂ClO₄

Fig. 2.



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Program Committee

NMR SESSIONS FOR 1985 EAS

from: Gwendolyn N. Chmurny
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301-695-1226

"NMR Spectroscopy in Two Dimensions"

Wednesday, November 20, 1985 AM (9:00 to Noon)

Chairman: Ray Freeman, Physical Chemistry Laboratory,
Oxford University, Oxford, ENGLAND.

- (1) "Introduction to Two Dimensional NMR". Ray Freeman, Physical Chemistry Laboratory, Oxford University, Oxford, ENGLAND.
- (2) "New Methods for the Assignment of Complicated NMR Spectra". Ad Bax, Arthritis Institute, NIH, Bethesda, MD.
- (3) "Pulse Games Played with DNA". R. Andrew Byrd, Office of Biologics, FDA, Bethesda, MD.
- (4) "Two Dimensional NMR of Glycopeptide Antibiotics". Luciano Mueller, Smith Kline & French, Philadelphia, PA.

"Applications of Modern NMR Methods"

Wednesday, November 20, 1985 PM (2:00 to 4:30)

Chairman: James A. Ferretti, National Heart, Lung and Blood Institute,
NIH, Bethesda, MD.

- (1) "Overview of Modern NMR Spectroscopy and Biology". James A. Ferretti, National Heart, Lung and Blood Institute, NIH, Bethesda, MD.
- (2) "Solid State Deuterium NMR: A Method for Studying Molecular Motion in Bulk Polymers". Lynn W. Jelinski,* J.J. Dumais and A. Kintanar, Polymer Chemistry Research Department, AT & T Bell Laboratories, Murray Hill, NJ.
- (3) "NMR Methods for the Structural Determination of Cell Surface Oligosaccharides". James Prestegard, Department of Chemistry, Yale University, New Haven, CT.
- (4) "Recent NMR Studies of Fluorinated Biological Probes". Robert E. London,* Elizabeth Murphy and Lewis A. Levy, National Institute of Environmental Health Sciences, NIH, Research Triangle Park, NC.

"Micro and Macro NMR Spectroscopy: Polymers to Man".

Thursday, November 21, 1985 AM (9:00 to Noon)

Chairman: Frank Bovey, AT&T Bell Laboratories, Murray Hill, NJ.

- (1) "¹³C and ¹⁵N NMR Analysis of Molecular Motion in Solid Polymers and Proteins". Jacob F. Schaefer, Monsanto Company, St. Louis, MO.
- (2) "Two Dimensional NMR Analysis of Polymer Microstructure and Conformation". Peter Mirau, AT&T Bell Laboratories, Murray Hill, NJ.

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- (3) "Microscopic and Spectroscopic NMR Imaging". Paul C. Lauterbur, Department of Chemistry, State University of New York, Stony Brook, NY.
- (4) "Magic Angle Spinning NMR in the Study of Surfaces," Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

"Advances in NMR Imaging Techniques".

Thursday, November 21, 1985 PM (2:00 to 4:30)

Chairman: David Hoult, Division of Research Services, NIH, Bethesda, MD.

- (1) "Understanding Advances in NMR Probe Design". David Hoult, Division of Research Services, NIH, Bethesda, MD.
- (2) "Techniques and Applications of NMR Chemical Shift Imaging". Paul A. Bottomley, G.E. Corporate Research and Development Center, Schenectady, NY.
- (3) "The Influence of the Macromolecular Matrix on Proton Relaxation Times in Hydrogels and Living Cells". Paula t. Beall, Pharmaceutical Division Ciba-Giegy, Ardsley, NY.
- (4) "Solid State Imaging Using Multiple Pulse NMR". Gerald C. Chingas, U.S. Naval Research Laboratories, Washington, D.C.

1985 EASTERN ANALYTICAL SYMPOSIUM (SHORT COURSES)

from: Robert E. Santini
Program Committee
317-494-5230

Monday, November 18, 1985

- (1) "Inside Your NMR: Introduction to Hardware Aspects of NMR Instrumentation". Robert E. Santini, Purdue University, West Lafayette, IN.

Tuesday, November 19, 1985

- (2) "1D, 2D, 3D Pulsed NMR of Liquids, Solids and Spaces: A Practical Approach". John Grutzner, Purdue University, West Lafayette, IN.

Wednesday, November 20, 1985

- (3) "Introduction to Laboratory Data Systems". Stannley Demming, University of Houston, Houston, TX.

Note: EAS is held at the Penta Hotel in New York City.

D. CANET
Professeur

Professor B.L. SHAPIRO
TEXAS A & M University
Department of Chemistry
COLLEGE STATION
TEXAS 7784-3255
U.S.A.

Cartesian vectorial representations for analyzing multipulse experiments.

Nancy, may 4, 1985

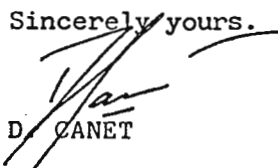
Dear Professor Shapiro,

Multipulse NMR experiments are conveniently analyzed by means of product operators (1) rather than by vectorial models which are known to lead, in some cases, to erroneous conclusions. In fact, two vectorial representations can be devised : a "classical" representation including magnetization vectors associated with each transition and a "total magnetization" representation, including vectors associated with the magnetization of each nucleus. By looking carefully at the properties of the above-mentioned product operators, it has proved possible to set up a correspondance between the latter and the two possible vectorial representations. The analysis of a sequence is then a matter of vector rotations in Cartesian axes (according to the situation at a given step of the sequence, one may have to switch from one representation to the other). No calculation is required and some physical insight is gained. This procedure is illustrated by the accompanying figure which describes the basic sequence of the INADEQUATE experiment (2) : only the behavior of the A nucleus is shown ; full and dotted vectors refer to "classical" and "total magnetization" representations, respectively. It is especially straightforward to realize how the phase of the last pulse acts.

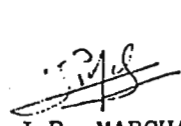
This graphical method should indeed be useful for devising appropriate phase cycles. Details will be published shortly.

We hope by means of this letter, re-establishing us as contributors, to be back on your mailing list.

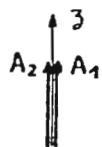
Sincerely yours.


D. CANET

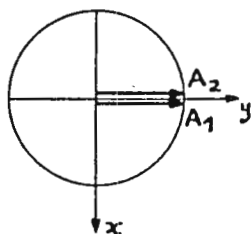

J. BRONDEAU


J.P. MARCHAL

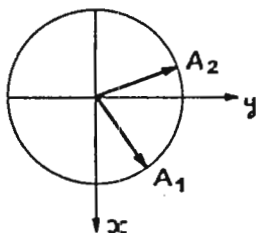
- (1) O.W. SØRENSEN, G.W. EICH, M.H. LEVITT, G. BODENHAUSEN and R.R. ERNST, *Progr. NMR Spectrosc.*, 16, 163 (1983)
- (2) A. BAX, R. FREEMAN and S.K. KEMPEL, *J. Am. Chem. Soc.*, 102, 48 49 (1980)



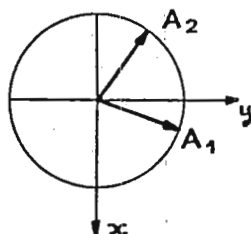
$$\left(\frac{\pi}{2}\right)_x$$



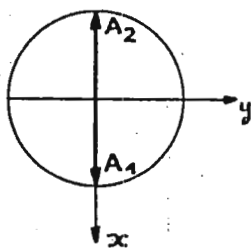
$$\frac{1}{4J}$$



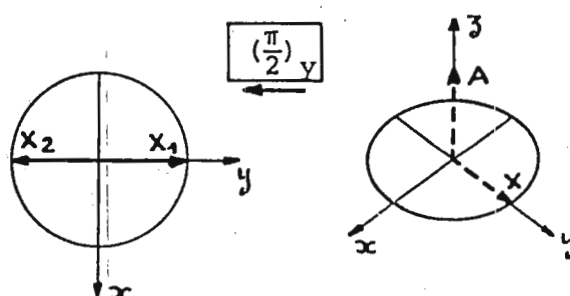
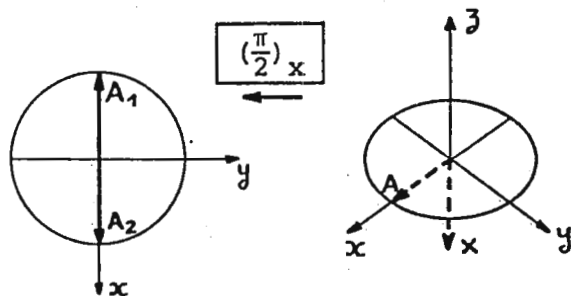
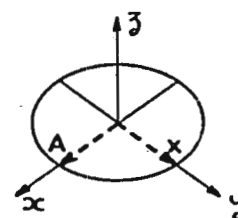
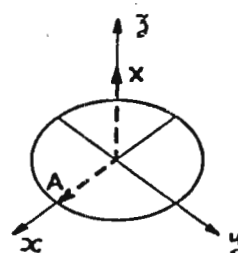
$$(\pi)_y$$



$$\frac{1}{4J}$$



$$\left(\frac{\pi}{2}\right)_x$$



May 7, 1985

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

Dear Barry:

Silica, Silicates and Silicones

We have recently been investigating structure and bonding in silica and silicates by means of ^{17}O and ^{29}Si NMR. We have found a very simple way to predict ^{29}Si chemical shifts in all types of silicates ($\text{Q}^0, \text{Q}^1, \text{Q}^2, \text{Q}^3, \text{Q}^4$) by use of a "group fragment electronegativity" approach. Noting a high correlation (0.992) between the group electronegativity sum and chemical shift for tetravalent silanes containing ligands with lone pairs available for backbonding, we have formulated the following relationship between group electronegativity sum and solution chemical shift:

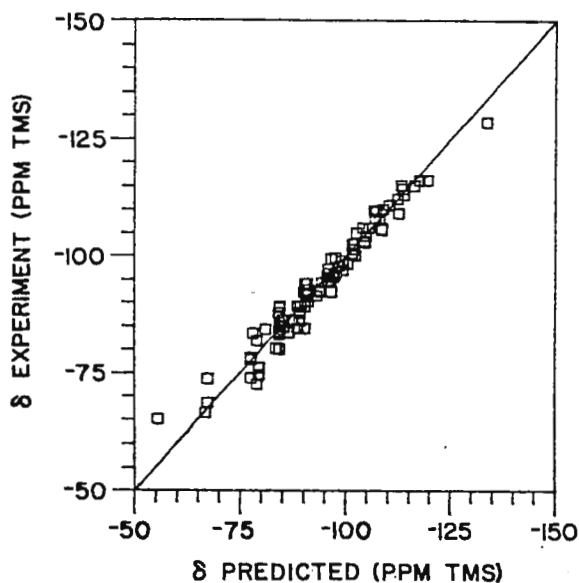
$$\delta_{\text{Si}} = -24.336 \sum \text{EN} + 279.27$$

Group electronegativities for oxymetal fragments are then derived empirically using the above equation. For instance, the OMg electronegativity is obtained from forsterite (Mg_2SiO_4 , $\delta = -61.9$, $\text{EN} = 3.5048$), the OCa from the average of $\alpha, \beta, \gamma\text{-Ca}_2\text{SiO}_4$ ($\delta = -71.73$, $\text{EN} = 3.6058$). The OSi electronegativities exhibit a structural dependence on SiOSi bond angle, derived from selected SiO_2 polymorphs as follows:

$$\text{EN}(\text{OSi}) = (\langle \text{SiOSi} / 136.79 \rangle + 2.9235$$

The chemical shift may now be predicted using the following relation:

$$\sum \text{EN}(\text{Q}^n) = \sum \text{EN}_f + (4-n) \sum (\text{EN}_{\text{nf}} z_{\text{nf}} / \sum z_{\text{nf}})$$

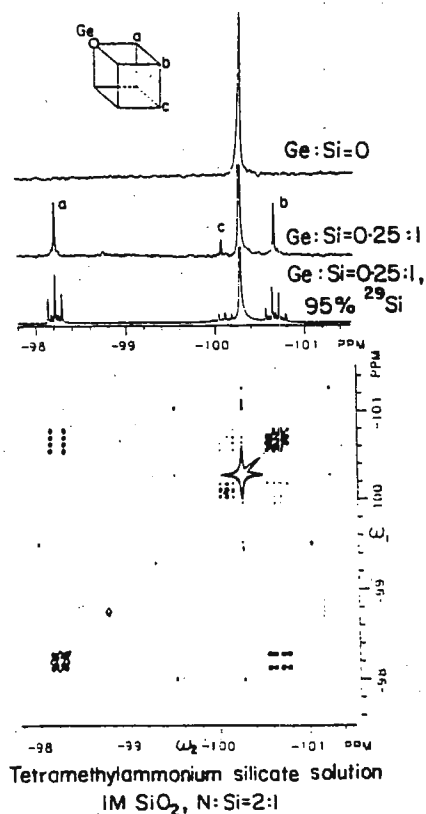
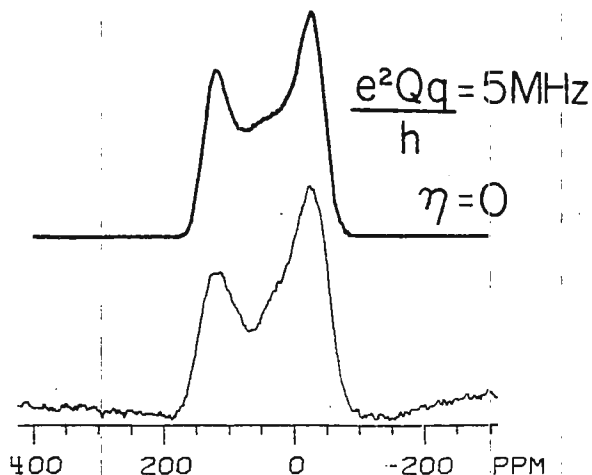


where Q^n refers to the degree of polymerization, f and nf are framework and nonframework sites, respectively, and z is the formal charge of the cation. For example, for the chain silicate diopside (Q^2 , $\text{CaMgSi}_2\text{O}_6$) the method works as follows:

$$\sum \text{EN}(\text{CaMgSi}_2\text{O}_6) = 2\text{EN OSi } (135.93^\circ) + 2 (\text{EN OMg } (2/4) + \text{EN OCa } (2/4))$$

The $\sum \text{EN}$ of 14.9450 corresponds to a chemical shift of -84.4 ppm (from TMS), which compares well with the experimental value of -84.7 ppm. Thus far we have tried 99 sites in 51 minerals and obtained a mean absolute accuracy of 2.0 ppm, as shown in the accompanying graph.

We have also obtained the ^{17}O quadrupole coupling constants of a number of minerals and used Townes-Dailey methods to investigate the (controversial) nature of the Si-O bond. We have found that (d-p) π -bonding must be included in order to adequately interpret the observed e^2qQ/h . The results are in accord with Pauling's model of 50% ionic σ -bonds and a total bond order of ca 1.55. Models that neglect (d-p) π -bonding predict ~2-fold larger e^2qQ/h values. These results indicate that caution should be used in ascribing the well-known bond-length--bond-angle correlation for bridging oxygens in silicates to σ -effects alone (e.g. Bent's rule), since the phenomenon may also be ascribed to changes in π -bond order (which has the added advantage of accounting for the generally shorter bond lengths observed for Si-O nonbridging bonds).



In addition to minerals, we have been applying ^{17}O NMR to the study of silicone polymers (all other possible nuclei having already been "taken"). The above shows the ^{17}O solid-state NMR spectrum (at $\sim -195^\circ\text{C}$) of $(\text{Me}_2\text{Si}^{17}\text{O})_n$, which displays a well-defined second-order powder pattern having $e^2qQ/h = 5$ MHz and $\eta = 0$.



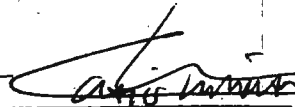

The inorganic chain silicates we've studied have $e^2qQ/h \sim 4$ MHz and $\eta = 0.4$, which implies, using Townes-Dailey reasoning, substantial charge donation from the bridging oxygen to e.g. Ca^{2+} and Mg^{2+} , which cannot of course occur in the polydimethylsiloxane.

We also hope to use the second-order lineshape to study hindered rotation about SiOSi and COC bonds in the future, which should complement the results of ^2H , ^{13}C and ^{29}Si studies of various high polymers.

Another aspect of our work has been on the solution NMR of various hetero-atom substituted silicate cages. We have been able to incorporate Ge into the double-four $[\text{Si}_8\text{O}_{20}]^{8-}$ ring, which lifts the degeneracy of the silicons. This leads to a nice candidate for a ^{29}Si COSY experiment, as shown in the spectra above, giving unambiguous assignment of all resonances and, inter alia, corroborating the long postulated existence of the double-four ring in solution.

With best regards.

Yours sincerely,

 Eric Oldfield
 Nathan Janes
 Christopher Knight
 Linda Reven

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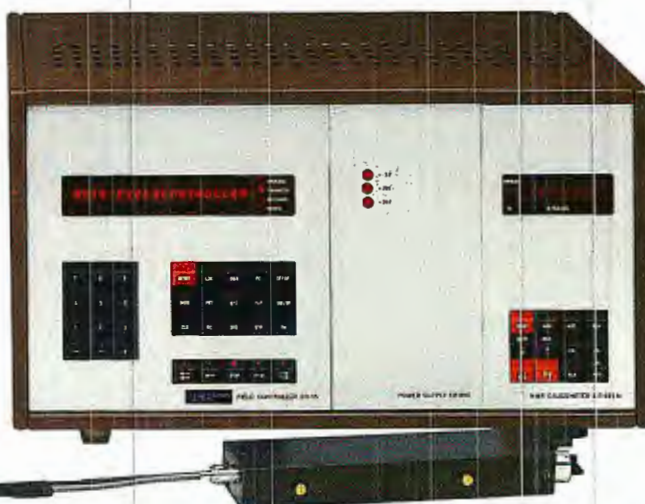
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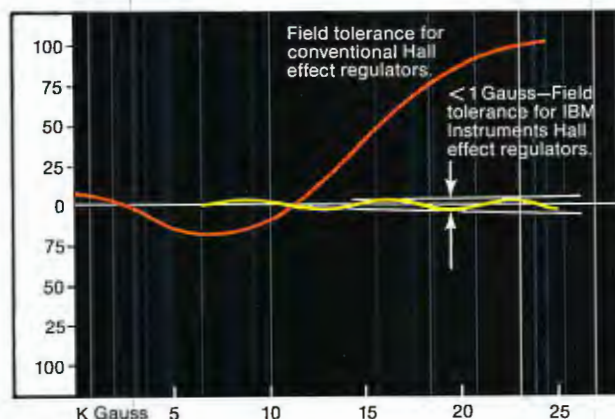
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RK/gf

GRONINGEN, May 2, 1985

Professor Barry Shapiro
Texas A & M University
College Station Texas 77843
U.S.A.

Dear Barry,

It is well known that the observation of CIDNP multiplet effects presents a problem in pulse FT NMR.¹ They disappear for a 90° pulse and undistorted observation is only accomplished at very small flip angles with concomitant loss of sensitivity. We have now explored two ways in which multiplet effects can be recovered in pulse NMR with full sensitivity. Both can be used to detect small multiplet effects in the presence of strong net polarization.

A $\theta(x)$ pulse applied to a spin system containing both net polarization and longitudinal spin-order (multiplet effects) creates both y-magnetization, which have different flip angle dependencies. Thus, FID's taken with $\theta = 45^\circ$ and 135° can be added to give spectra with pure net polarization and subtracted to yield multiplet effects. This method works well, but for small multiplet effects in the presence of strong net polarization artifacts may arise due to imperfect cancellation of large signals.

The second method makes use of the fact that a mixture of double and zero quantum coherence is created from the multiplet effect component by a 90° pulse, which can be transformed in observable magnetization by a second 90° pulse. A 2D experiment of this kind has been suggested by Bodenhausen² and Pouzard.³ Now net and multiplet effects occur at different ω_1 frequencies, which provides a cleaner separation. The Figure shows the result of a 2D experiment of the form light pulse - 90° - t_1 - 90° (Acq.) applied the photo-reaction of flavin with tyrosine.

Best wishes,

Yours sincerely,

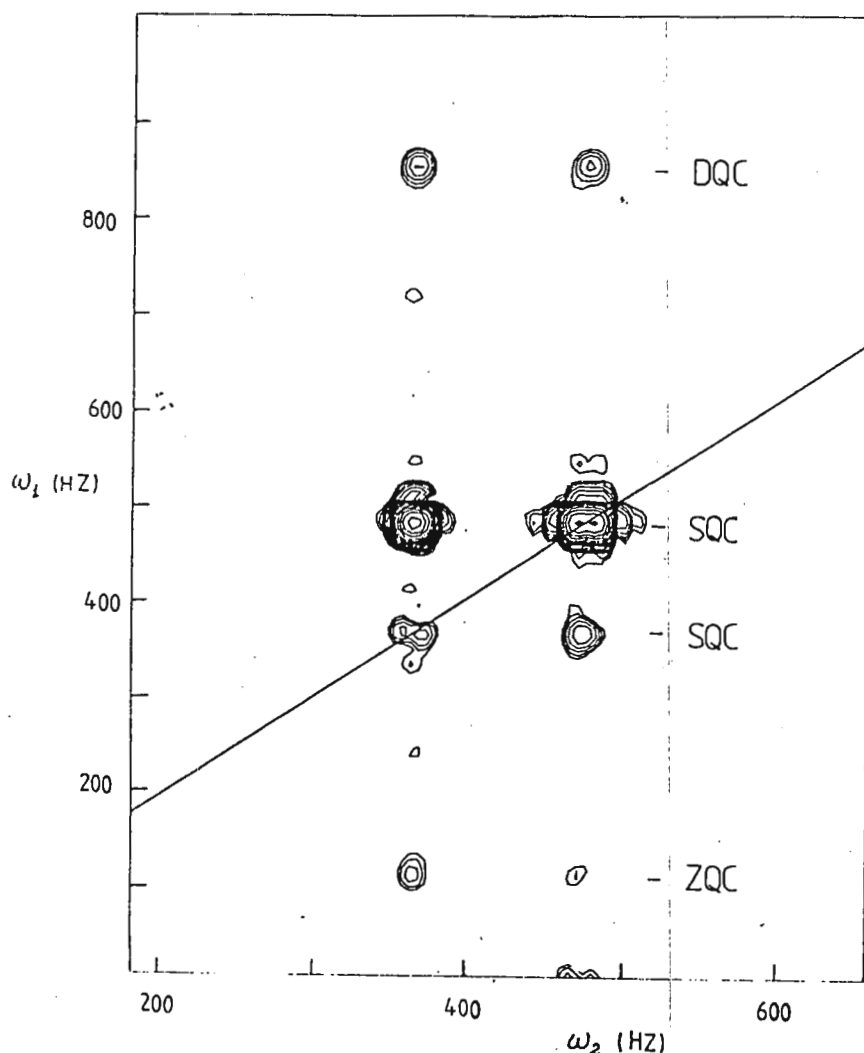
Rolf Boelens,

Alexei Podoplelov,

Robert Kaptein

Please credit this contribution to the account of Dr. W. Weringa.

1. Schaublin, S., Hoehener, A. and Ernst, R.R., J. Magn. Reson. 13, 196 (1974)
2. Bodenhausen, G., Progr. in NMR Spect. 14, 137 (1981)
3. Allouche, A., Martinelli, F. and Pouzard, G., J. Magn. Reson. 53, 65 (1983).



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May 22, 1985

Dear Dr. Shapiro,

While studying natural abundance, proton-decoupled deuterium spectra of a set of seventeen methylcyclohexanes, we had occasion to perform a stepwise multiple regression analysis to determine shift parameters for structural features. Initially the values of the four parameters for ring hydrogens with vicinal methyl groups (see Figure 1) appeared anomalous. With the exception of A(2a), which has a trans relationship to the vicinal methyl, the ring hydrogens have very similar spatial and structural relationships with the neighboring methyl group, and yet the values for these three remaining parameters given in Figure 1 vary from negligible to -0.309.

Treating E(parent) as the default case and cataloging only differences in substitutions at vicinal carbons as perturbations, the important parameters which affect the shielding are found to be the vicinal gauche C-C bonds as modified by the inductive effect of a vicinal methyl (see Table I). There is a large correlation (0.95 from a regression analysis) between the numbers of gauche C-C bonds and the shift differences. Addition of the inductive effect then accounts for the relative values of A(2a) and A(parent). The ring flattening induced by an axial methyl^{1,2} could be expected to modify the interactions between the vicinal gauche bonds, and to account for the difference between E(2e) and E(2a). For simplicity, this angular dependence is assumed to relate to the overlap integrals between gauche carbon bond orbitals. Using values for the angles between ring hydrogens and vicinal gauche bonds from reference 2 and the corresponding values for the overlap integrals³, OI, the c_i were calculated from these OI's with the given angular correction and then normalized to the parent as follows:

$$c_i = OI_i / OI_{E(\text{parent})}$$

A linear regression fit with a multiple R of 0.9844 and a standard error of the estimate of 0.0288 ppm yielded the values for the shift effects in Table II.

Acknowledging the rather crude estimates of angles and considering that the overlap assumption is also crude, we were pleased with the parameters obtained for the gauche interactions and two inductive terms. Although the largest correlation is with the number of gauche C-C bonds, the inductive terms are significant. The trans effect appears in only one entry (see Table I) and would not be well determined statistically. Additionally it is comparable, within experimental error, to the gauche inductive effect.

Best regards,

Janet Curtis
Janet Curtis

David M. Grant
David M. Grant

1. Altona, C.; Sundaralingam, M. Tetrahedron, 1970, 26, 925.
2. Geise, H.J.; Mulhoff, F.C.; Altona, C. J. Mol. Struct. 1972, 13, 211.
3. Mulliken, R.S.; Rieke, C.A.; Orloff, D.; Orloff, H. J. Chem. Phys. 1949, 17, 1248.

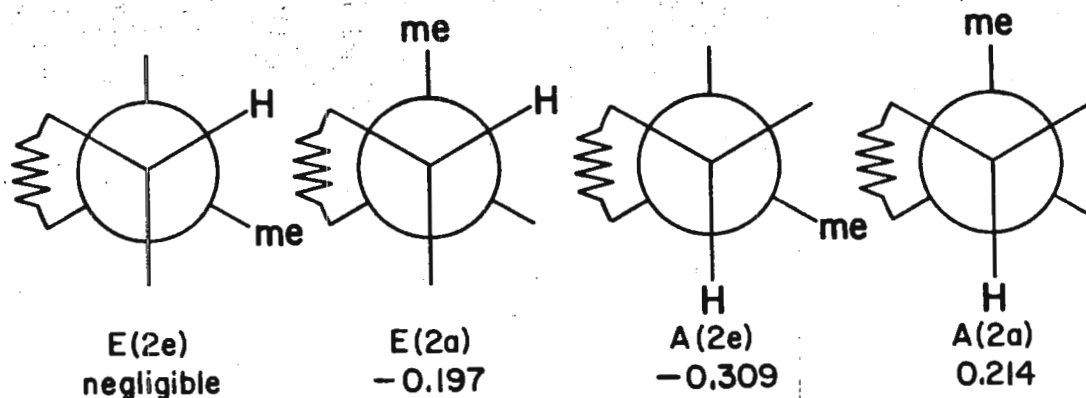


Figure 1. A comparison of the spatial and structural relationships of the four vicinal parameters. Values from the regression analysis are included.

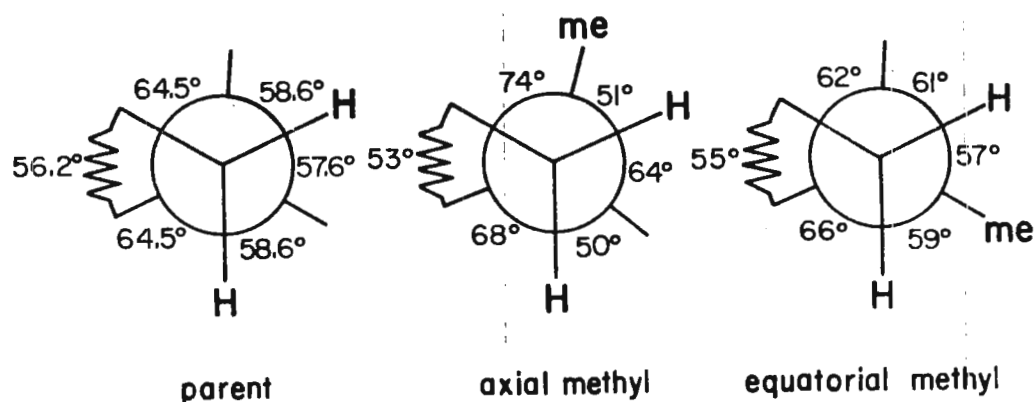


Figure 2. A comparison of the angular distortions to the cyclohexane ring induced by methyl substitution. The values are from force-field calculations from reference 2.

Table I. Total Shift Differences and Shift Effect Coefficients for Vicinal Sites

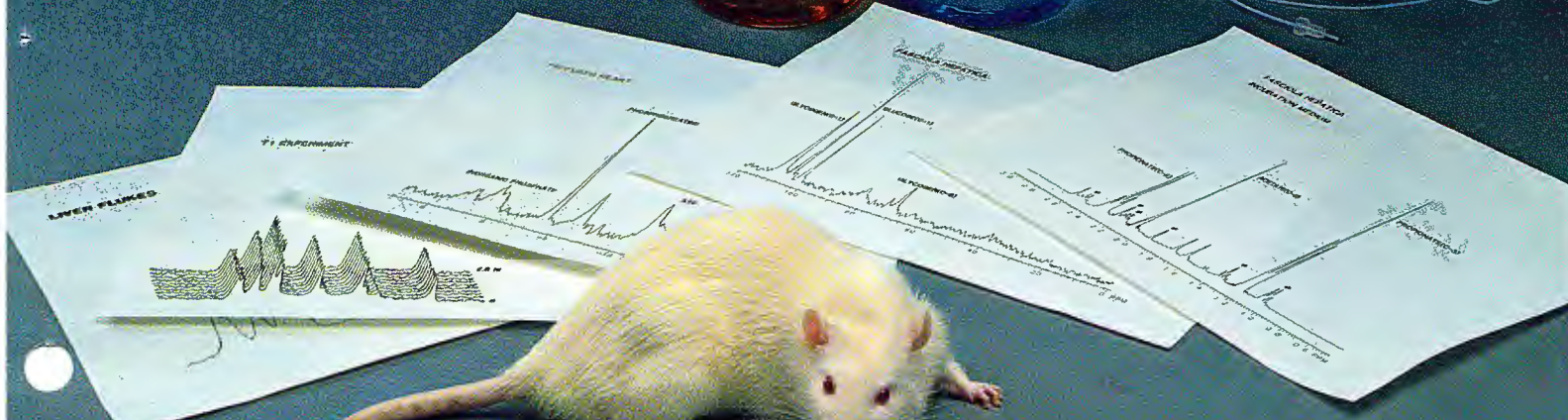
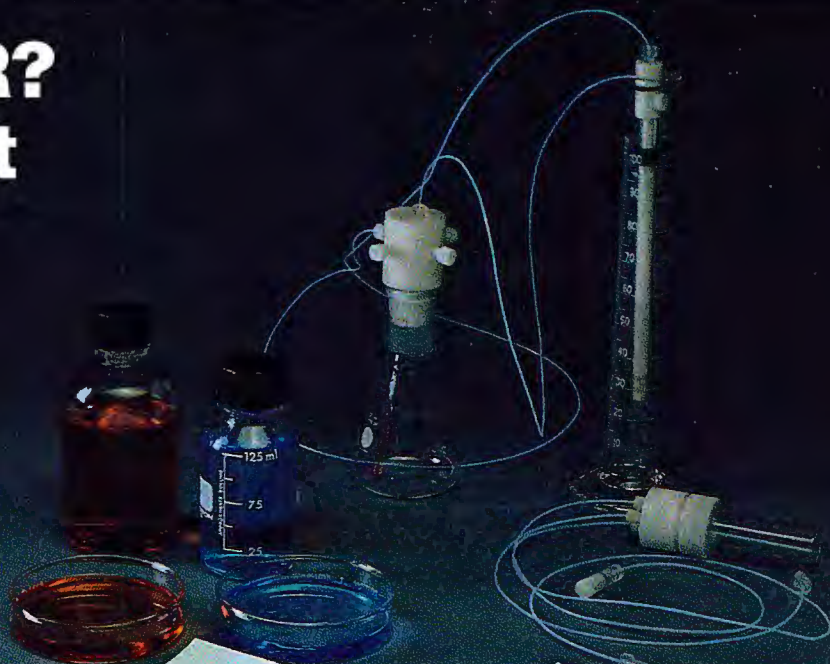
Site	Shift	$\Delta\delta$	Number of C-C	Coefficients		
				$\delta_{\text{ind-G}}$	$\delta_{\text{ind-T}}$	$\delta_{\text{C-C}}$
E(par)	1.642	0	0	0	0	0
E(2e)	1.632	-0.010	1	1	0	1.00
E(2a)	1.445	-0.197	1	1	0	1.10
A(2a)	1.376	-0.266	2	0	1	1.66
A(par)	1.162	-0.480	2	0	0	1.77
A(2e)	0.853	-0.789	3	1	0	2.82

Table II. Shift Effect Parameters for Vicinal Sites

$\delta_{\text{C-C}}$	$\delta_{\text{ind-G}}$	$\delta_{\text{ind-T}}$
$-0.319 \pm .053$	$-0.190 \pm .111$	$-0.263 \pm .149$

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ISTITUTO DI CHIMICA DELLE MACROMOLECOLE

20133 MILANO, may, 6, 1985

VIA E. BASSINI, 15/A

TEL. 29.28.93 - 29.30.97 - 29.36.04 - 29.37.81

29.52.78 - 29.54.82 - 29.60.71 - 23.53.10

No. Rif. Prot. N.

Dear Prof. Shapiro

by using the photo-CIDNP technique applied to ^1H -NMR we showed that Met-enkephalin, human and camel β -endorphin interact to various extent with C_{12}PN (dodecylphosphorylcholine), the binding efficiency being considerably lower for the shorter peptide⁽¹⁾.

Recently, we run a series of ^{31}P spectra of C_{12}PN at variable concentration, alone and in the presence of Met-enkephalin, camel β -endorphin and morphine. While the chemical shift changes are small and not easy to rationalize, the linewidth of the ^{31}P signal appears to be sensitive to the state of micelles, and is also modulated by the interaction between opiate and lipid. Fig. 1 shows that for C_{12}PN alone a progressive line sharpening is observed by increasing the lipid concentration; the curve has an abrupt inflexion near 13 mM, most likely corresponding to the critical micell concentration (cmc). Addition of Met-enkephalin does not affect this trend, whereas in the presence of β -endorphin and morphine the ^{31}P signal is already sharp at the initial C_{12}PN concentration. This may suggest a lowering of the cmc, owing to formation of mixed micelles.

By increasing the lipid/opiate ratio, the linewidth slightly increases, to reach a maximum, after which all curves are nearly superimposable, as the concentration of mixed micelles becomes negligible.

Sincerely,

Lucia Zetta

Antonio De Marco

Pierluigi Gariboldi

(1) A. De Marco, L. Zetta and R. Kaptein (1985) Eur.Biophys.J. 11, 187-193.

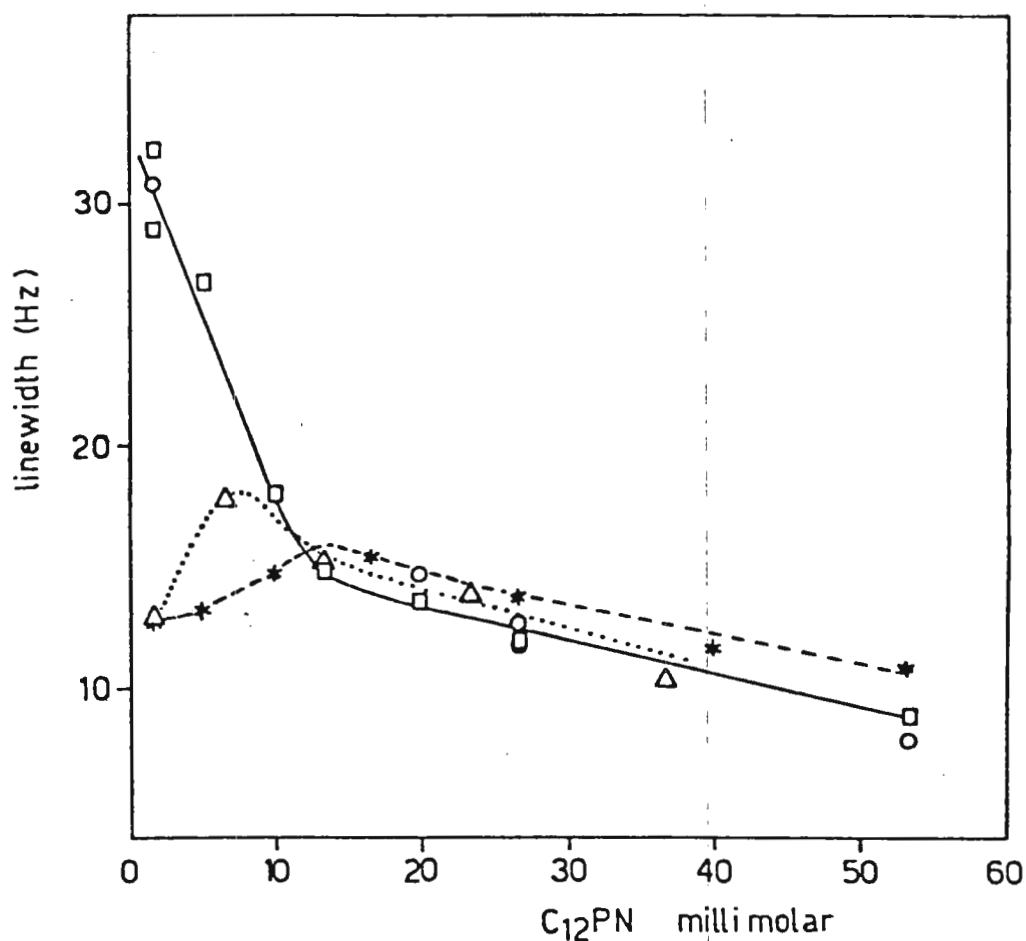


Fig. 1. Linewidth of the ^{31}P signal vs. the lipid concentration, for:

(□, —) C_{12}PN .

(○, —) C_{12}PN in the presence of 1 mg of Met-enkephalin

(* , ---) C_{12}PN in the presence of 1 mg of camel β -endorphin

(Δ,) C_{12}PN in the presence of 1 mg of morphine.

The curves are free interpolations between points.

Spectra were run with a Varian XL-200 spectrometer.

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University of Illinois
at Urbana-Champaign

School of Chemical Sciences
505 South Mathews Avenue

Urbana
Illinois 61801

May 8, 1985

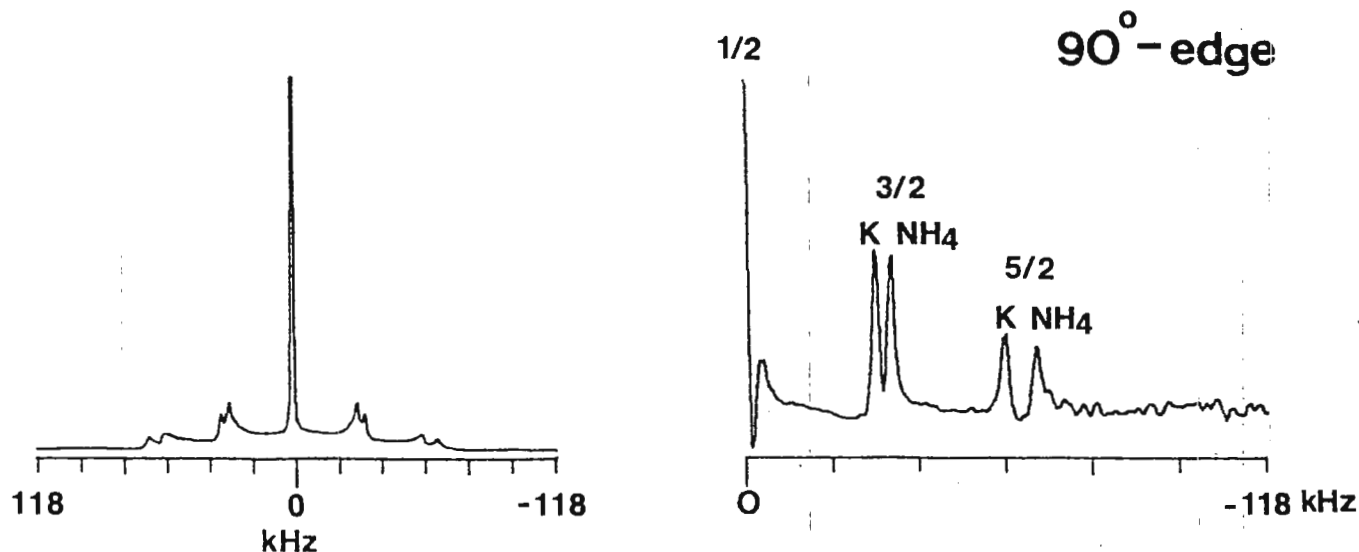
Professor B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

Non-Integral Spin Quadrupolar Echoes

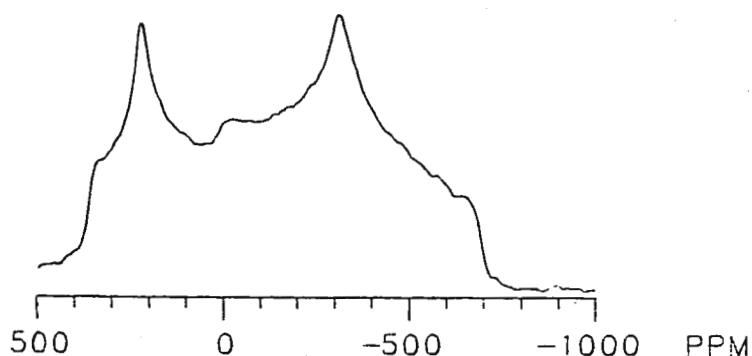
We have recently been reading the literature, and have noted that there exists a fairly wide body of information on the use of various quadrupolar echo sequences to refocus magnetization of our favorite nonintegral spin quadrupolar nuclei. Everyone knows of the early work of Solomon (1), which has led to the extensive use of ^2H quadrupole echoes (2), but we believe it's generally thought that FTs of the quadrupole echoes of, say, ^{127}I or ^{27}Al , will lead to a rather confused spectrum. That's not necessarily so, however, because the 2τ -echo can be selectively enhanced by judicious use of pulse sequence.

The following shows the FT of the 2τ -echo in a mixture of K^+ and NH_4^+ -alums, in the presence of ^1H dipolar decoupling:



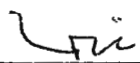
together with a "de-Paked" half spectrum. Clearly, such experiments should yield useful quadrupole coupling constant resolved spectra from, e.g., some minerals and aluminosilicate catalysts, and can in principle be readily implemented on a commercial instrument.

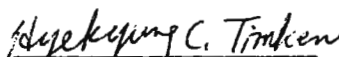
We've been similarly surprised by our ability to refocus second-order interactions, which helps alleviate instrumental dead-time problems, as shown in the following ^{39}K spectra of 18-crown-6 ether. KNO_3 , at 23.3 MHz:




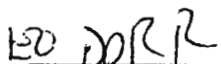
With best regards.

Yours sincerely,


Eric Oldfield


H. K. C. Timken


A. C. Kunwar


R. Ramachandran


B. Montez

References

1. I. Solomon, Phys. Rev. 110, 61 (1958).
2. J.H. Davis, K.R. Jeffrey, M. Bloom, M.I. Valic, and T.P. Higgs, Chem. Phys. Lett. 42, 390 (1976).

Coordinator - NMR Facility

Southern Illinois University, Carbondale seeks a specialist in magnetic resonance spectrometry to coordinate the operations and management of a high-field NMR facility. This facility will include two new high-field NMR spectrometers and related equipment. The coordinator must be a person with advanced level training, preferably with a Ph.D. in chemistry or physics, and must have a strong background in RF electronics with considerable experience with state-of-the-art NMR spectrometers. Responsibilities will include: (a) oversight of the operation of the facility, (b) supervision of other facility staff, (c) performance of routine maintenance, (d) training and advising NMR users in chemistry, physics, plant physiology, biochemistry, and medical physiology among others, and, (e) assisting researchers in developing research protocols using NMR spectroscopy. Applicants should desire to work in the academic setting, and although neither independent research nor formal teaching is required, the opportunities for collaborative research and teaching are numerous. The coordinator will report to the director of the Office of Research Development and Administration. Salary is competitive based on experience and credentials. Please submit a complete curriculum vita and the names, addresses, and phone numbers of at least three references to: Michael R. Dingerson, Assistant Vice-President for Academic Affairs and Research, Office of Research Development and Administration, Southern Illinois University at Carbondale, Carbondale, Illinois 62901. Applications are desired as soon as possible. It is unlikely that candidates whose materials are received after 15 August will be considered.

TAMU NMR Newsletter Readership Survey

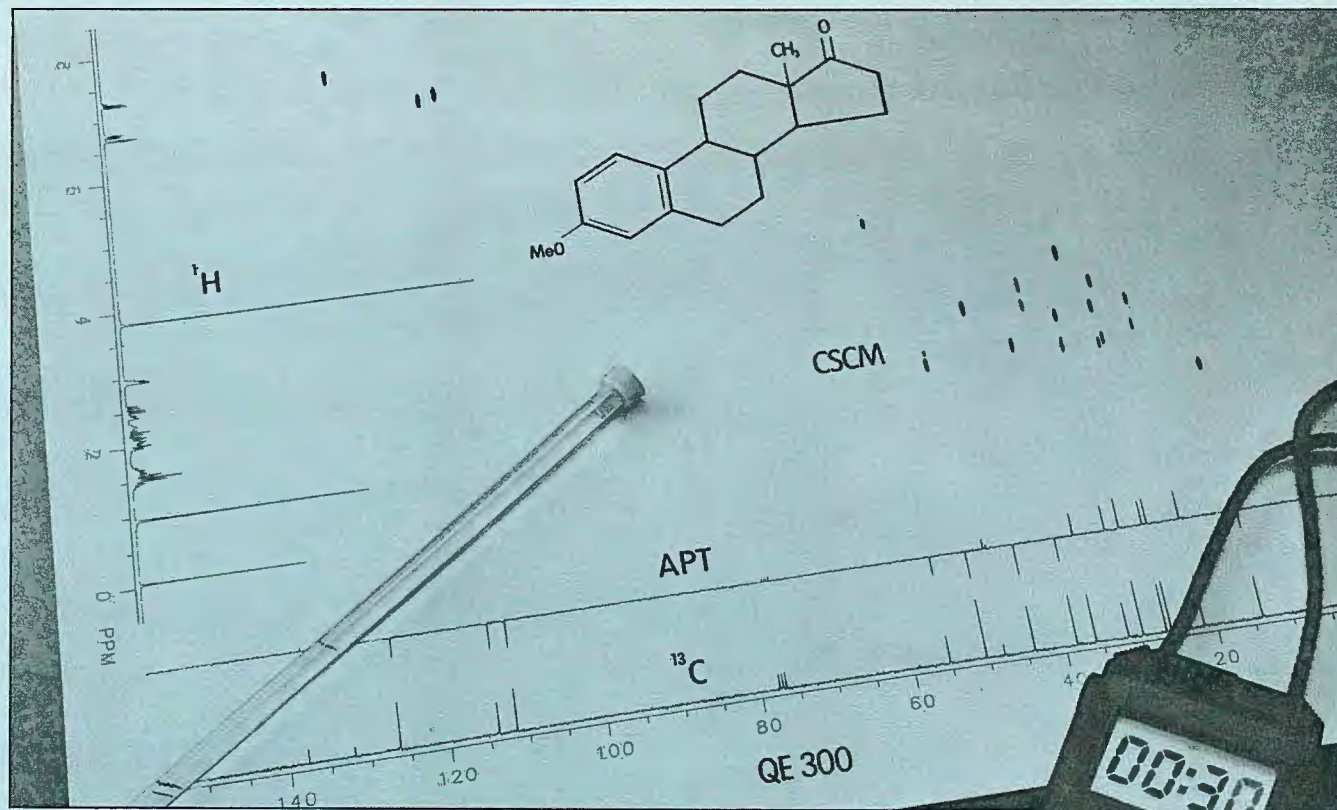
Let me use this page to give a brief report on the readership survey cards which were sent out with the February 1985 issue. While returns are still incomplete, it appears that the readership of the Newsletter has not changed in the sense that there are still approximately 6+ readers for every copy of the Newsletter mailed out - just as it was several years ago when we last did such a survey. If you have not returned a readership survey card, please drop me a postcard or whatever, letting us know the number of persons who routinely read, inspect, or have the opportunity to make significant use of your copy of the Newsletter. Thanks for your cooperation with this request.

The survey cards returned have in many instances contained useful comments and suggestions, which are being acknowledged and/or acted upon as time permits. Some of the cards also contained somewhat plaintive but useless messages, mainly having to do with the time it takes for the mails to deliver the Newsletter to the subscriber. Of course we have no influence over this delay time, other than to suggest that if you can stand the cost, we will be happy to send your copy by either first class or air mail. Just let us know of your needs in this regard.

Also, let me thank all those who said so many kind things about the Newsletter and the purposes it apparently continues to serve. We greatly appreciate your words of encouragement and support.

Let me end with a repeated request that contributors provide their own titles for their contributions. This will ensure accuracy and suppress our tendencies here to be cute.

B.L. Shapiro



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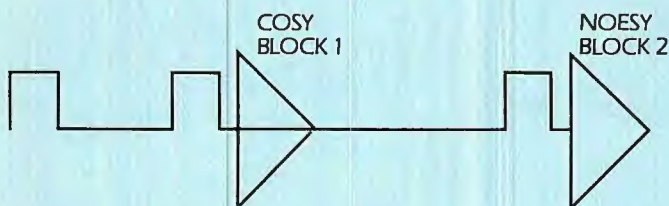
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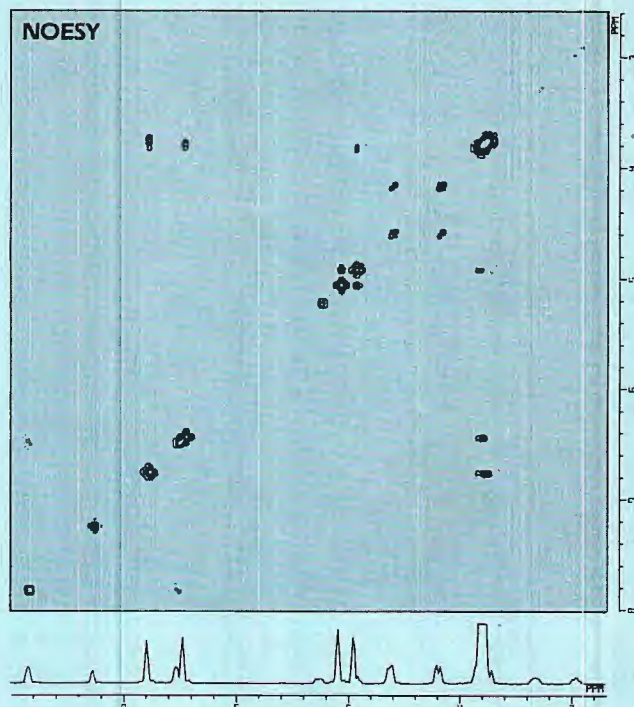
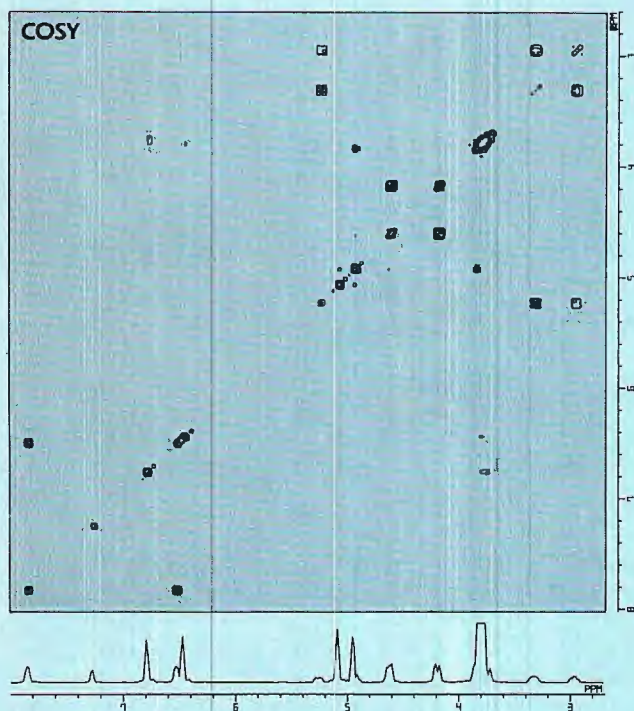
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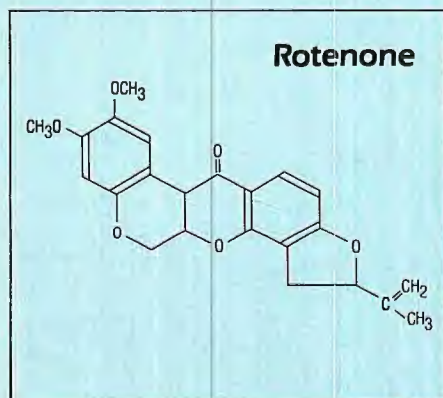


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