BRIAN SYKES

TEXAS A&M UNIVERSITY

NMR NEWSLETTER

No. 352

January 1988

Continued on page 80

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FORTHCOMING NMR MEETINGS

39th Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, February 22-26, 1988; New Orleans, Louisiana; contact Mr. J. P. Auses, Exposition Chairman, Pittsburgh Conference, 12 Federal Drive, Suite 322, Pittsburgh, PA 15235.

NMR-88 - Feb. 14-18, 1988; Thredbo Alpine Hotel, Thredbo, N.S.W. Australia. Chairman: Dr. L.R. Brown, The Australian National University. For further information, contact: Leslie Harland, Research School of Chemistry, The Australia National University, Canberra, A.C.T. 2601, Australia. Telex: AA62172. Facsimile: (61-62)-49-7817. Telephone: (61-62)-49-2863. See Newsletter 349, 20.

* Symposium on Quantitative NMR Spectrocopy, March 29, 1988, in Las Vegas, Nevada, at the 9th Rocky Mountain Regional A.C.S. Meeting (March 27 - 30, 1988); contact Donald M. Wilson (415-620-2415) or Daniel A. Netzel (307-721-2370); For details, see this Newsletter issue, pp. 78-79.

BRSG Meeting on Magnetic Resonance Spectroscopy of Colloidal Systems, April 5-7, 1988; Bristol, UK; contact Dr. N. Boden, Dept. of Physical Chemistry, The University, Leeds LS2 9JT, U.K.

Magnetic Resonance in Colloid and Interface Science, April 6-8, 1988; Bristol, UK; contact Dr. T. Cosgrove, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

29th ENC (Experimental NMR Conference), Apr. 17-21, 1988; Rochester, New York; Chairman: Professor Stanley J. Opella, Dept. of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, (215) 898-6459. For information, contact Professor Edward O. Stejskal, ENC Secretary, Dept. of Chemistry - Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204; telephone (919) 737-2998.

9th EENC (European Experimental NMR Conference), May 16-20, 1988; Bad Aussee, Austria; For further information, write Professor H. Sterk, Karl-Franzens-Universitaet Graz, Institut fuer Organische Chemie, Heinrichstrasse 28, A-8010 Graz, Austria. See Newsletter 348, 15.

2nd European Congress on NMR in Medicine and Biology, June 23-25, 1988; Berlin, West Germany; contact Prof. R. Felix, Dept. of Radiology, Charlottenburg University Hospital, Spandauer Damn 130, D-1000 Berlin 19, West Germany.

XIII Intl. Conference on Magnetic Resonance in Biological Systems, Aug. 14-19, 1988; Madison, Wisconsin. See Newsletter 349, 60.

* New listing.

Additional listings of meetings, etc., are invited.

All Newsletter Correspondence
Should be Addressed to:

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303 U.S.A.

(415) 493-5971

DEADLINE DATES

No. 354 (March) ------ 19 February 1988
No. 355 (April) ------ 18 March 1988
No. 356 (May) --------- 22 April 1988
No. 357 (June) ---------- 20 May 1988

352-2

THE ROYAL INSTITUTE OF TECHNOLOGY
Dept. of Inorganic Chemistry

Stockholm, November 17, 1987
(received 11/27/87)

Prof. Bernard L. Shapiro
966 Elsinore Court
Palo Alto,
California 94303, USA

^{205}Tl NMR on a High Field Spectrometer

Dear Professor Shapiro,

According to our knowledge there are only a few ^{205}Tl probes for high field NMR spectrometers (here meaning higher than 2.3 T) and there is only one published work in which such a probe is used.[1] In this paper[1] CSA relaxation mechanism is considered to be very important for broadening ^{205}Tl-NMR signals at high field. This is certainly true. However, this result does not mean that it is useless to measure ^{205}Tl NMR at high magnetic fields, as might be inferred from a recent NMR handbook.
One example from our experience: Some years ago, we have studied the Tl(III)-Cl^- system in water using ^{205}Tl-NMR at low field (2.1 T) and determined the equilibrium constants and the individual ^{205}Tl chemical shifts for the various $TlCl_n^{3-n}$ complexes (n = 1-6).[2] For n = 0-1 the chemical exchange was slow and the determination of chemical shifts and equilibrium constant was straight forward. For the higher complexes the chemical exchange was fast on the NMR timescale and the above mentioned parameters had to be calculated. Recently, we have measured ^{205}Tl-NMR at high field (9.4 T) for a solution containing the complexes $TlCl^{2+}$ and $TlCl_2^+$. As can be seen in the Figure, the two peaks can now be resolved and the individual chemical shifts for the complexes can be obtained. These shifts agree satisfactorily with the previously calculated shifts (2198±4 ppm for n=1 and 2201±4 ppm for n=2).[2]
At high field, we can also record ^{205}Tl spectra for dilute solutions (μmolar) and this has not been possible at 2.1 T.

Yours sincerely,

Bányai István

István Bányai

Julius Glaser

Julius Glaser

1.) Brady, F. et al. Inorg.Nucl.Chem.Lett. 1981, 17, 155.
2.) Glaser, J. and Henriksson, U. J.Am.Chem.Soc. 1981, 103, 6642.

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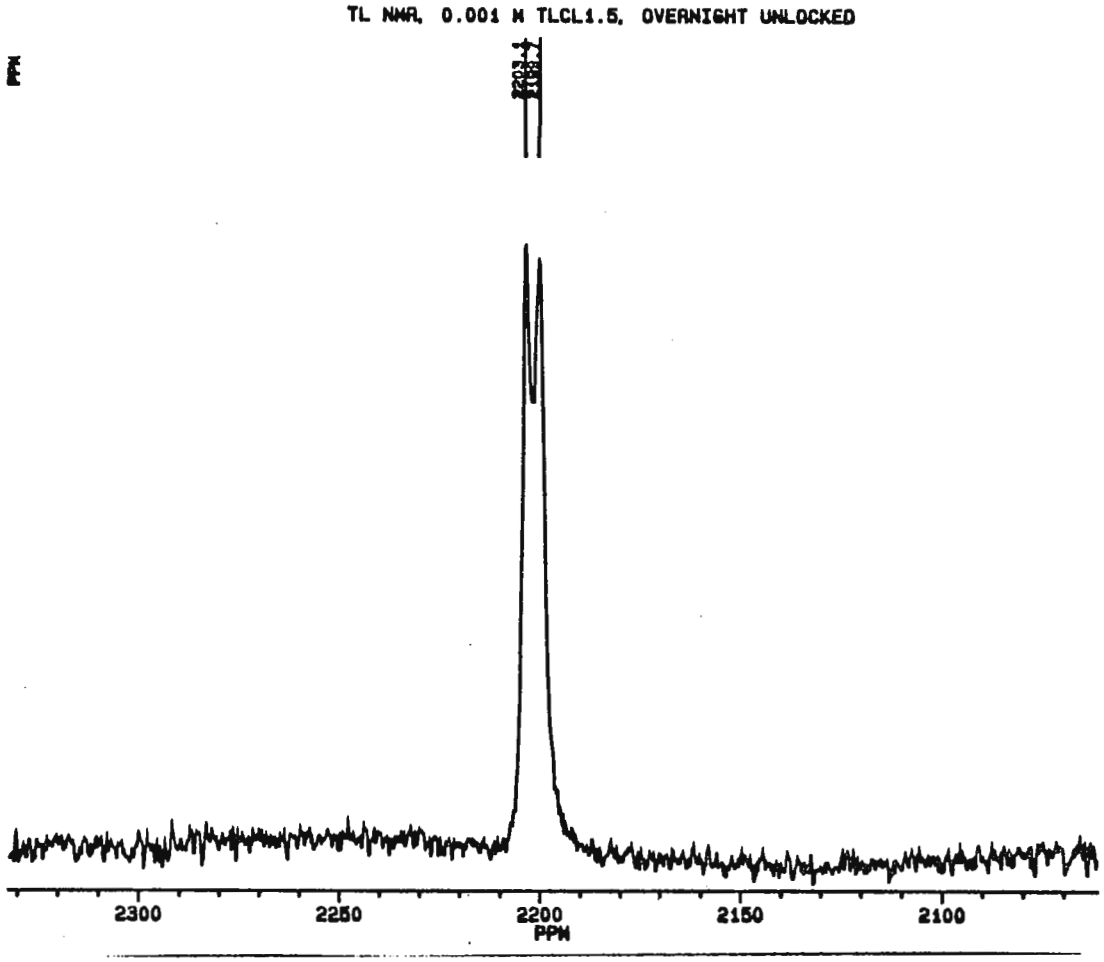

230.8 MHz ^{205}Tl-NMR spectrum for a 1 mM acidic aqueous solution of thallium(III) . Average composition is $TlCl_{1.5}(ClO_4)_{1.5}$; room temperature; linewidth at half height ~1500 Hz.

Postdoctoral Position Available

There is an opening in my lab for a postdoctoral research associate with a Ph.D. in Chemistry and experience with modern FTNMR techniques. Familiarity with Varian XL and/or VXR instruments is advantageous. Expected salary will be $16,000-20,000/year depending on qualifications. A one year appointment is available immediately, with renewal for a second year dependent upon availability of funds and mutual agreement. Projects include the use of 2D-NMR techniques to determine structure and conformation of small model molecules, peptides, and polymers; development of new 2D-NMR techniques, and use of multi-nuclear NMR (including N-15, Li-6, Cd-113, and Tl-205) to study metal ion and organic substrate binding to macromolecules. For this work we have a Varian VXR-300 liquids instrument, a Chemagnetics 200 MHz multinuclear solids instrument, and have access to a Varian widebore XL-400 liquids instrument. Interested applicants should have at least two letters of reference, cv, and copies of publications sent to: Dr. Peter Rinaldi, Department of Chemistry, The University of Akron, Akron, Ohio 44325; by Feb. 15, 1988.

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20th October, 1987
(received 12/3/87)

Professor B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 90303

One-Bond C-H Coupling Constants in Methylene Groups

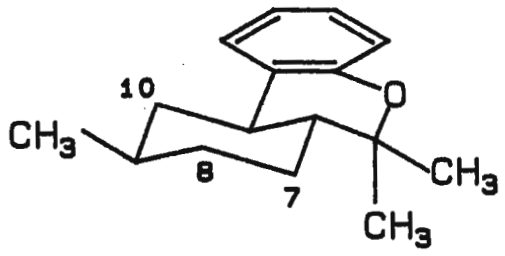
Dear Professor Shapiro:

It is well known that $^1J(C-H)$ is influenced by the carbon hybridization and by the geometry of the coupled proton. In particular, in alicyclic compounds the heteronuclear coupling constants have been found to be different for axial and equatorial protons [1].

$^1J(C-H)$ can be measured by 1- and 2-D NMR experiments, e.g. DEPT or INEPT spectra without proton decoupling during acquisition, heteronuclear J-resolved 2-D spectra obtained with the gated decoupling technique, or with the so-called "spin flip" method.

While any of the first three experiments provides the desired information for CH and CH_3 groups, we find that the last one is very suitable in order to measure the $^1J(C-H)$ in methylene groups. In fact, multiple coupling and second order effects may complicate the appearance of CH_2 multiplets in undecoupled ^{13}C spectra to the extent of preventing any significant evaluation of the heteronuclear interactions. A variation of the "spin flip" method first introduced by Bax in 1983 [2], then reproposed by Rutar in 1984 [3] (semiselective 2D J-spectroscopy) makes it possible to remove the long range coupling constants from the spectrum, which causes great spectral simplification and the evidentiation of a possible difference between the two $^1J(C-H)$'s in methylene groups.

The hexahydrocannabinol derivative (-)-(6aR,9R,10aR)-6,6,9-trimethyl-6a,7,8,9,10,10a-hexahydro-6H-dibenzo[b,d]pyran (HHC)



contains three CH_2 groups in positions 7, 8 and 10. Spectrum (A) in the figure shows the cross-section for C-7 in the ^{13}C J-resolved spectrum of HHC obtained with the gated-decoupling technique. Despite a long signal averaging and the application of a resolution enhancement routine, the spectrum appears as an

unresolved triplet, due to multiple coupling to neighbour protons across two and three bonds. Spectrum (B) shows the same trace in a 2D semiselective J-resolved experiment obtained with the spin-flip technique and suppression of the long range interactions. Two distinct ^{1}J(C-H)'s are now measurable, of 123.4 and 127.6 Hz, for the axial and the equatorial proton, respectively. Similar results are obtained for C-8 and C-10. Spectrum (C) shows the result of the same experiment on the CH_2 of ethylbenzene, in order to prove that the splitting in spectrum (B) is not an artefact at zero frequency.

1. V.A. Chertkov and N.M. Sergeyev, J.Amer.Chem.Soc. **99**, 6750 (1977).
2. A. Bax, J.Magn.Reson. **52**, 330 (1983).
3. V. Rutar, J.Magn.Reson. **56**, 87 (1984).

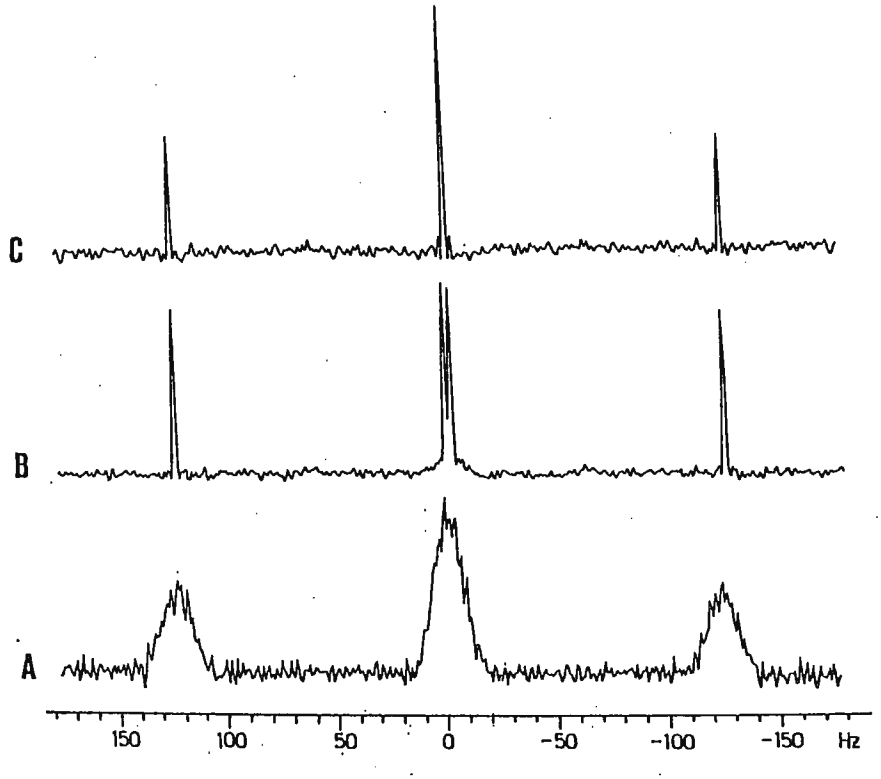


Figure: 67.88 MHz ^{13}C J-resolved spectra, selected columns, of: (A), HHC, carbon-7, obtained with the gated decoupling technique; (B), same, obtained with spin-flip of directly attached protons; (C), ethylbenzene, methylene carbon, obtained with spin-flip of directly attached protons.

Antonio De Marco Roberto Consonni Lucia Zetta

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Department of Chemistry
Faculty of Science
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November 25, 1987
(received 12/1/87)

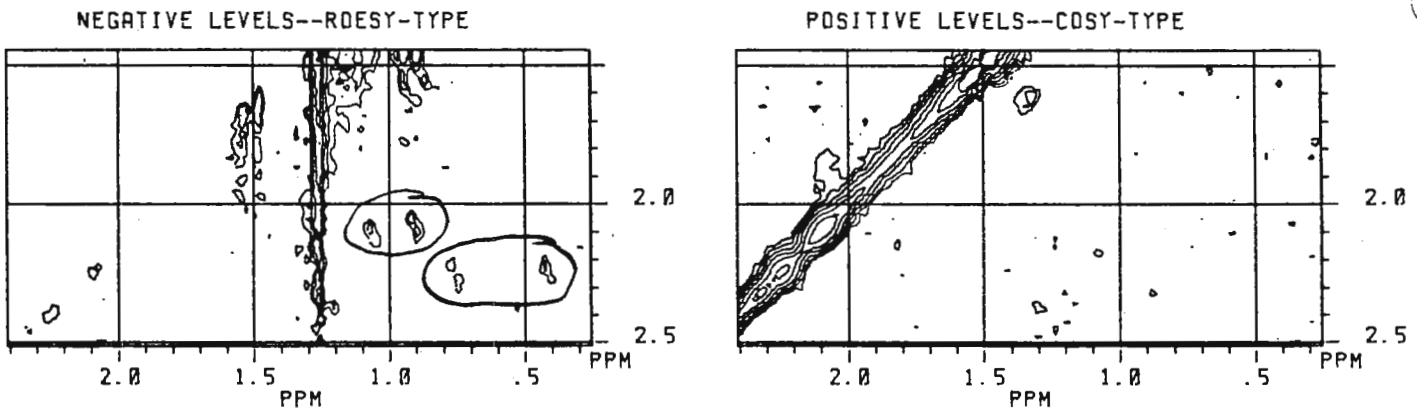
Dr. B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
PALO ALTO, California
U.S.A. 94303

Cheap and Easy ROESY

Dear Barry:

We recently attempted Kessler's[1] variation of the ROESY technique (spin locking by a rapid series of 30° pulses for typically 0.25 sec. with a 10% duty cycle), unfortunately the mismatch control circuit in our AM-300 promptly shuts down the pulse amplifier. A solution was to simply desensitize the mismatch circuit by replacing C5 (10 nF) at IC4 (7242) with a 500 pf. capacitor. This reduces the sensitivity to high repetition rates but retains the protection against long pulses (> 400 μs). There is a minor drawback to this method in that garbage is injected into the deuterium lock channel during the spin locking sequences.

Shown in the figure is a portion of the ROESY spectrum obtained from a medium sized peptide (2 mM). Circled are the β-γ cross peaks of two valines.



Please credit this to Tom Nakashima's subscription.

Yours truly,

Glen Bigam

(1) Kessler, H.; Griesinger, C.; Kerssebaum, R.; Wagner, K.; Ernst, R.R. JACS, 1987, 109, 607.

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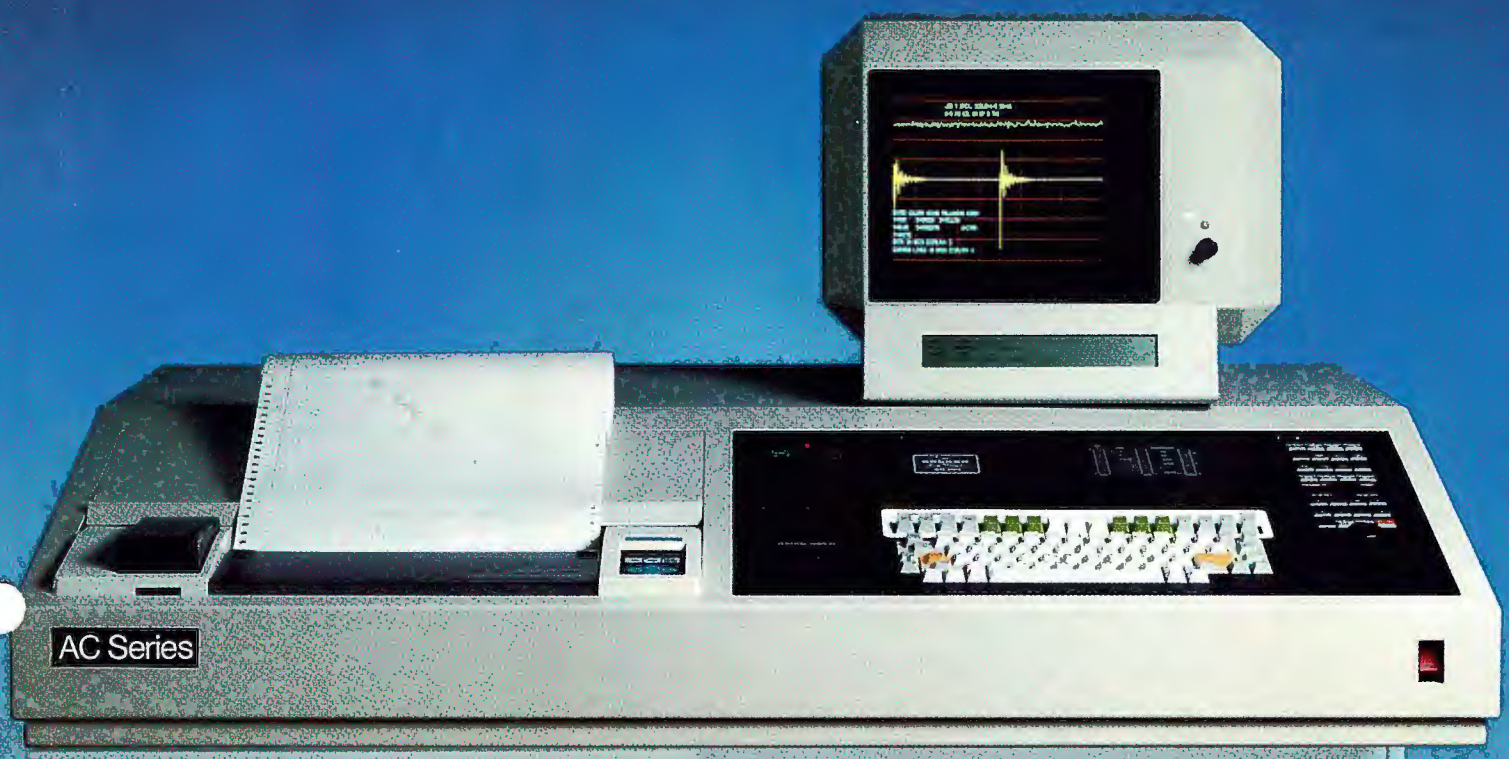

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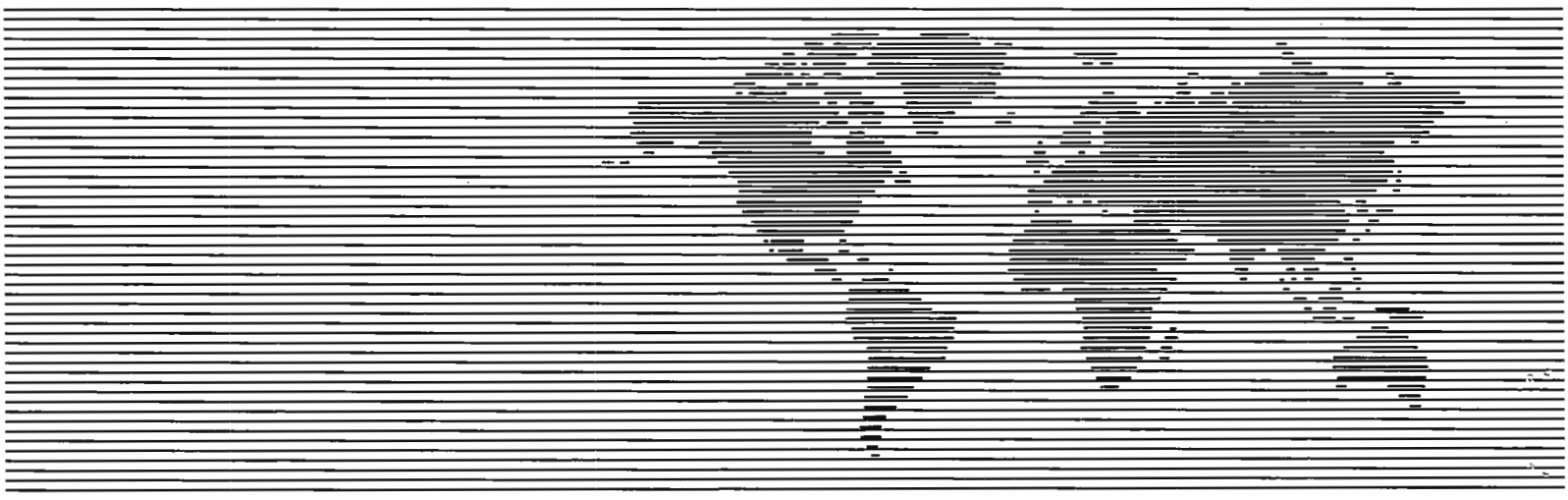

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LABORATOIRES DE CHIMIE

Département de Recherche Fondamentale de Grenoble

Grenoble, le 28 Octobre 1987
(received 12/14/87)

N/référence : DRF/CH/87-817/mjc

Dear Dr. Shapiro,

Possibility of adding several 2D INADEQUATE matrices to improve the sensitivity of the 2D INADEQUATE experiment.

The two dimensional INADEQUATE experiment appears to be a very powerfull tool for the structural characterization of organic molecules (1). Especially in its last version, where a cosy-like symmetry representation can be edited, thus adjacent carbons may be directly observed. With slightly soluble molecules or molecules with a large number of chemically different carbons, it is not possible to run such experiments within reasonable recording times. By using ^{13}C enriched molecules this drawback can be overcome and in our laboratory we succeeded in recording lignins and cellulose 2D-INADEQUATE spectra. The results have been already published (2).

In lignins samples, due to differences in the values of the $^{1}J13_{C-}{}^{13}_{C}$ coupling constants, ranging from 50 to 70 Hz, we run several experiments with different values of D_2, delays on which rely, in the pulse sequence, the double quantum coherence transfers. Each of these experiments took about 30 hours. In fact, the maps we got after Fourier transformation in both directions were very similar and only one of them was published (2). Thus we tested the possibility of adding the initial matrices, in order to get a final matrix (named "sum matrix") with a better signal to noise ratio.

Centre d'Etudes Nucléaires de Grenoble, DRF-LCH, 85 X, 38041 GRENOBLE CEDEX, France.
Téléphone : 76.88.44.00 - Télex CEN Grenoble n° 320.323

The following program with the Bruker software was written :

```
1  ZE
2  RE ≠ 1
3  AT ≠ 2
   AT ≠ 3
4  WR ≠ 4
5  IF ≠ 1
      ≠ 2
      ≠ 3
      ≠ 4
6  IN = 1
EXIT
```

Then the 2D Fourier transformation of the sum matrix was performed. The final map presented a much better signal to noise ratio than any of the original ones.

This can be further illustrated by the spectra Figure 1 : these are cross sections, in the F_1 direction, through the same carbon chemical shift (50 ppm/TMS) of the three initial matrices (spectra a, b and c) and of the sum matrix (spectrum d). 2D Fourier transformations of all these matrix were accomplished by using the same parameters. It does appear that the marked correlation which was just above the noise on the cross sections through any of initial matrix become perfectly distinct on the one plotted through the sum matrix. Thus weak correlation can be detected, which demonstrates the efficiency of this data summation.

Sincerely yours,

M. BARDET M.F. FORAY D. ROBERT

(1) J. BUDDRUS and H. BAUER, Angew. Chem. Int. Ed. Engl. 26, 625-642 (1986) ; see also M. BARDET, Thesis, Grenoble University (1987).

(2) M. BARDET, D. GAGNAIRE, R. NARDIN, D. ROBERT and M. VINCENDON, Holzforschung 40, suppl. 17-20 (1986).

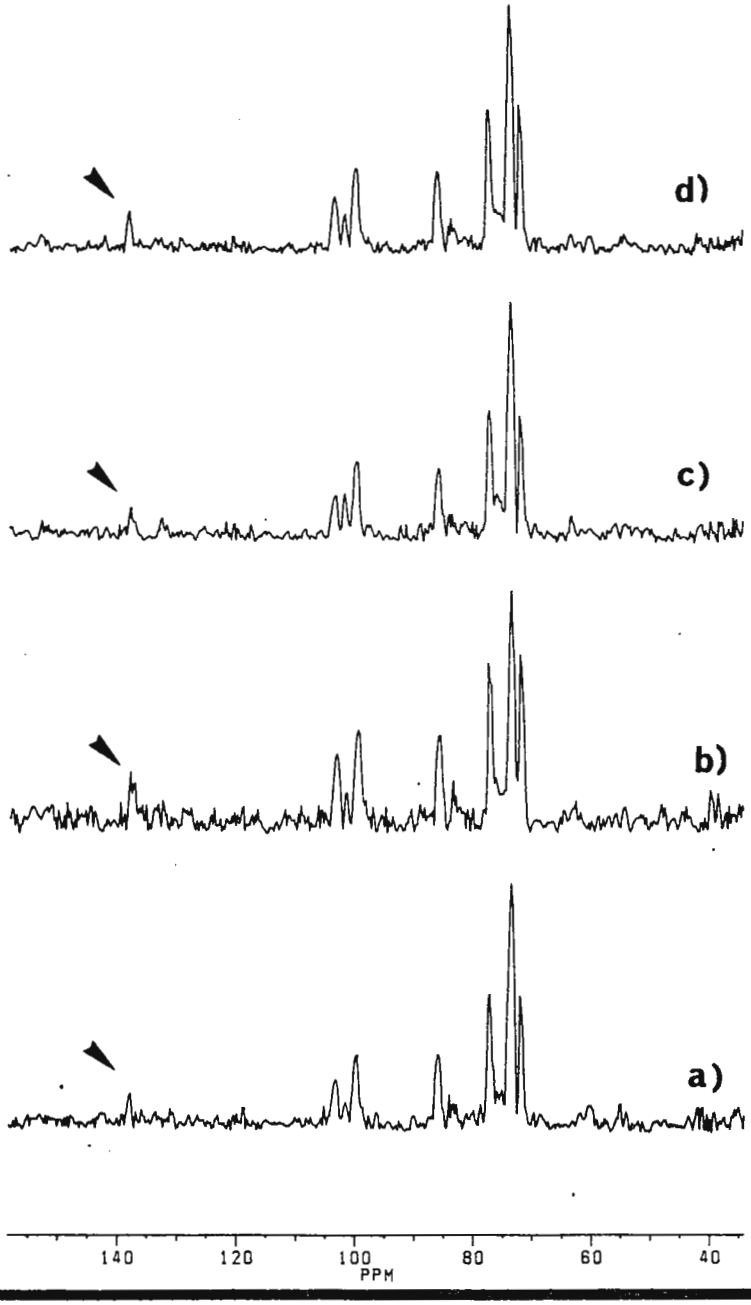

Fig.1 : Cross sections through a same chemical shift (50 ppm/TMS) of the three initial matrices (spectra a, b and c) recorded with the Bruker program INADSYM.AU and of the sum matrix (spectrum d).

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20 November 1987

Dr. Barry Shapiro
TAMU Newsletter
966 Elsinore Court
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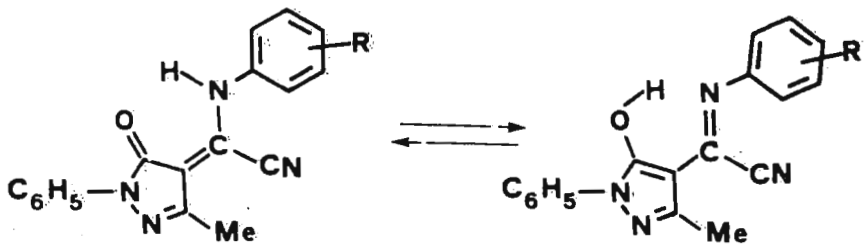
(received 12/9/87)

Prof. Bernhard L. SHAPIRO
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Isomerization as a regulation process for polarization transfer and scalar coupling.

Dear Professor Shapiro,
we will show that some interesting exceptions besides of fast isomerization processes ($\tau \ll 1/2J$) within different molecular structures exist which not only diminishe both the effect of the polarization transfer and the scalar coupling. In some instances the time scale of the isomerization process is such that the polarization transfer is operative whereas the scalar coupling is averaged out.

Experimental: The following differently substituted phenylamino-3-methyl-1-phenyl-2-pyrazolin-5-ones (3'chlorphenylamino **1**, phenylamino **2**, and 4'methoxyphenylamino **3**) as well as the following substituted phenylamino-3-n-propyl-1-phenyl-2-pyrazolin-5-ones (3',5-dichlorophenylamino **4** and 4'methoxyphenylamino **5**) have been investigated and characterized by means of ^{1}H, ^{13}C, and ^{15}N nmr spectroscopy.



Thereby three distinct types of the ^{15}N signals in the INEPT 1,2 spectrum could be observed. The compounds 1,2,4 show neither a polarization transfer - no INEPT spectrum detectable - nor a scalar coupling with the proton attached to the ^{15}N. In compound 3, at least at low temperatures, the ^{15}N experiences a weak polarization transfer resulting in an observable line in the spectrum. In compound 5, however, the polarization transfer leads to a signal enhancement in the INEPT spectrum of about 3, whereas, no scalar coupling between the nitrogen and the attached proton can be observed.
The measurements have been performed on a Varian XL 200 and a Bruker 400 spektrometer.

Discussion: The above cited behavior of the phenylamino (1) nitrogen can be monitored and understood if the magnetization vector in the INEPT experiment is described by the well known pulse operators techniques 3-5 and the averaging dynamics of the scalar coupling is expressed by the Gutowsky formula 6-8.
As can be seen in case of the INEPT experiment one ends up for the magnetization with a term like $\sigma = \sin \pi J_{KL} \tau \; 2 I_{KL} S_{Ly}$. The average of the coupling according to Takeda and Stejskal 8 is $\Delta\delta / J = [[4Q(1/2t + 1/Q)^3 + (Q^2 + 8)(1/2t + 1/Q)^2 + (Q^2 + 2)(1/2t + 1/Q) + 1]^{1/2} - 4(1/2t + 1/Q)^2 - (1/2t + 1/Q)Q]^{1/2}$; $Q = T_2 J$; $t = J\tau$ From a graphical representation one derives that $\Delta\delta/J$ decays to 0 for values of $(\tau J)^{-1}$ in the range 0.3 to 0.5. From these two equations one is able to deduce that in a small time interval where the isomerization is not too fast - lifetimes approximately 2/J - no scalar coupling can be observed. The polarization transfer, however, is operative as long as the lifetime of the species is longer than the evolution time which is fixed to 1/2J.
We think that measurements done with respect to this situation, will open some additional insight into time dependence of isomerization processes.

References:
1 G.A.Morris and R.Freeman, J.Am.Chem.Soc. 101,760 (1979)
2 A.G.Avent and R.Freeman, J.Magn.Reson. 39,169 (1980)
3 E.Königsberger, Diplomarbeit 1983 Karl Franzens Universität Graz
4 O.W.Sorensen and R.R.Ernst, J.Magn.Reson. 51,477 (1983)
5 F.J.M. van de Ven and C.W.Hilbers, J.Magn.Reson. 54,512 (1983)
6 H.S.Gutowsky, D.W.McCall and C.P.Slichter, J.Chem.Phys. 21,279 (1953)
7 H.M.McConnell, J.Chem.Phys. 28,430 (1958)
8 M.Takeda and E.O.Stejskal, J.Am.Chem.Soc. 82,25 (1960)

With our best regards,

H.Sterk H.Junek M.Klade

H.Fritz
(Ciba Geigy AG Basel)

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Your file *Votre référence*

Our file *Notre référence*

Title: Multivariate Analysis and NMR Spectroscopy

(received 12/3/87)

Dear Dr. Shapiro, Nov.26, 1987

As an addition to our studies of oil emulsion stability, we have recently begun to explore the use of multivariate analyses as applied to nmr characterization and correlations with the relative effectiveness of wax crystal modifiers and demulsifiers. Ideally, one would hope to obtain correlations of predictive value based on such factors as geographical location of the crude or heavy oil source and / or chemical composition of the oil. As in many techniques however, we quickly acquire more data than the human mind can effectively assimilate. Although it may be expedient, it is also not generally wise to ignore those data that we assume to be of no consequence for the problem at hand.

Therefore, we are using principal component analysis (PCA) and factor analysis (1,2,3) in the following areas of interest: (i) determining the relationship among structures of the chemicals tested, ie, which chemicals in a series are the best candidates for extensive testing, based on an objective and quantitative analysis of total composition of the base concentrates, (ii) the origin of the chemicals, (iii) lot - to - lot variability and polymer stability in relation to efficiency of separation, (iv) determination of active ingredients(s) in complex mixtures, (v) synergistic / antagonistic interactions with solvents, and (vi) effects of emulsion aging on chemical treatment.

To illustrate these studies we show results relating to parts (i) and (iv) above. The raw data set comprises rows and columns representing the individual additive and the corresponding intensities of the chemical shifts observed. (3) All peaks are included (as many as 100 in the present case), both solvent(s) and active ingredient(s). In many cases, when dealing with concentrates supplied by the manufacturers, it is difficult to determine accurate assignments by inspection of the nmr data alone. In terms of field performance, the nature of the solvent is of prime concern also. Therefore, we must consider all the data in the intial analyses.

'The major step in PCA is the extraction of the eigenvectors from the variance - covariance matrix to get uncorrelated new variables called principal components (PC). The first principal component (denoted PC1) is the linear combination of variables in the original data set that accounts for most of the variation in the data. The second principal component (PC2) is that linear combination of variables that accounts for the next largest variation in the original data set, and so on. In this manner the complexity / dimensionality of the original problem may be reduced significantly.

Interpretation of a single principal component is possible through the connection to the original variables. For each principal component one obtains the values of the coefficients (loading) of each variable in the linear combination. A nice feature of PCA is that nearly every result can be represented graphically. One such representation is the 'score plot', which is a projection of the loading coefficients along the principal component

axes. The scores along the principal components reveal relationships among the variables. Similar samples group together in clusters (classes) in the score plot. Since the PC's are orthogonal, the (Euclidean) distance between the samples can be used to measure similarity quantitatively.

A loading plot displays both the importance of each variable to the interpretation of a PC and the relationship among variables in that PC. The coordinates of a variable in a loading plot are its loadings along the (orthogonal and normalized) PC's. A variable's contribution to a PC is directly proportional to the squared loading. Thus, the distance of a variable to the origin along a PC is a quantitative measure of the importance of that variable in the PC. The mutual location of the variables reflects the coherence among them. Variables grouped together hold the same information in the PC. Variables located on the same side of the origin are positively correlated, while variables located on opposite sides are negatively correlated.

Figure 1 shows the score plot for 13 wax crystal modifiers. Clusters are immediately apparent, eg samples 2,4,5 and samples 7 - 12 form two such classes. The location of the data points reflects the relative intensity of the peaks at 30 ppm (horizontal axis, PC2) and 126.8 ppm (vertical axis, PC1), as well as some of the finer details of the nmr data. The active ingredients are long chain branched hydrocarbons, hence the presence of a dominant peak at 30 ppm due to methylene sequences. The solvents are aromatic in nature and comprise alkyl-substituted benzenes. On the basis of these data it would not be necessary, for instance, to test / screen all 13 samples in the field, but rather only 4 or 5 chosen to be representative of the clusters observed.

Figure 2 is a plot of the PC2 loadings against each variable (chemical shift). Six of the loadings are negative. As it happens, these represent the loadings of the chemical shifts assigned to the active ingredient in the complex mixtures investigated. The positive loadings are assigned to the solvent peaks. Thus, PCA can be of use in assigning nmr chemical shifts in complex mixtures.

More detailed multivariate studies also incorporate data concerning the nature of effect of each chemical on a given emulsion, ie, the rate of separation, water content in the oil phase, oil content in the water phase, temperature, pH, etc.

References :

(1) M.A.Sharaf, D.L.Illman and B.R.Kowalski, "Chemometrics", Wiley Interscience, New York, 1986
(2) D.L.Massart and L.Kaufman, "Interpretation of Analytical Chemical Data By The Use Of Cluster Analysis", Wiley Interscience, 1983
(3) O.M.Kvalheim, D.W.Aksnes, T.Brekke, M.O.Eide and E.Sletten, Anal. Chem., 57, 2858-2864(1985)

Yves
Y.Theriault

Dave
D.E.Axelson

Figure 1

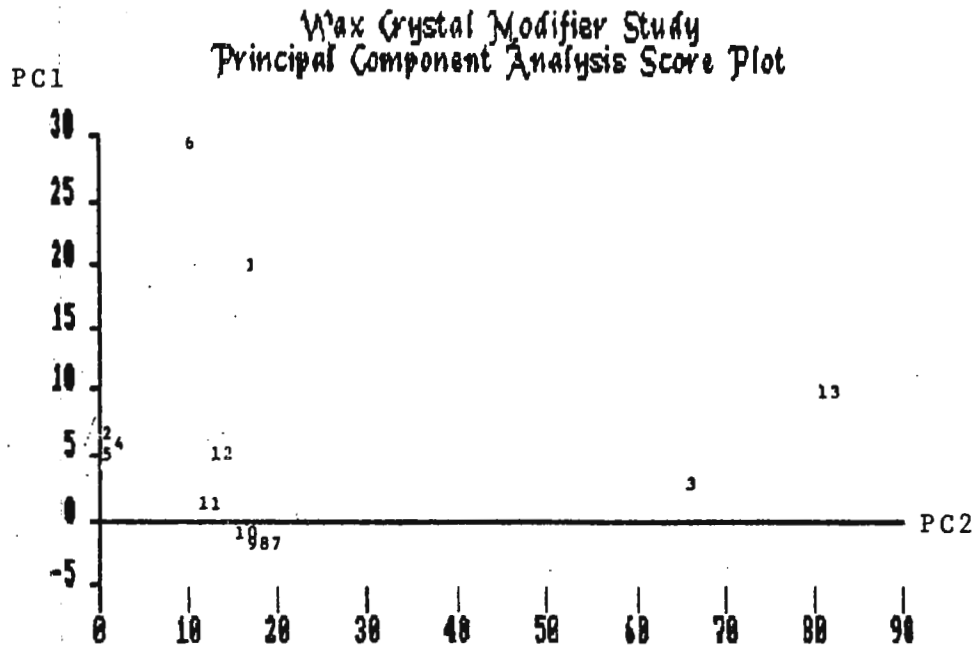
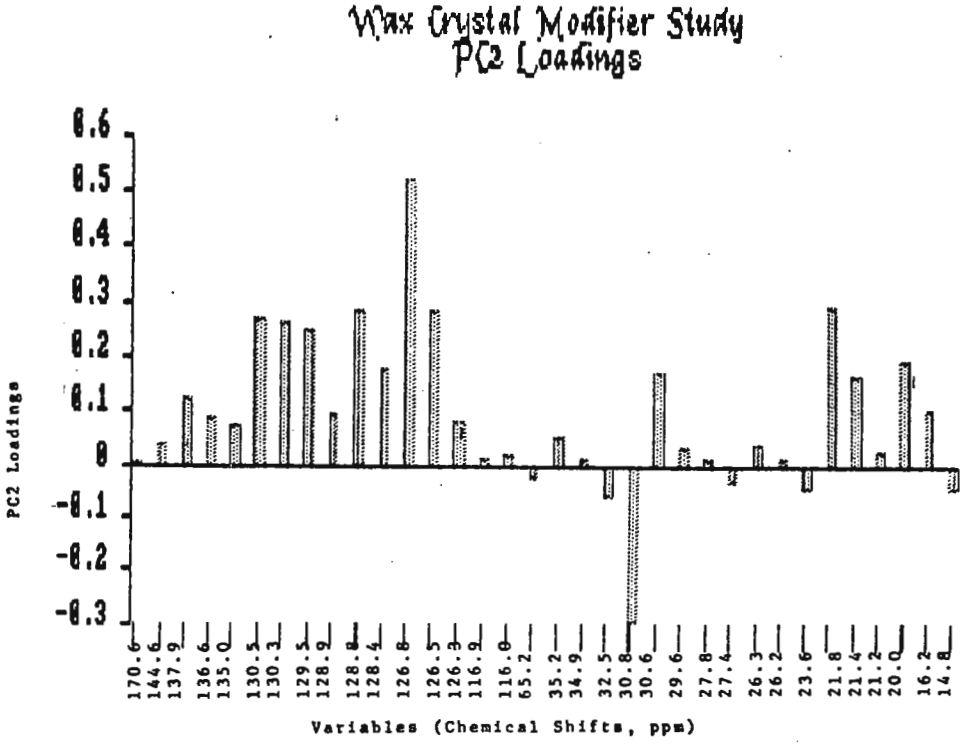


Figure 2



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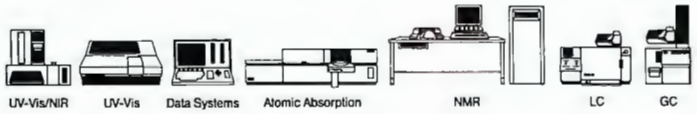

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HB/JL

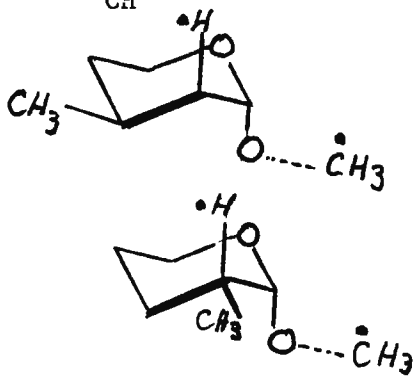
17th November 1987
(received 12/1/87)

Professor B.L. Shapiro,
966 Elsinore Court,
Palo Alto,
California 94303,
U.S.A.

Dear Professor Shapiro,

Stereospecificity of $^{4}J_{CH}$ couplings

In our attempts to use coupling constants to indicate rotameric preference, we have measured (and identified) the following $^{4}J_{CH}$ values (in addition to $^{1}J_{CH}$ and $^{3}J_{CH}$ values):-



$^{4}J_{CH}$ 0.98 Hz (± 0.15)

$^{4}J_{CH}$ 0.63 Hz (± 0.15)

The appreciable values for $^{4}J_{CH}$ suggest a preference for a W-type bond arrangement,[1,2] as illustrated. Alas, we are not yet able to use such information quantitatively.

Yours sincerely,

H. Booth.

Dr. H. Booth
S.A. Readshaw[3]

1. P. Ayras and C-J. Widen, Org.Magn.Reson., 1978, 11, 551.
2. E.G. Sundholm, Acta.Chem.Scand.(B), 1978, B 32, 177.
3. Present address: Beecham Pharmaceuticals, Great Burgh, Epsom, Surrey, U.K.

CLARK UNIVERSITY
950 Main Street Worcester Massachusetts 01610-1477

Department of Chemistry

Telephone (617) 793-7116

November 20, 1987
(received 11/27/87)

Dr. Barry L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

RE: MOTIONAL NARROWING OF ^{31}P CSA IN POLYMER BLENDS

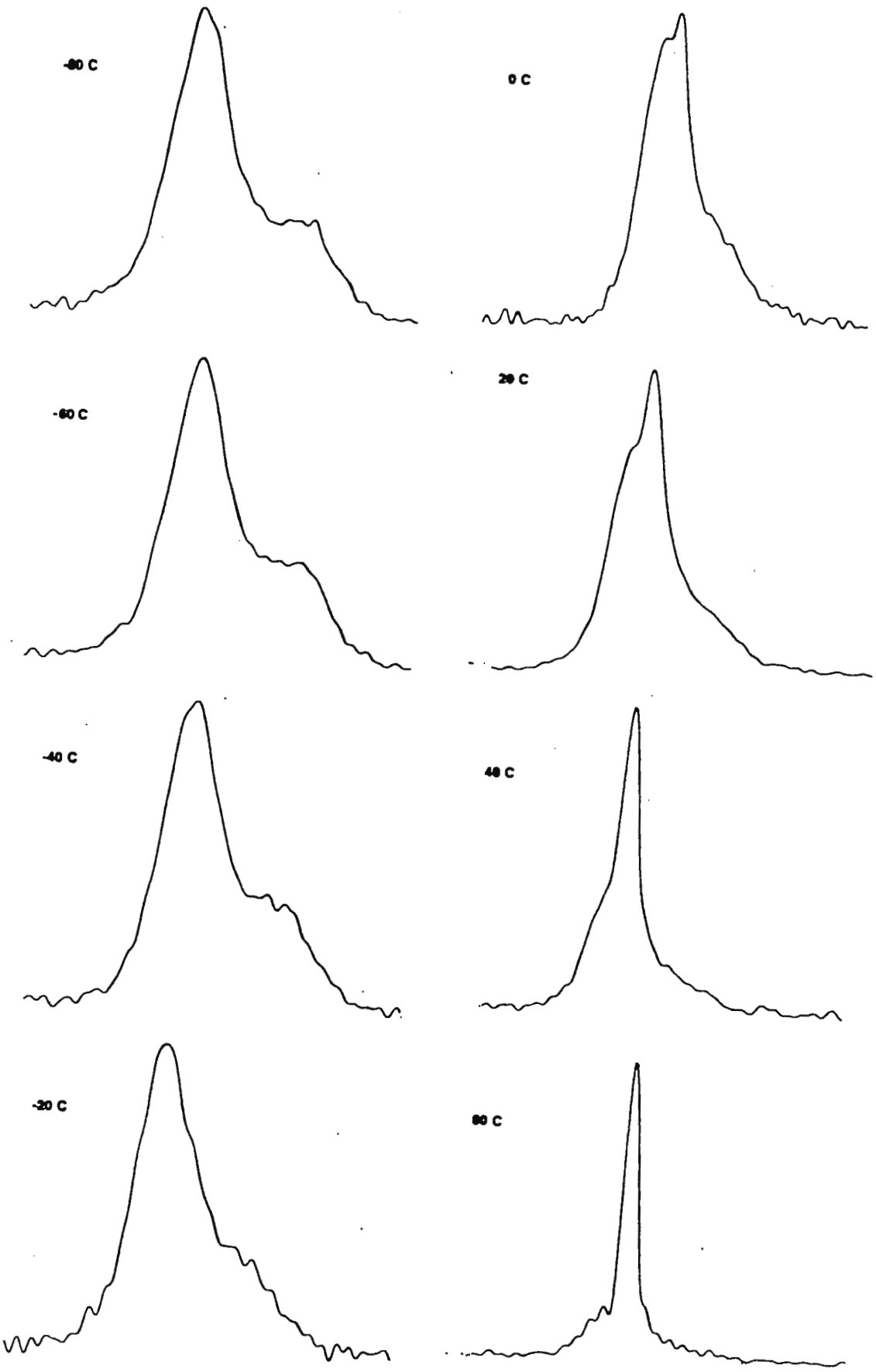
Dear Barry:

We have been recently studying the influence of low molecular weight diluents in solid polymer systems using NMR, with the intention of probing the effects of plasticization and antiplasticization at the molecular level. In this example the polymer system is polystyrene and polyphenylene oxide (50:50) and the diluent is trioctyl phosphate (TOP). The ^{31}P spectra at 101 MHz and 100 kHz sweep width are shown as a function of temperature. The low temperature spectra are classic examples of an axially symmetric CSA, consistent with the electronic environment in a trialkyl phosphate. As the temperature is raised evidence of TOP motion is clearly seen and the nature of the lineshape collapse allows for identification of the features of the motion. All the spectra shown are below the glass transition and the high temperature spectra indicate TOP is undergoing isotropic reorientation with a correlation time shorter that tenths of milliseconds. The intermediate temperatures show a superficially bimodal character indicative of heterogeneous motion often characteristic of glassy polymers. We have made measurements on a number of similar systems; the ^{31}P spectra was easily obtained, the lineshapes showing negligible dependence on proton decoupling and quantification of the lineshape collapse can often be compared to the macroscopic properties of the blend.

Regards,

Paul T. Inglefield Bonnie J. Cauley

P.S. We have a postdoctoral position available for the study of solid polymer structure and dynamics using NMR, anyone interested can contact me (PTI) at (617) 793-7653 for further details.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TEXAS A&M UNIVERSITY

DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843-3255

A. I. SCOTT
Center for Biological NMR
(409) 845-3243

November 20, 1987
(received 11/27/87)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Dr. Shapiro:

Recently we had difficulty performing plant cell culture metabolism studies on our Bruker WM 300 spectrometer due to bacterial contamination which consistently outgrew the plant cells. Addition of carbon dioxide/oxygen bubbling increased plant cell growth significantly but added to contamination problems and added lock problems as well.

A recent report by Santos and Turner (1) described a pumped flow cell design which offered better lock stability and improved culture mixing. Our design shown in Figure 1 adds further modifications which prevent contamination. A sterile plastic 0.1μ filter removes foreign particles from the airstream and Luer connectors hold parts of the cap apparatus in place. The syringe needle, NMR tube and teflon insert are autoclaved before use. NMR tube caps melt under these conditions so they are sterilized with alchohol and allowed to dry in a laminar flow hood. As originally designed, the teflon plug was press-fit size and was positioned in the NMR tube only with difficulty. After three trips through the autoclave it fit loosely which turned out to be animprovement. A length of 5 lb monofilament tied through two holes in the plug is held in place by the cap, allowing easy pump height adjustment with minimum risk of contamination.

Due to problems which may arise in handling gas cylinders near NMR magnets, we find it expedient to extend the air line to tanks mounted outside the NMR laboratory. Nupro®S series metering valves allow precise airflow control.

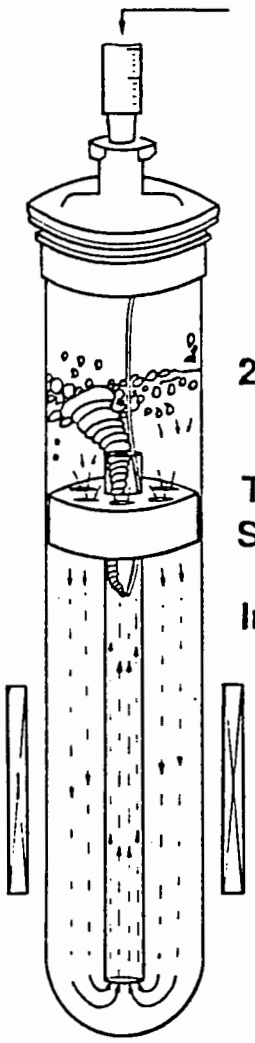
1. H. Santos and D.L. Turner, *J. Magn. Reson.*, 68, 345 (1986).

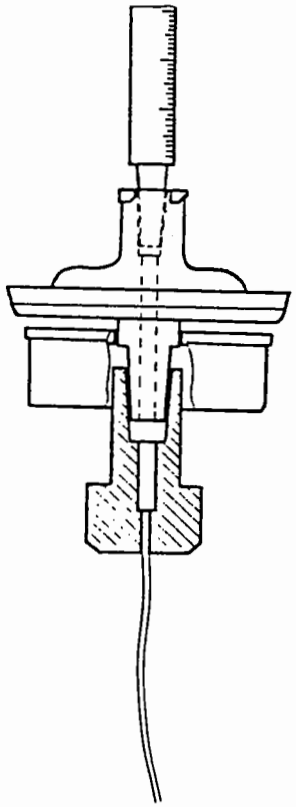
Sincerely yours,

Howard Williams, Senior Scientist

Yanding Gao, Research Assistant

A. Ian Scott, Davidson Professor of Science & Head, CBNMR





NON-CONTAMINATING PUMPED SYSTEM FOR NMR CELL CULTURE STUDIES

352-24

SYRACUSE UNIVERSITY
NMR and DATA PROCESSING LABORATORY
GEORGE C. LEVY, DIRECTOR (315) 423-1021

DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, N.Y. 13244-1200

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

Multivariate Techniques for Enhancement of Two Dimensional NMR Spectra

Dear Barry,

Recently we have introduced the concept of using multivariate techniques in a new pattern recognition strategy designed to isolate and identify the spin connectivities in 2D correlated spectra.[1] The basis of the approach involves tabulating position and height information for all peaks in a 2D spectrum in a multidimensional way. By using principal component analysis (PCA), we reduce this multidimensional space into two or three dimensional hyperplanes which forms projections oriented along directions of maximum variance in the data.

When this method is applied to representations of spectra containing more than one spin system, signals from different spin system are projected into mutually orthogonal planes or hyperplanes; this is due to the specifics of the data representation. Therefore, PCA can be used as a tool to separate mixed spin systems, allowing independent analysis.

In a further exploration of multivariate representations of 2D NMR spectra, it is shown that systematic noise such as t1 and t2 ridges can be modeled by a principal component analysis . Later these noise models can be subtracted from the original data without distorting the spectral features. In addition, PCA can generate reconstructions of 2D spectra, which are solely based on the systematic information from the data, and thus exclude random noise. This leads to a pronounced enhancement of spectral quality. These methods can be used to optimize data in preparation for automated, multivariate-based spectral analysis procedures, which benefit greatly from such improvements. Both of these latter applications are exemplified on the attached figure. In F, the spectral improvement possible by removal of component 2 is not shown.

It should be pointed out that these are only preliminary results showing various applications of multivariate techniques. Other applications will deal with multivariate pattern recognition procedures for NOESY spectra of RNA and DNA.

Yours sincerely,

Hans Grahn Frank Delaglio George C. Levy

Hans Grahn — Syracuse University

Frank Delaglio — New Methods Research

George C. Levy — Either

[1]. H. Grahn, F. Delaglio, M. A. Delsuc and G. C. Levy, *J. Magn. Reson.* (in press).

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For further information from NMRi, turn over.....

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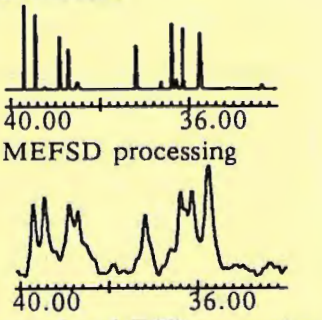

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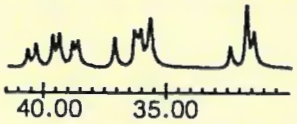
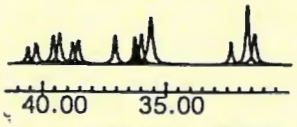


complex ^{13}C spectrum



automatic curve fitting

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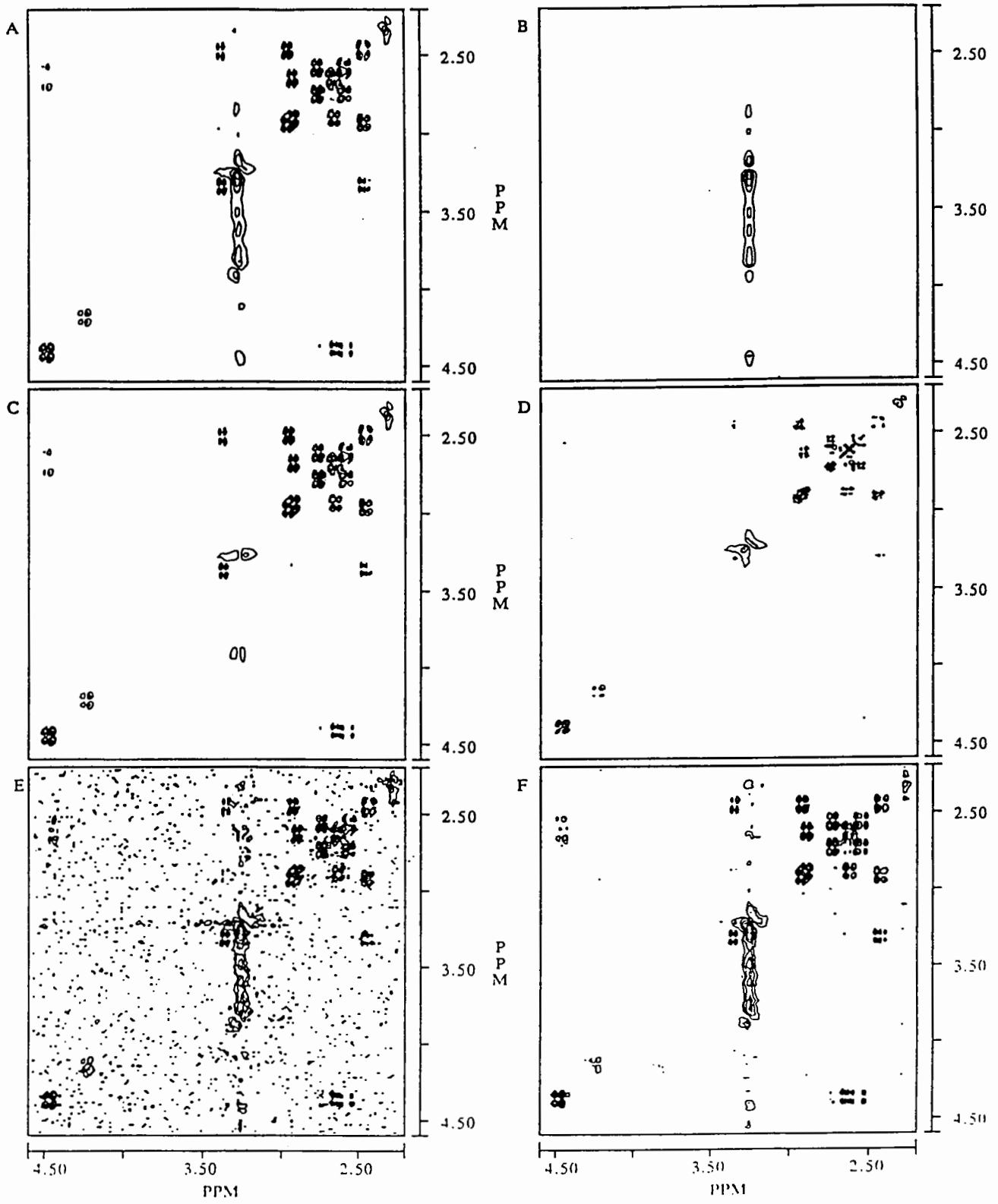

Example of PCA Analysis and Improvement of 2-D Spectra

(A) Here, the aliphatic region of the DQF-COSY spectrum of Trp-Ala-Trp-Phe in DMSO is shown. (S:N-50:1) (B) The second principal component, reconstruction of region shown in A. (C) Original data with noise-ridge component subtracted. (D) Standard symmetrization of original data. (E) Original data plus simulated noise, S:N - 5:1 (F) Reconstruction of spectrum in E, with 10 principal components. S:N -12:1.

P. BERNIER

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November 23, 1987
(received 12/7/87)

Dear Pr. Shapiro,

our work concerning the CP-MAS ^{13}C NMR of conducting organic crystals is still in progress. After our first studies of the Bechgaard salts $(TMTSF)_2X$ (X = ClO_4, PF_6, ReO_4) (see NMR newsletter n° 311 and 331) we have recently investigated new TMTSF compounds, namely the $(TMTSF)_2$ $(Ni(tds)_2)$ (tds = bis (trifluoromethyl ethylene diselenato-)).

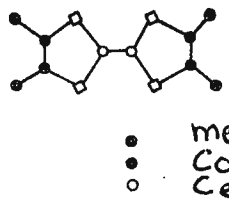
This compound experiences a structural phase transition at ∿ 272K with an increase of conductivity when the temperature is decreased, while with Bechgaard salts phase transitions generally imply a decrease of conductivity. Then we expect some new behaviour when studying the temperature dependence of the various ^{13}C resonance positions.

The figure shows three groups of resonances concerning the corner carbons (Co), the center carbons (Ce) and the methyl carbons (Me) respectively. When the temperature is lowered through the transition temperature, the Ce and Me resonances do not move but the Co ones are significantly changed. The remarkable feature is that some lines are displaced upfield and some downfield, showing that there is a redistribution of the electronic density among these carbons. At the moment we are working to interpret in detail these features.

Sincerely yours,

P. BERNIER, A.K. WHITTAKER, P.C. STEIN, W.B. HEVER*, B.M. HOFFMANN*

* Evanston, IL.60201, U.S.A.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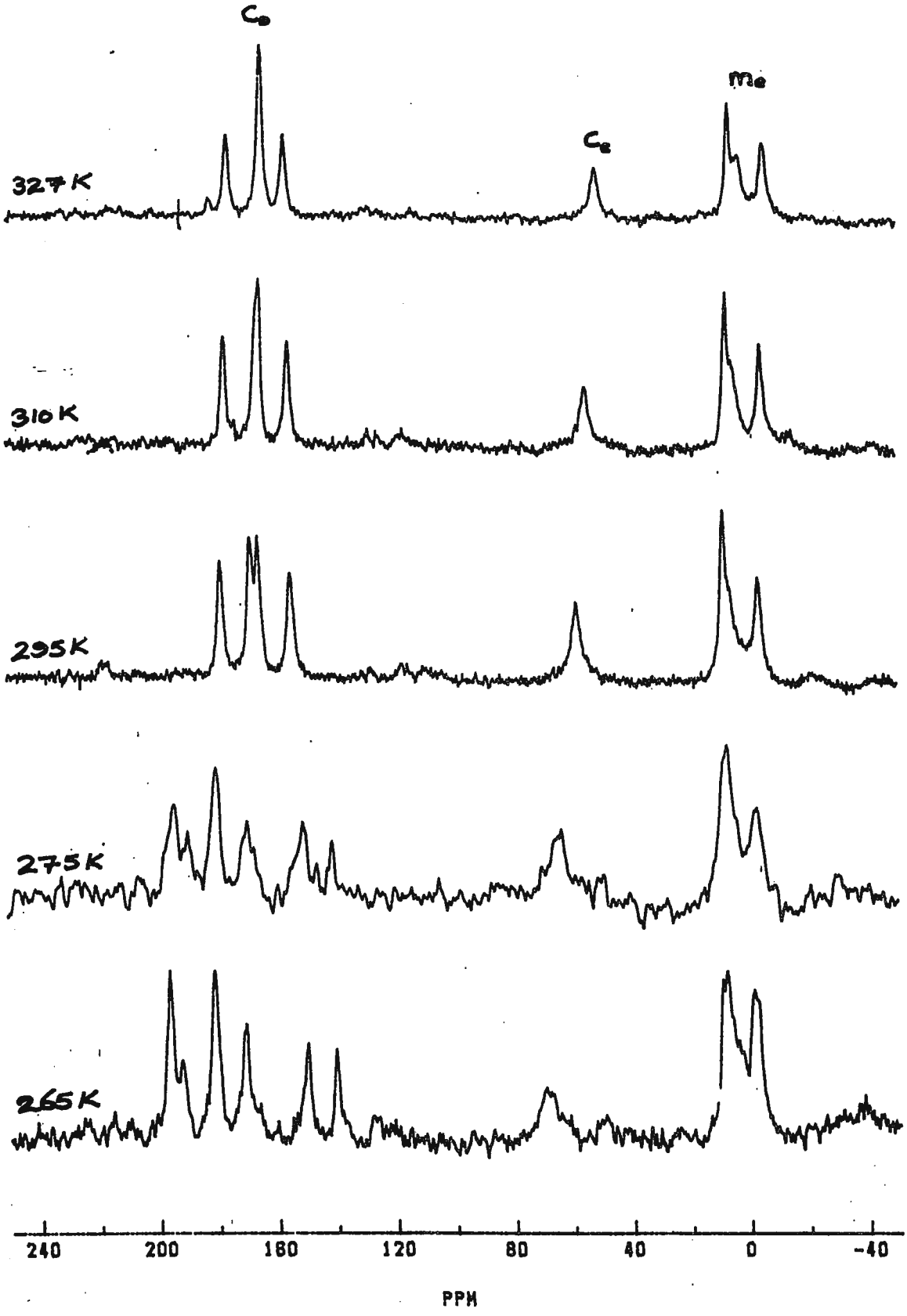
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PPM

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Sherbrooke, November 25th, 1987.
(received 12/3/87)

Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303
U.S.A.

^{1}H NMR Studies of Thermally Induced Volume Changes in a Block Copolymer of Propylene Oxide and Ethylene Oxide in Aqueous Solution.

Dear Dr. Shapiro:

Recently some temperature induced molar volume changes have been reported for solutions of block copolymers of propylene oxide (P) and ethylene oxide (E) with structures of the type $(E)_m$-$(P)_n$-$(E)_o$ (1). We have studied with ^{1}H NMR (250 MHz) the expansibility of a 5% solution of the polymer with P/E = 0.289/1, a molecular weight of 11,300 and a transition temperature range of 20° to 30°C. The resonances of the E and P monomers are well resolved thereby permitting to monitor the microscopic environments in the different blocks of the polymer. We show the temperature variation of T_1 in figure 1 for the methyls (P) and methylenes (E) and their respective lineshapes in figures 2 and 3. In the transition temperature range changes are observed for the methyls' T_1 and the doublet lineshape due to CH_3-CH- scalar coupling broadens, while the methylenes show uniform behavior. We therefore infer that volume changes can be associated with the P block of the polymer. The apparent energies of activation for the methyls are 2.35±0.33 kcal/mole (5°-21°), 3.06±0.48 kcal/mole (27°-70°) and 5.39±0.36 kcal/mole (5°-70°) for the methylenes. In the same temperature range (5° to 70°) the solvants T_1s and lineshapes for H_2O, HDO, and D_2O all show uniform behavior. We are currently studying the concentration dependence of the same system. When completed, we hope to have a better understanding of the volume changes in this block copolymer.

(1) R.K. Williams, M.A. Simard and C. Jolicoeur. J. Phys. Chem. 89, 178 (1985).

Sincerely,

Franco Cau

Serge Bérubé

Serge Lacelle
Département de chimie

Please credit this to S. Lacelle's account.

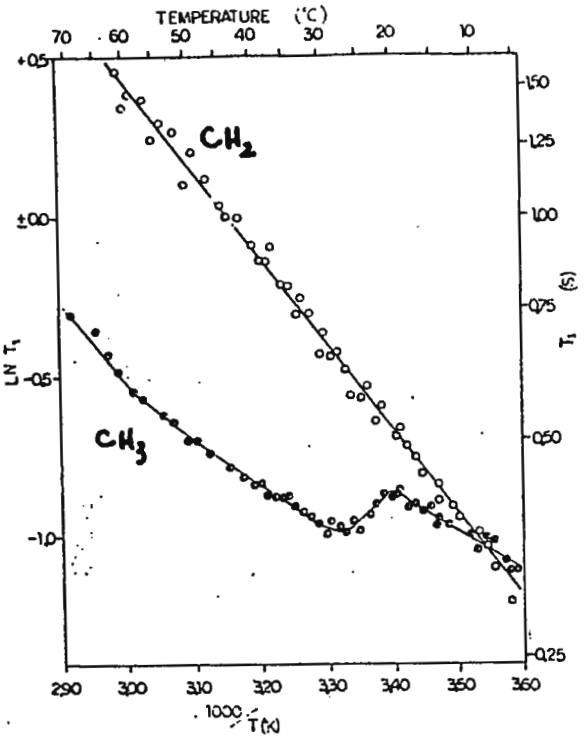

FIG. 1

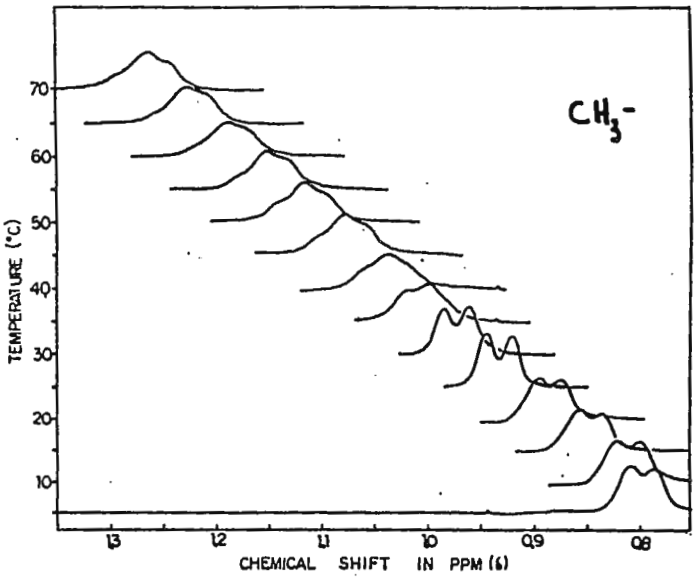

FIG. 2

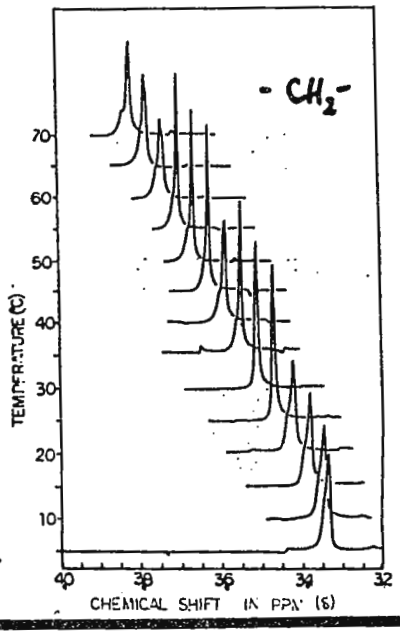

FIG. 3

Position Available

NMR Spectroscopist at the Laboratory for Molecular Spectroscopy, School of Chemical Sciences, University of Illinois-Urbana. Requirements for this position include a PhD in chemistry or extensive equivalent experience with state-of-the-art NMR spectrometers; a thorough familiarity with modern FT-NMR spectroscopy; and the ability to work independently and collaboratively in a stimulating research environment. Experience in devising or implementing new FT-NMR experiments (e.g. 2D NMR; new pulse sequences), and a working knowledge of CP or FT solid state NMR is also desired. Duties will include the operation of several high-field FT-NMR instruments, the supervision of instrument operators, and the instruction of graduate students and postdoctoral fellows in NMR techniques. The successful applicant will have the opportunity to engage in NMR research independently or in collaboration with faculty of the School of Chemical Sciences. Starting salary is competitive and commensurate with experience. January 19, 1988 starting date although other starting dates could be negotiated. Submit resume and three letters of recommendation, preferably by January 5 to Dr. Vera M. Mainz, Department of Chemistry, Box 34 Noyes Laboratory, University of Illinois, 505 S. Mathews Ave., Urbana IL 61801 (Tel: 217/244-0564). The University of Illinois is an affirmative action/equal opportunity employer.

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BIOPHYSICS RESEARCH DIVISION

November 23, 1987
(received 11/27/87)

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Advantages of Time Proportional Phase Incrementation (TPPI)

Dear Dr. Shapiro:

We have recently set up a NMR laboratory at the University of Michigan where we are involved in a *Program for Protein Structure and Design.* When implementing standard 2D NMR experiments on our new GN-500 spectrometer we have used two methods for discrimination of the frequency sign along ω_1: (1) time proportional phase incrementation (TPPI) (Redfield and Kunz, 1975; Marion and Wüthrich, 1983) with a real Fourier transform, and (2) quadrature detection by simultaneous acquisition of two data sets phase shifted by 90^0 and a complex Fourier transform along t_1 (Aue et al., 1976; States et al., 1983). Initially we were favoring the latter technique since the 2D Fourier transform is faster with standard GE software. We have realized, however, that for certain 2D experiments where the phase cycles for axial peak suppression do not work perfectly it is advantageous to use TPPI.

When the discrimination of the frequency sign along ω_1 is achieved by acquisition of a complex data set, the overlap of the spectrum with its quadrature image is eliminated by recording a second 90^0 phase shifted data set, and a complex Fourier transform is performed. In essence, this means that a cosine modulated time domain signal is subject to a cosine Fourier transform, and a sine modulated time domain signal is subject to a sine Fourier transform. Both transforms yield the same spectrum, but the quadrature images have opposite signs. Thus, coaddition of the two transforms eliminates the quadrature image. Axial peaks are not affected by this procedure, they stay in the center of the spectrum at the carrier frequency. If they are not completely suppressed by phase cycling, they interfere with the signals of interest.

With TPPI the quadrature image along ω_1 is eliminated by application of a phase modulation along t_1 with the frequency of half the spectral width. Thus the spectrum and its quadrature image are shifted to directions away from the carrier at $\omega_1 = 0$. Axial peaks are not affected by the phase modulation, they stay in the center between the spectrum and the quadrature image and do not interfere with the signals of interest.

Therefore, it is advisable to use TPPI for all 2D experiments where the schemes for axial peak suppression are not perfect. In addition, the TPPI data may be recorded sine modulated in t_1, circumventing the t_1-ridge problem associated with the Fourier transformation of cosine-modulated data (Otting et al., 1985).

Gerhard Wagner Sven Hyberts Gaetano T.Montelione

W. P. Aue, E. Bartholdi and R.R. Ernst, J. Chem. Phys. 64, 2229 (1986).
D. Marion and K. Wüthrich,Biochem. Biophys. Res. Comm. 113, 967 (1983).
D.J. States, R.A. Haberkorn and D.J. Ruben, J. Magn. Reson. 48, 286 (1982).
G. Otting, H. Widmer, G. Wagner and K. Wüthrich, J. Magn. Reson. 66, 359 (1986).

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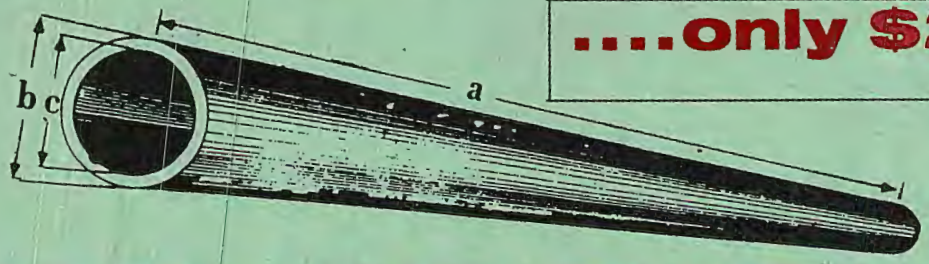

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Institut de Chimie
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Professor B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966, Elsinore Court
Palo ALto, CA 94303, USA

December 2, 1987
(received 12/12/87)

Nitromesitylene Corrected

Dear Barry,

As you know, we work at upgrading electrophilic aromatic substitution. We came upon an ambiguity in the attribution of the ^{13}C NMR spectrum of nitromesitylene. A German group assigns the 129.5 ppm signal to C-4 (1). For Japanese workers (2), this nucleus resonates at ca. 140.5 ppm. From careful signal integration and signal multiplicity, we must take issue with the erroneous attibution of Bremser (1) (Table). This work was done with A. Cornélis, A. Gerstmans, and J. Grandjean. You have moved closer to the Zinfandel : congratulations and best personal regards.

Sincerely yours,

Pierre Laszlo

(1) Bremser, W., Hardt, A., Ernst, L., Fochinger , W., Gerhards, R. and Lewis, P., Carbon-13 NMR Spectral Data, 4th ed., VCH, Weinheim, 1987.
(2) Mishima, M., Fujio M. and Tsuno, Y., Memoirs of the Faculty of Science, Kyushu University, Ser. C., 15, 99 (1985)

	δ (ppm)		
carbon	ref. 1	ref.2	this work
C-1	150.10		149.92
C-2	140.40		129.57
C-3	129.50		129.52
C-4	129.50	ca 140.5	140.39
C-5	129.50		129.52
C-6	140.40		129.57
C-7	17.30		17.45
C-8	21.00		20.98
C-9	17.30		17.45

TABLE 1 : ^{13}C-NMR chemical shifts for 1

Washington
WASHINGTON·UNIVERSITY·IN·ST·LOUIS

Department of Chemistry
Washington University
Campus Box 1134
One Brookings Drive
St. Louis, Missouri 63130

November 25, 1987
(received 12/4/87)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

'Tis the Season for Pumpkin (Pie?) Slices

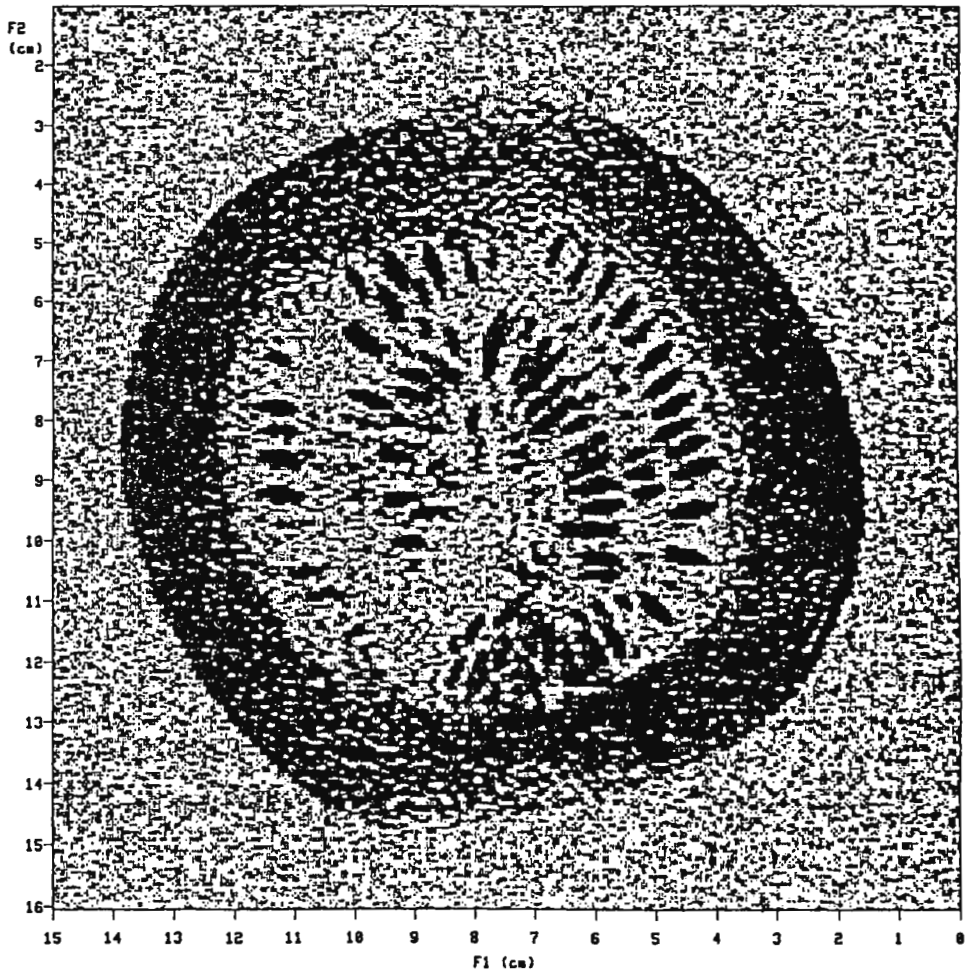
Dear Barry,

Our new SIS 200/400 imaging spectrometer has recently been installed by Spectroscopy Imaging Systems (a joint venture of Varian and Siemens, located in Fremont, California) and is now operational. The 4.7 tesla horizontal magnet has a 40-cm bore (32 cm with gradients installed), large enough to accomodate dogs, and is equipped with gradients of 2 G/cm field strength. While there have been the usual startup bugs, as expected with any prototypical instrument, we are currently obtaining proton images and multinuclear specra on a routine basis, and are exploring the multinuclear imaging capabilities of the system.

Shown below is a spin-warp proton image of a pumpkin, taken using the large imaging coil supplied by SIS (28 cm i.d., 23 cm o.d.). The pixel size is 0.6 mm x 1.2 mm and the slice thickness is 2.4 mm. While this image was obtained in the single slice mode, the system has multislice capabilities as well. We will submit further updates as progress is made.

Position Available

We are currently seeking to fill a research position in advanced imaging and spectroscopy techniques which requires an advanced degree in physics, engineering, or physical chemistry. Anyone interested in this position please apply to Joseph J. H. Ackerman at the above address.



Sincerely yours,

Nancy N. Becker

Joseph J. H. Ackerman

College of Physicians & Surgeons of Columbia University | *New York, N.Y. 10032*

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630 West 168th Street

November 25, 1987
(received 12/5/87)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Dear Barry:

TITLE: ADVENTURES WITH ROESY EXPERIMENTS ON A BRUKER AM-500 SPECTROMETER

The rotating frame Overhauser enhancement experiment (ROESY)[1] or CAMELSPIN[2] experiment are useful alternatives to the more traditional NOE experiments for obtaining distance information in intermediately sized molecules. If the product of the rotational correlation time (τ_c) and angular Larmor frequency (ω) are approximately equal to unity ($\tau_c \omega \approx 1$) then no NOE occurs. In contrast, the rotating frame NOE is positive and monotonically increases with increasing values of τ_c.

Recently, I was given less than a milligram of a steroidal compound isolated from fetal bile extracts. My task was to structurally characterize the compound by NMR. Previous NMR work done by my collaborators used DMSO-d_6 as a solvent, so I therefore decided to perform my work in the same solvent. Unfortunately, as I somewhat expected, at 500 MHz for a molecule of this size in DMSO the one dimensional NOE's were horrible being a mixture of very weak positive and very weak negative NOE's. Therefore, I next turned my attention to the ROESY experiment as a means for obtaining the needed proton-proton distance information.

The spin lock field in the ROESY experiment requires a field strength of about 2-5 kHz. However, it has been recommended that a weaker field be used since this can minimize effects due to homonuclear Hartmann-Hahn type transfer. Normally, one uses the proton decoupling channel for generating the spin lock field as this allows an adjustment of power output for obtaining the desired field strength. Unfortunately, on all of our Bruker spectrometers the proton decoupling channels are not phase coherent with the receiver electronics and one must resort to other means for performing the ROESY experiment. Bruker now has a so called fast TLO switch or "ROESY box" as an upgrade option which allows one to use both high power (50 watts) and low power (2 watts) transmitter pulses directly without adding extra delays normally required for relay switching between high and low power modes.[3]

Since we do not have a phase coherent proton decoupler nor a fast TLO switch, I resorted to using low power mode (TLO, 0.5 watts) for the entire ROESY experiment which provided a field strength of about 4.6 kHz. I used a slightly modified spin lock pulse scheme which had been described to me earlier by Dr. Allen Kline of Professor Wuthrich's group. This modification used a series of 32° pulses during the spin lock period; I used seven 32° pulses followed by a final 180° pulse, the latter pulse was necessary to

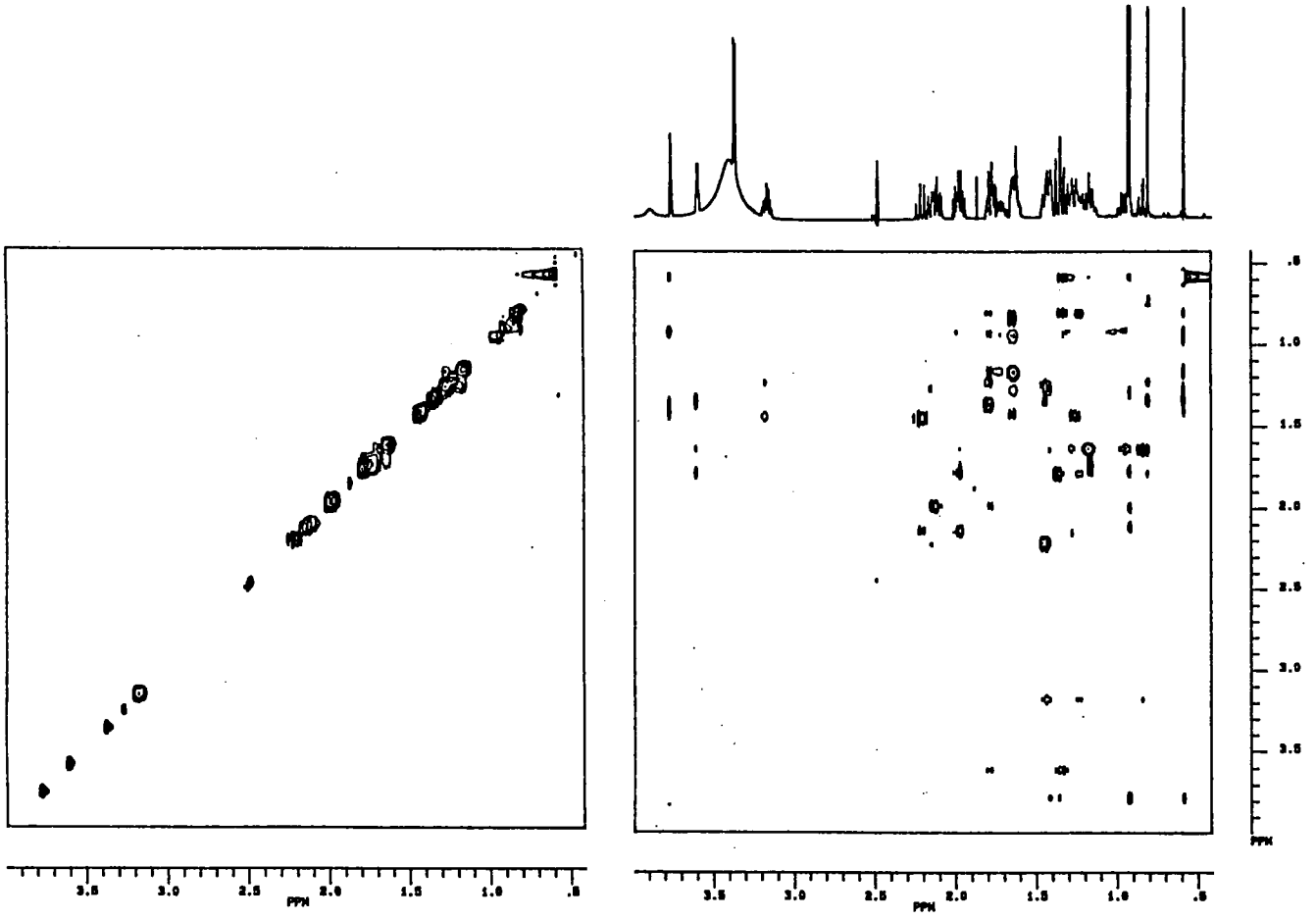
remove phase distortions in the spectrum. Shown in the figure is the result of using this scheme on the steroidal compound in DMSO-d_6 at 40°C. The total spin lock time was 300 ms and the data was processed in the standard 2-D hypercomplex format. The carrier was positioned in the downfield spectral region as suggested by Bax[1], et.al. to minimize undesirable cross peaks in phase with the diagonal due to Hartmann-Hahn transfers. Clearly, the data is quite good and cross peaks due to Hartmann-Hahn couplings are absent. I am currently further examining the relationship of this spin lock scheme and carrier positioning on Hartmann-Hahn peak intensity.

Sincerely yours,

Michael G. Zagorski

Michael G. Zagorski

Reference
(1) Bax, A.; Davis, D.G. J. Magn. Reson. 1985, 63, 207-213.
(2) Bothner-By, A.A.,; Stephens, R.L.; Lee, J.; Warren, C.D.; Jeanloz, R.W. J. Am. Chem. Soc. 1984, 106, 811-813.
(3) Contact Mike Gekel or Henry Luhrs, Bruker Instruments, for details about this upgrade.



Michigan Technological University

Houghton, Michigan 49931

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

December 1, 1987
(received 12/5/87)

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

Fixed Capacitors for low temperatures

Dear Professor Shapiro,

In the not too distant past I have used Sprague series 10TCC NPO ceramic disc capacitors for temperatures down to 4K. While this is well outside the specifications for these capacitors, they worked well and the capacitance changed little below 77K. A few years ago, however, the coating was changed from a dull orange phenolic dip ("Durez") to a shiny orange epoxy. The epoxy coating evidently has a significantly different thermal expansion coefficient as the newer capacitors frequently will split at lower temperatures.

A phone call to Sprague sent me to a company called Cera-mite (who actually make the capacitors) and they suggested two possible solutions.

1. They will run a special batch with the old coating at $150 per line item. That is, roughly 1000 capacitors of each value desired. The major advantages of these capacitors are their low cost and spectrum of values available (particularly from 1 to 10pF), and hence this solution does not seem particularly useful for a single small user.

2. They told me that the epoxy coating can be removed and the capacitor either used bare or with a coating of your own choice. One simply gently heats the capacitors in a bath of the oily solvent called "M-pyrol" (N-methyl-2-Pyrrolidone manufactured by GAF) to about 90°-100°C for an hour or two. Then rinse the capacitors in distilled water. I have tried this and it does indeed work. I used a water bath on a hot plate in a fume hood. The only problem one might have is obtaining the solvent in small quantities. Our chemistry storeroom just happened to have some in their "used chemical supplies" but it is not a regularly stocked item.

Sincerely,

BH Suits

Bryan H. Suits
Assistant Professor
Department of Physics

BHS/krc

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Minneapolis, Minnesota 55455

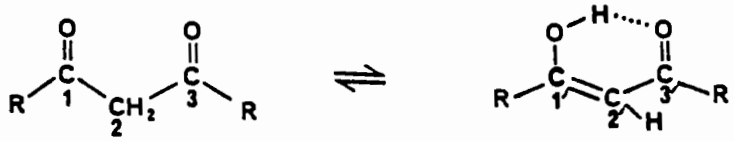
December 9, 1987
(received 12/12/87)

Professor Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 94303

Title: ^{13}C CP/MAS NMR of ß-Di- and Triketo Compounds

Dear Dr. Shapiro:

We are studying the ^{13}C CP/MAS NMR spectra of symmetrically substituted ß-di- and tri-ketomethanes with special interest in using the isotropic ^{13}C chemical shift values (σ) as indicators of tautomeric structures and asymmetry in the local environment of multiple carbonyl groups. These compounds are particularly well suited for solid-state studies since rapid keto-enol tautomeric equilibrium in solution causes the carbonyl carbons to be averaged, so C(1) and C(3) can not be studied independently in solution.



Also, in solution, C(1) and C(3) are always equivalent if the structure is keto, while in the solid-state C(1) and C(3) keto carbons can have different environments giving rise to resolvable ^{13}C peaks.

In this letter , we report anomalously large ^{13}C CP/MAS NMR $\Delta\sigma_{C(1)-C(3)}$ values found for 2-ethyl- and 2-methyl-1,3-diphenyl- 1,3-propanedione (I) and (II) respectively, which exist in the solid state in the keto form.[1,2] These $\Delta\sigma$ values of 5.65 and 6.06 ppm respectively are compared to $\Delta\sigma_{C(1)-C(3)}$ values of 1.2 ppm for indanedione (III) and 2.43 ppm for Meldrum's acid (IV) both of which exist in the keto form in the solid state.[3,4] Previously we had found that a $\Delta\sigma_{C(1)-C(3)}$ range of 5-25 ppm was expected for these compounds (V) and (VI) in their enolic forms, and that solid-state asymmetric packing forces accounted only for $\Delta\sigma$ values less than 3 ppm.

It is not immediately clear from the crystal structure of I why its $\Delta\sigma$ value should be so large. It may be that a C-H···O intermolecular interaction exists between the α-H and one of the carbonyl oxygens. We are doing further

studies of this and related compounds to examine this possibility.

We also show here the spectrum of tribenzoylmethane, which has a $\Delta\sigma$ value of 0.0. We have been unable to solve the crystal structure of this compound due to poor crystal quality, but we did determine that it has a trigonal unit cell, and that the crystals themselves have trigonal morphology. The ^{13}C CP/MAS NMR spectrum show that the chemical environments of the three carbonyl groups are nearly if not precisely equivalent and that the molecule itself may have trigonal symmetry. In the absence of a crystal structure analysis, we have thus been able to extract crystallographic information from the ^{13}C CP/MAS NMR spectrum of VII.

Sincerely,

Margaret C. Etter

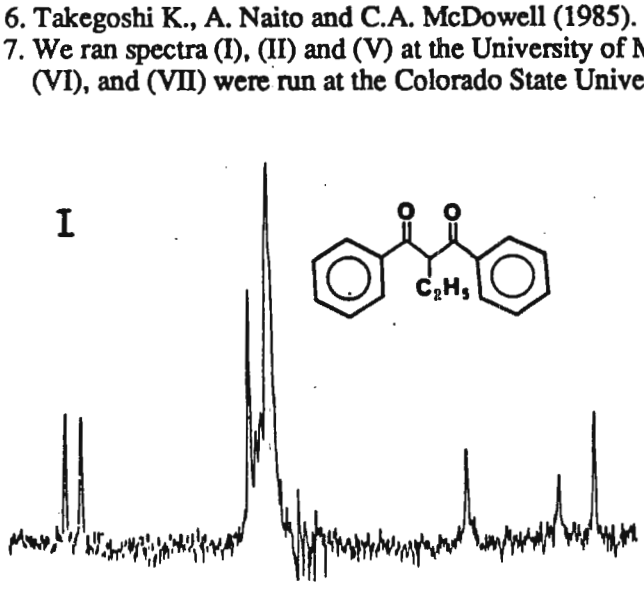
Margaret C. Etter
Associate Professor of Chemistry

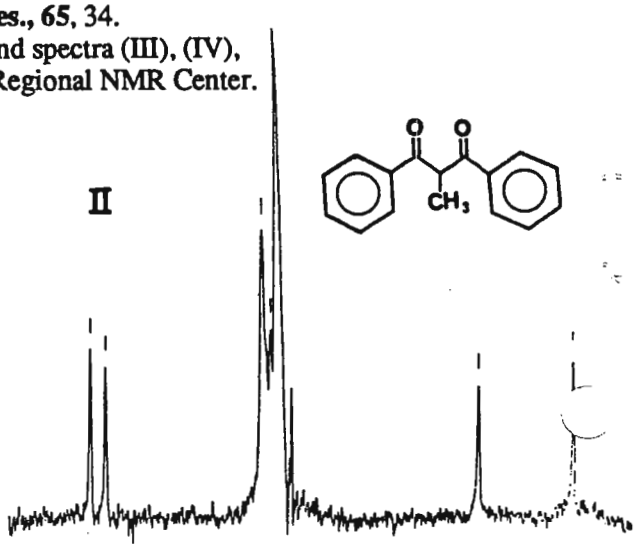
Gail M. Vojta

Gail M. Vojta

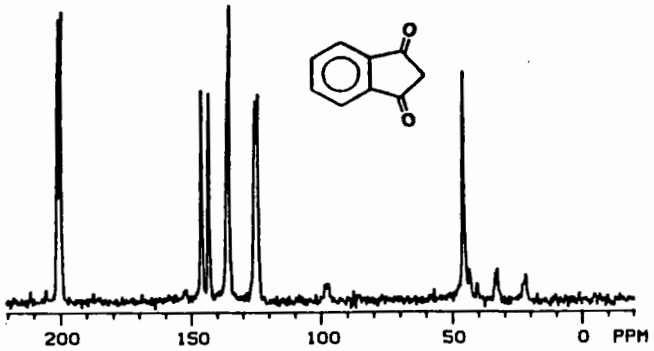
Please credit Stephen Philson's account.
cc: Stephen Philson, U. of MN
Jim Frye, Colorado State University

1. Mullica D.F., J. W. Karban and D.A Grossie (1987). **Acta. Crystallogr.**, C43, 601. Crystal structure of 2-ethyl-1,3-diphenyl-1,3-propanedione.
2. No crystal structure has been done on the methyl derivative; however, the chemical shift at 49.8 ppm for C(2) indicates that this carbon is a methine group, so it must be in the keto form.
3. Bravic G., F. Bechtel, J. Gaultier and C. Hauw (1976). **Cryst. Struct. Comm., 5,** 1.
4. Takegoshi K. and C.A. McDowell (1986). **J. Am. Chem. Soc., 108,** 6852.
5. Imashiro F., S. Maeda, K. Takegoshi, T. Terao and A. Saika (1982). **Chem Phys. Lett., 92,** 642.
6. Takegoshi K., A. Naito and C.A. McDowell (1985). **J. Magn. Res., 65,** 34.
7. We ran spectra (I), (II) and (V) at the University of Minnesota, and spectra (III), (IV), (VI), and (VII) were run at the Colorado State University-NSF Regional NMR Center.

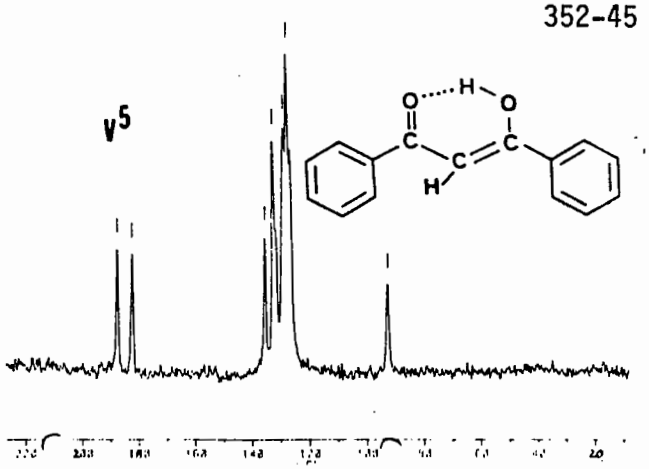




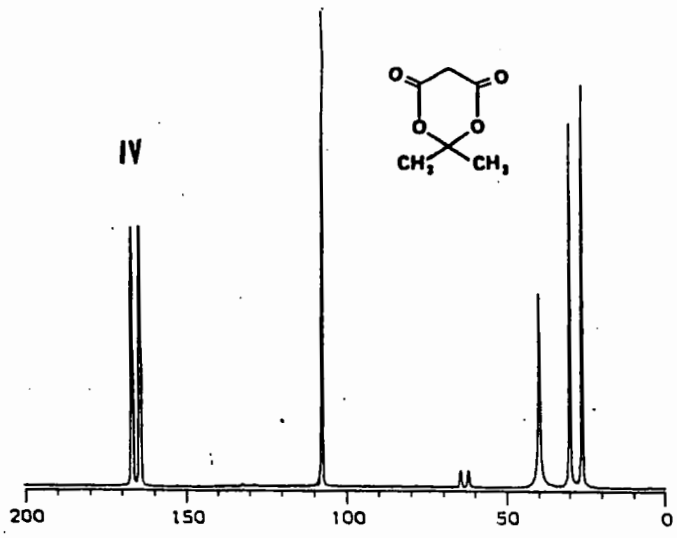
III



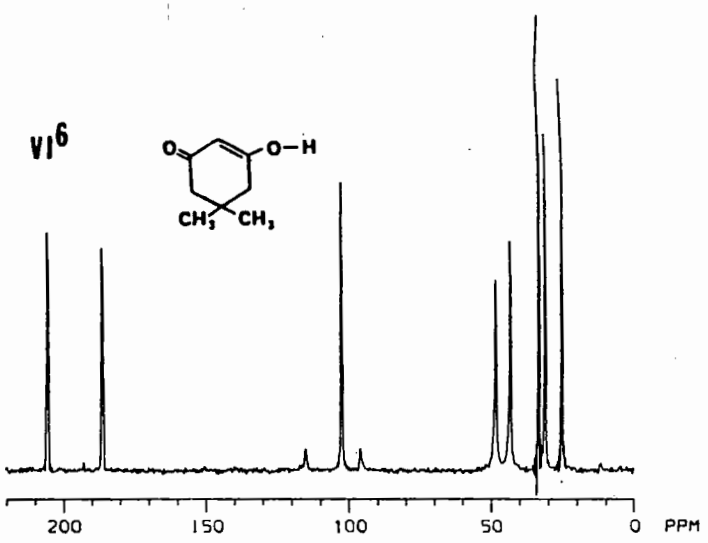
V[5]



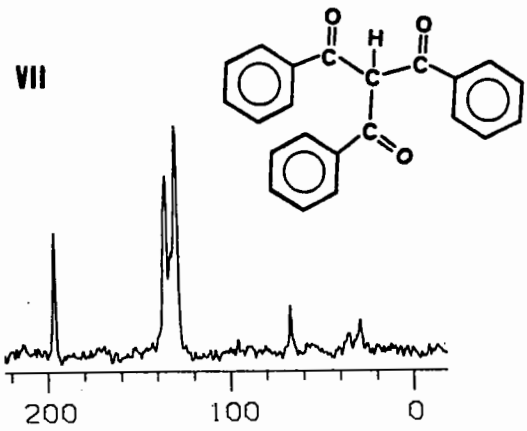
IV



VI[6]



VII



PURDUE UNIVERSITY

SCHOOL OF SCIENCE
at INDIANAPOLIS

PHYSICS DEPARTMENT
1125 East 38th Street
P.O. Box 647
Indianapolis, Indiana 46223
(317) 274-6900

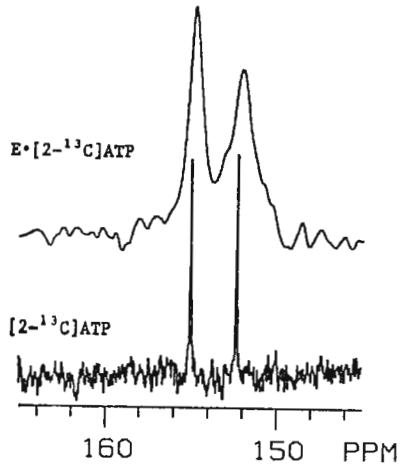
December 2, 1987
(received 12/4/87)

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

DIFFERENTIAL BROADENING REVISITED: POSITION AVAILABLE

Dear Barry:

Thank you for your pink reminder. Some time ago Dr. Bruce Ray working in my laboratory, ran the ^{13}C NMR of [2-^{13}C]-ATP bound to 3-phosphoglycerate kinase. (The labelled substrate was synthesized with the help of Dr. Wilmer Fife of our Chemistry Department.) The proton coupled doublet in the free and enzyme-bound forms is shown in the figure. The differential broadening of the doublet in E•ATP arises from the well-known interference between ^{13}C chemical shift anisotropy (CSA) and ^{13}C-^{1}H dipolar interaction. We have confirmed this by the field dependence of the observed broadening.



The history of the differential broadening arising from the interference effect make interesting reading. The effect was first calculated by Hiroshi Shimizu (J. Chem. Phys. 40, 3357 (1964)) in analogy with well-established results in ESR. This was the time when a Varian 60 MHz spectrometer represented the state of the art and CSA did not figure seriously as a relaxation mechanism. Although some people were thinking about the interference effects in general, observation of the CSA-dipolar interference began to occur frequently only after high-field spectrometers became common.Somewhere along the line, Shimizu's work appear to have been forgotten. Goldman (J. Mag. Res. 60, 437 (1984)), apparently unaware of Shimizu's paper, presented a closely-related reformulation of the problem. (Shimizu considered an axially symmetric CSA tensor. Goldman derived the equations for the case of a general anisotropy as well.) Recent papers by Farrar (e.g., J. Am. Chem. Soc. 108 8190 (1986)) recall Shimizu's original contribution (as did Withers *et. al*, J. Mag. Res. 61, 545 (1985)). Unfortunately, however, Farrar's paper contained a number of errors. If his expressions for linewidth are used as given, they will lead to the anomalous result that the linewidth exclusively due to CSA (not due to interference terms) depends on the angle between the dipolar vector and the symmetry axis of the CSA tensor! We killed at least a couple of weeks muddling through the theory given by different people. I think we have managed to clear up the confusion.

We are now scratching our heads to see if we can learn something about the binding site of

ATP on the enzyme by an analysis of this interference effect. If we can find any useful information, TAMU will hear about it.

Sincerely yours,

Durga

B. D. Nageswara Rao
Professor of Physics

P.S. Position Available. A postdoctoral position is immediately available for applying NMR and EPR techniques to explore structure-function relationships in the matalloenzyme alcohol dehydrogenase (ADH). This is a multidisciplinary project involving myself, Barry Muhoberac (Chemistry) and Bill Bosron (Biochemistry). Bill Bosron's group have succeeded in cloning and over-expressing rat, mouse and human ADH in *E. Coli*. Site-directed mutagenesis of the enzyme is being done. Multinuclear (^{31}P, ^{13}C, ^{15}N and ^{1}H) NMR (using a Nicolet 300 MHz machine) and spin-label ESR (using a Bruker X-band machine) experiments are planned. The appointment will be initially for one year and can be renewed for two additional years based on mutual agreement. Salary is negotiable and will be funded by a NIAAA training grant and the recently funded NIAAA Alcohol Research Center at the Medical School in our University. Ph.D.'s with experience in using NMR/ESR spectroscopy and a good background in biochemistry/biophysics are encouraged to apply. Those interested may please contact me ((317) 274-6897) or Barry Muhoberac ((317) 274-6885) in our Chemistry Department.

THE UNIVERSITY OF MANITOBA DEPARTMENT OF CHEMISTRY Winnipeg, Manitoba
Canada R3T 2N2

December 02, 1987 (received 12/9/87)

Dr. Bernard L. Shapiro
966 Elsinore Court
Palo Alto, CA
94303 U.S.A.

Dear Barry,

A bit of whimsey with apologies to J. Dryden; Zee before Eee.

In classic days, e'r 2-D specs were in
Before 1-D became a sin,
When sharp on sharper multiplied our lines;
E'r blobs on blobs were, cursedly, designs...
Then, oh what joy it was, at heart,
With vigorous warmth to, variously, impart
To peaks and valleys, jumbled (grains of sand),
A set of J's and shifts throughout the band.

Now, double, double beats the drum:
Rotate the axes, shift the sum;
Do not, for Pete's sake, undercut
This contour, or you'll miss, you slut.

Enough of that, you will be saying, and I agree. So, I'll proceed in the usual broken English.

The spectra on the diagram (no need to say, they are 1-D) arise from lonely protons in some phenyl esters made from somebody's aunt's acid. The bit in A should be ignored, it's explanation's sure to leave you bored. However, that in B evinces carnal knowledge of protons five, six and seven bonds removed. The other parts display the proof, experimental and theoretical, that all is postive and true, though small (one part in twenty is the one). It seems that, were it flat, this molecule would render little, littler yet. In short, the fullish adumbrations (one hopes to publish in Can. J. Chem.), tell you its zed* and, furthermore, the twist** of zed, its depth and width.

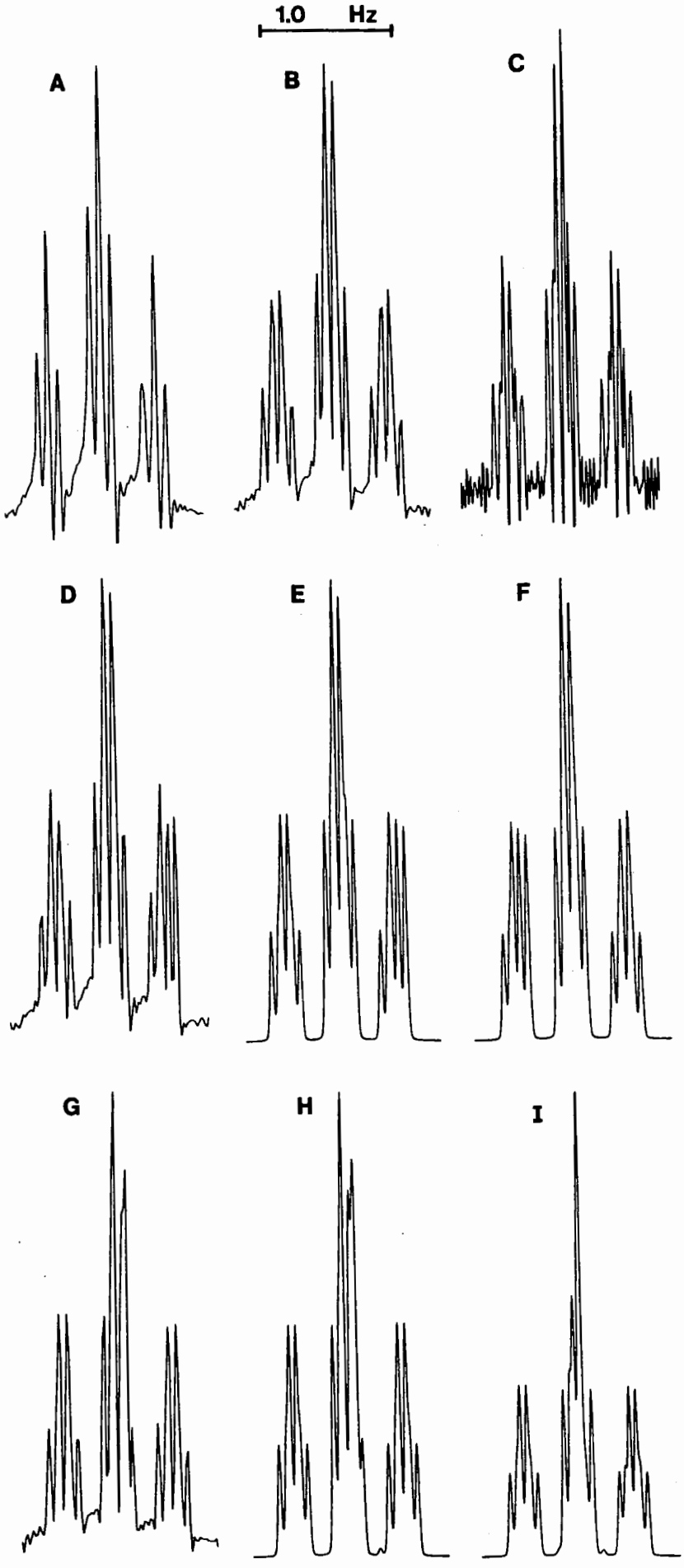
So, Barry, note: this information on the zed is meant to cancel out all red; and of course to wish you all the best at your abode out in that west.

Yours sincerely,

Ted

Ted Schaefer

* Read as zee below the 49th parallel
** A twist of about 60° at 300K about the C (phenyl) -O bond


1.0 Hz
A
B
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H
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CONSIGLIO NAZIONALE DELLE RICERCHE

ISTITUTO DI CHIMICA DELLE MACROMOLECOLE
20133 MILANO - VIA E. BASSINI, 15
TEL. (02) 26.66.071 - 26.63.604 - 23.88.93 - 26.64.378 - 29.28.93 - 23.53.10

3rd December, 1987
(received 12/12/87)

Professor B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, California 90303

photo-CIDNP NMR in Milano

Dear Professor Shapiro:

The present is to announce the opening of the first Italian Facility for photo-CIDNP NMR spectroscopy.

Last week we were finally able to connect our 270 MHz Bruker spectrometer to the Spectra Physics Argon Laser 171 located in a laboratory across the courtyard, via a fiber-optic cable fifty meter long. A second cable, which carries the triggering signal for a mechanical shutter, runs together with the fiber. Despite the distance, the light which hits the sample is still sufficient to produce an acceptable good photo-CIDNP spectrum in standard conditions, as shown in the figure. Actually, the insert shows that it is possible to observe the photo-CIDNP effect on single transitions, as those forming the 5,6,7,8 quartet in the A_2B_2 spin system of the para-disubstituted benzene ring.

The probe is a standard 5 mm proton probe, in which the beam from the fiber-optic cable is reflected by a prism through the loops of the radiofrequency coil, as often described previously. The diameter of the fibers is 600 microns.

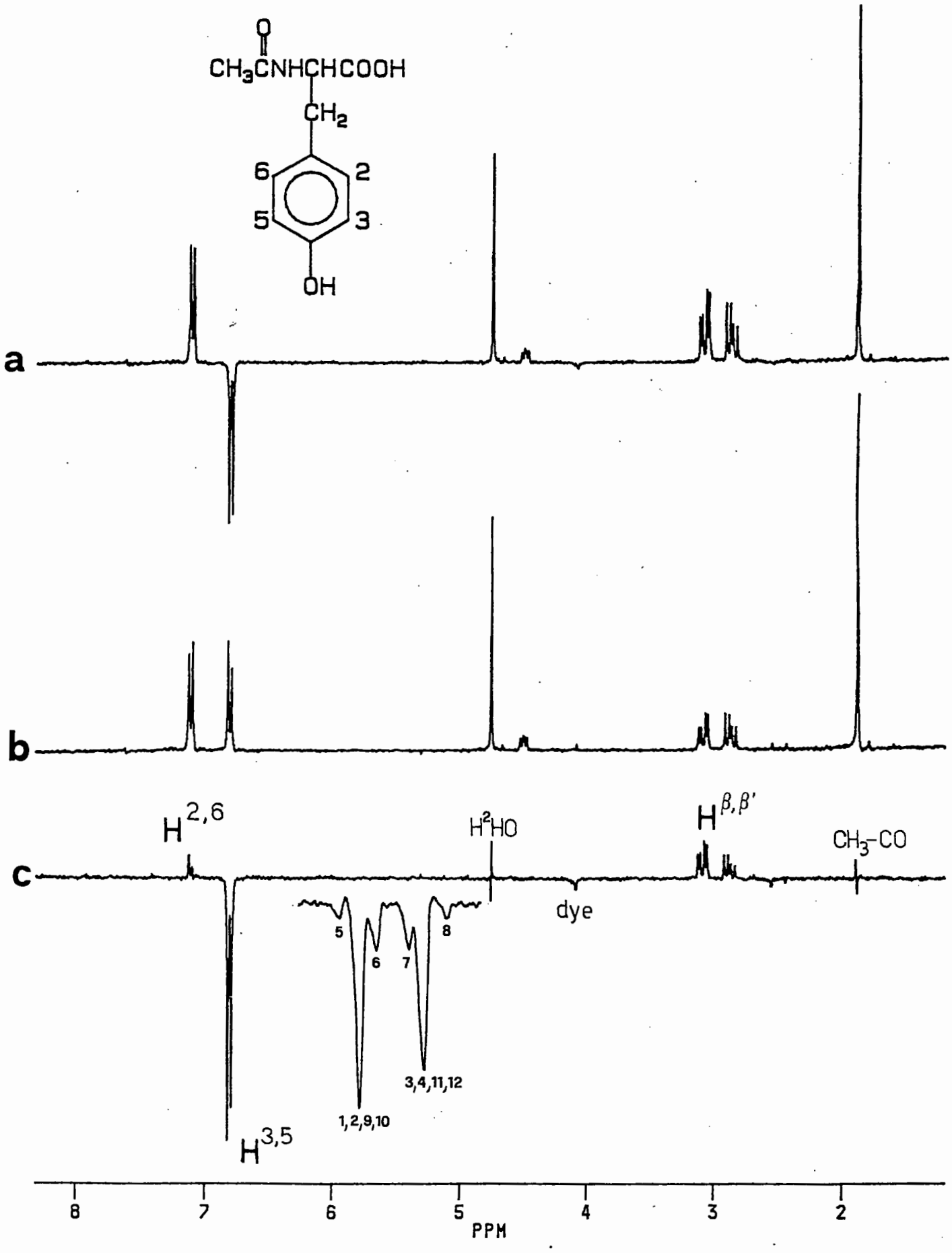
Since our spectrometer is an SY version, for which no output line is available to control an external device, in order to produce the pulse required to trigger the shutter for the laser light, the cable was connected to the BB/CW modulator in the decoupler unit. The switching on and off was then simply piloted by the two microprogram commands (1) D1 BB DO (2) D2 CW DO, where D1 is the irradiation time and D2 is a few milliseconds. This enables concomitant use of the decoupler channel in HG or HD mode to saturate a solvent line between scans or to perform a homonuclear decoupling during acquisition, which may help the interpretation of the photo-CIDNP spectrum [1].

We are extremely grateful to Klaas Dijkstra (University of Groningen), who built the experimental set-up, and to prof. Robert Kaptein (University of Utrecht), for having introduced us to the many capabilities of this technique through several years of fruitful collaboration.

[1] L. Zetta, A. De Marco, G. Casiraghi, M. Cornia and R. Kaptein (1985) Macromolecules 18, 1095-1100.

Lucia Zetta Roberto Consonni Antonio De Marco

Figure caption: 270 MHz photo-CIDNP NMR spectra of a solution of 10 mM acetyltyrosine and 0.4 mM 3-N-carboxymethyllumiflavin in ^2H_2O, 1 scan; (a) "light" spectrum, (b) "dark" spectrum, (c) difference (a)-(b). The insert to (c) shows a horizontal expansion of the $H^{3,5}$ multiplet, after the application of a gaussian window to the FID, in which the resolved transitions are indicated. The laser power at the beginning of the optical pathway was 4 watts (multiline); the laser pulse was 0.5 s.


CH3CNHCHCOOH
CH2
6
2
5
3
OH
a
b
c
H2,6
H2HO
Hβ,β'
CH3-CO
dye
5
6
7
8
1,2,9,10
3,4,11,12
H3,5
8
7
6
5
4
3
2
PPM

UNIVERSITY OF FLORIDA - NMR or Mass Spec Research Scientist to join Chemistry Department MS/NMR Facility as a permanent staff member. Responsibilities will involve providing NMR or MS services, including training and supervising users, running specialized samples, consulting with users in experimental design and spectral interpretation, overseeing maintenance, and collaborating with users as well as other research groups active in MS or NMR. Departmental instrumentation includes XL-200, VXR-300, and NT-300 multinuclear NMR's and Kratos MS30 and Finnigan 4515 MS's. Required is a Ph.D. in Chemistry or a related discipline, or equivalent experience in modern MS or NMR instrumentation and applications. Send resume and arrange to have three letters of recommendation sent by January 30, 1988 to Richard A. Yost, University of Florida, Chemistry Department, Gainesville, FL 32611. EO/AA Employer.

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO — SANTA BARBARA • SANTA CRUZ

December 15, 1987

University of California Service
Veterans Administration Medical Center
4150 Clement Street (11D)
San Francisco, California 94121
(415) 750-2146

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

RE: Position Available for Associate Professor of Radiology in Residence

Dear Dr. Shapiro:

A position is available for an Associate Professor of Radiology in Residence in the Magnetic Resonance Unit at the Veterans Administration Medical Center, Department of Radiology, University of California, San Francisco. This individual should be recognized as an international authority in the development, implementation, optimization, and evaluation of new hardware and software techniques for in vivo magnetic resonance imaging, magnetic resonance spectroscopy, and especially spectroscopic imaging.

Sincerely,

MICHAEL W. WEINER, M.D.
Associate Professor of Medicine and Radiology

MWW/let

DUPONT
ESTABLISHED 1802
E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
WILMINGTON, DELAWARE 19898

CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
EXPERIMENTAL STATION

E. I. DuPont de Nemours & Co., Inc.
Central Research and
Development Department
Experimental Station, Bldg. 328
Wilmington, DE 19898
1987 December 5
(received 12/11/87)

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

Asymmetry Parameter Transformations

Dear Dr. Shapiro,

This modest missive contains only some simple algebra. It might save some time for anyone interested in solid-state NMR lineshapes, particularly those interesting in fitting powder patterns.

Each anisotropic interaction in NMR is readily expressed in the form of a second-rank tensor, **R**. Each has a principle axis system in which it is diagonal. Its diagonal components are R_{xx}, R_{yy} and R_{zz}.

It's handy to define a little guy called the asymmetry parameter, η. He allows the number of variables to be reduced by one, and leads to a simpler form for the Hamiltonian. η arises naturally in the quadrupole interaction[1], because the electric field gradient tensor is traceless by virtue of the LaPlace equation ($R_{xx} + R_{yy} + R_{zz} = 0$). If one expresses the elements of the chemical shift tensor relative to its isotropic shift, this condition also holds[2]. The same is true of indirect (**J**) coupling.

An asymmetry parameter η' is then defined as

$$\eta' = (R_{xx} - R_{yy}) / R_{zz}.$$

The traditional, hallowed and time-honored definition of the asymmetry parameter η, oft-seen haunting Hamiltonians, is obtained if we further select the principle axes such that

$$|R_{zz}| \geq |R_{yy}| \geq |R_{xx}|, \text{ and } \eta = \eta', \text{ then } 0 \leq \eta \leq 1.$$

Now we can express our Hamiltonian in terms of only two variables (R_{zz} and η) instead of three (R_{xx}, R_{yy} and R_{zz}).

The whole point of this note is "what happens if this inequality is violated?" In other words, what if we arbitrarily interchange the axes? This leads to $\eta' < 0$ or $\eta' > 1$. But we can still compute the "traditional" η directly from the apparent η' by a simple transformation.

There are six possible cases depending on the relative magnitudes of R_{xx}, R_{yy} and R_{zz} (or, equivalently, depending on the value of η') . . .

(1) if $|R_{xx}| > |R_{yy}| \geq |R_{zz}|$ or $-\infty \leq \eta' < -3$ then $\eta = (\eta'+3)/(\eta'-1)$

(2) if $|R_{xx}| \geq |R_{zz}| > |R_{yy}|$ or $-3 \leq \eta' < -1$ then $\eta = (\eta'+3)/(-\eta'+1)$

(3) if $|R_{zz}| \geq |R_{xx}| > |R_{yy}|$ or $-1 \leq \eta' < 0$ then $\eta = -\eta'$

(4) if $|R_{zz}| \geq |R_{yy}| \geq |R_{xx}|$ or $0 \leq \eta' \leq 1$ then $\eta = \eta'$

(5) if $|R_{yy}| > |R_{zz}| \geq |R_{xx}|$ or $1 < \eta' \leq 3$ then $\eta = (-\eta'+3)/(\eta'+1)$

(6) if $|R_{yy}| > |R_{xx}| \geq |R_{zz}|$ or $3 < \eta' \leq \infty$ then $\eta = (-\eta'+3)/(-\eta'-1)$

(These are easily derived by a bit of algebra, but I haven't seen these transformations stated elsewhere. I have a nagging suspicion that someone has known them since the days of Decartes. Had I taken a few more math courses, I might have known them as well!)

Why, you may well ask, would anybody give a care about such simple transformations? They can come in very handy in our pragmatic age of "discrete mathematics". To fit a solid-state NMR powder pattern, one needs to vary η'. Any unconstrained least-squares fitting machine will check values of η' outside of the range 0 to 1, as it knows not η' from η. To keep your Hamiltonians happy, you'd have to artificially constrain the fit by applying some arbitrary punishment (*ugh!*) for venturing outside of the limits $0 \leq \eta' \leq 1$. What these transformations allow you to do instead is to easily compute the correct η and the correct lineshape, without a constraint.

In a numerical simulation of the powder pattern, efficient use can be made of computer time if the ratio of number of steps in the Euler angle ϕ (ϕ=0 on x) to the number of steps in θ (θ=0 on z) is chosen to be $\sqrt{\eta}$.

Using these tricks, one can more easily fit solid-state NMR spectra exhibiting chemical shift[3] or quadrupole[4] interactions, with or without magic-angle spinning. The program **FTNMR**[5], written by that maestro of robust NMR processing, **Dennis Hare**, can now iteratively fit any of these lineshapes, in addition to any combination of Lorentzian, Gaussian or Voigt lineshapes. A couple of pictures are attached.

Best wishes[6],

Rod Farlee

Rod Farlee

[1] Das, Hahn, Solid State Physics, 1958, Suppl. 1.

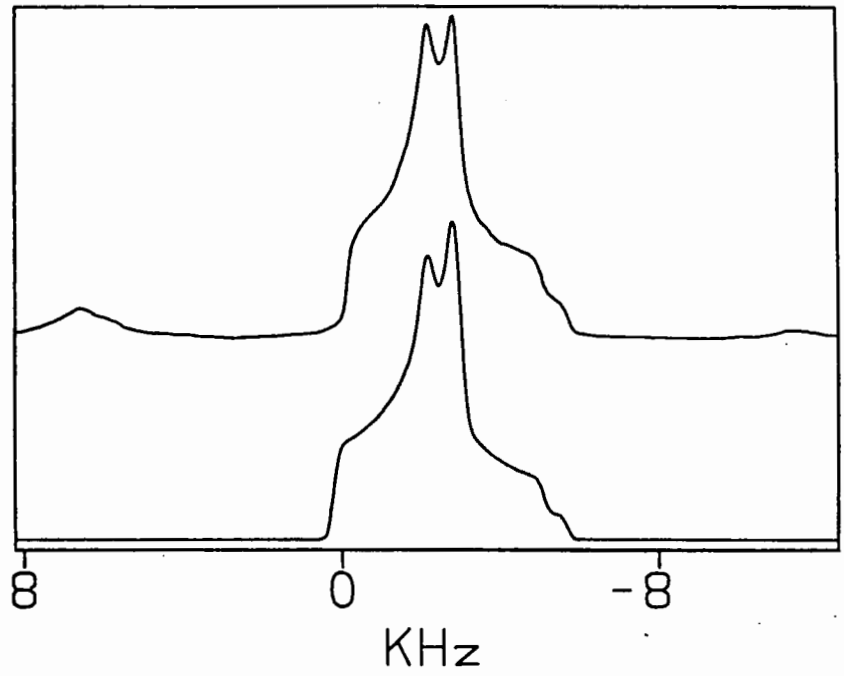
[2] Haeberlen, Adv Magn Reson, 1976, Suppl. 1, p. 9.

[3] it can be shown that transformation (2) also applies directly to Alan Berger's parameter ρ, which is a measure of the chemical shift asymmetry during MAS, in his program SQUARE. Herzfeld, Berger, J Chem Phys, 1980, **73**, 6021.

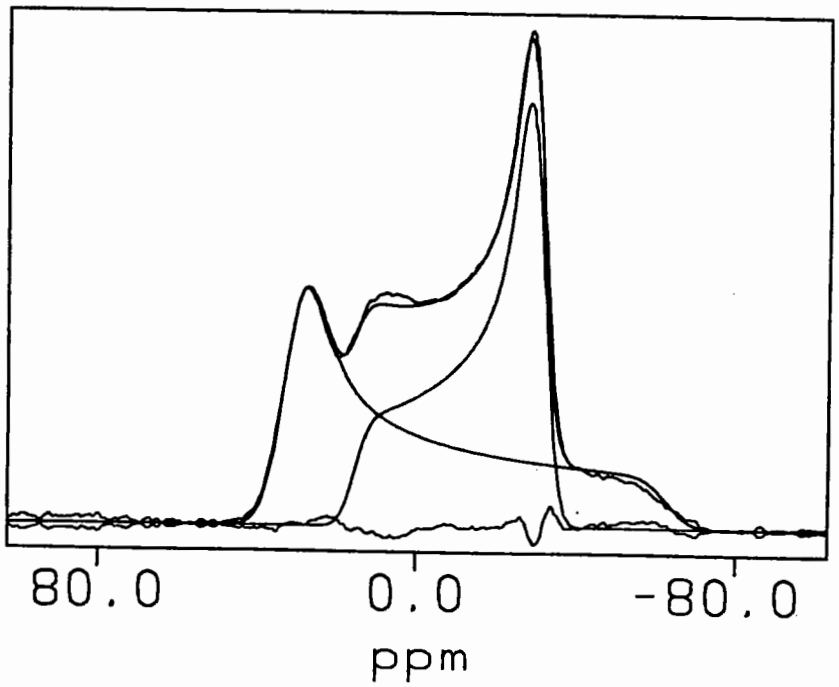
[4] Taylor, Baugher, Kriz, Chem Rev, 1975, **75**, 203; Kundla, Samosan, Lippmaa, Chem Phys Lett, 1981, **83**, 229.

[5] M-R Resources, P.O. Box 642, Ashburnham, MA 01430.

[6] may the tiresome climate of Palo Alto relent, and give you a white Christmas!



Na-23 MAS spectrum of sodium oxalate -
top: experimental (5 mm Doty probe, 8.8 kHz spin rate, 7 T., 79.4 MHz),
bottom: FTNMR fit (e^2qQ/h = 3.6 MHz, η = 0.77, δ_{iso} = -14 ppm vs NaCl)



P-31 NMR nonspin spectrum of Keggin salt $Na_{12}W_{15}P_2O_{56}.xH_2O$,
overlay plot of -
- experimental (7 T., 121.4 MHz),
- FTNMR fit to $O=P(OW)_3$ site

(δ_{11}, δ_{22}, δ_{33} = +31, +31, -63 ppm, area 1.0, FWHH 12 ppm Gaussian),
- fit to $P(OW)_4$ site (+15, -31, -31 ppm, area 1.0, FWHH 8 ppm Gaussian),
- sum of both fits to both sites, and residual.

Olin
RESEARCH CENTER
350 KNOTTER DRIVE, P.O. BOX 586
CHESHIRE, CT 06410-0586
(203) 271-4000

November 19, 1987
(received 12/18/87)

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

Subject: Modifying Bruker's BSV-3 Broadband Amplifier for Indirect Detection

Dear Dr. Shapiro:

A number of methods have been recently published which involve pulsing X-nuclei with subsequent detection of ^{1}H resonances (1-3). The simplest of these is the reverse H-X correlation technique shown in Fig. 1. Bruker's BSV-3 broadband amplifier when used with their spectrometers gives the spectroscopist a limited capability to perform these techniques. However, the amplifier cannot be switched from the continuous wave mode (for pulsing) to the broadband mode (for decoupling) by computer. Therefore, one cannot pulse and decouple in the same sequence. Also, the power levels are not computer controlled, so the user cannot attenuate the r.f. level for broadband decoupling. We describe two simple modifications to the BSV-3 to address these problems.

Fig. 2 shows the installation of a digital controlled switch in the broadband modulation unit for alternating between continuous wave and broadband modes. The switch terminals of the AD7510 (pins 11,12,15,16) were connected to the front panel switches of the broadband modulation unit. The digital broadband signal was taken from connection 27 of the Homo-Hetero decoupling unit in the spectrometer console (on-off commutation section).

To change power levels when switching to the broadband mode, the circuit shown in Fig. 3 was added to the attenuator section of the BSV-3. The connection between the collector of T5 and the resistor at the base of T8 was broken. The spf2b input to the base of T5 was also disconnected and two AND gates were installed. The inverse broadband signal was taken from Q1 of Fig. 2. The pulsing power could then be controlled by the variable resistance switch and the decoupling power by the potentiometer situated at the bottom of the attenuator unit.

Fig. 4 is an ^{15}N Indirect Detection 2D spectrum of formamide taken with the sequence of Fig. 1 at 200 MHz. The ^{15}N shift of 110 ppm. is seen on the F1. The fully ^{15}N decoupled syn and anti proton resonances are displayed along F2.

Very truly yours,

Gary P. Juneau

William T. Lefebvre

GPJ/WTL/skp
Attachments

1. A. Bax, S. Subramanian, J. Magn. Reson., 67, 565 (1986).
2. A. Bax, M. Summers, J. Am. Chem. Soc., 108, 2093 (1986).
3. L. Lerner, A. Bax, J. Magn. Reson., 69, 375 (1986).

FIGURE 1
PULSE SEQUENCE FOR INDIRECT DETECTION

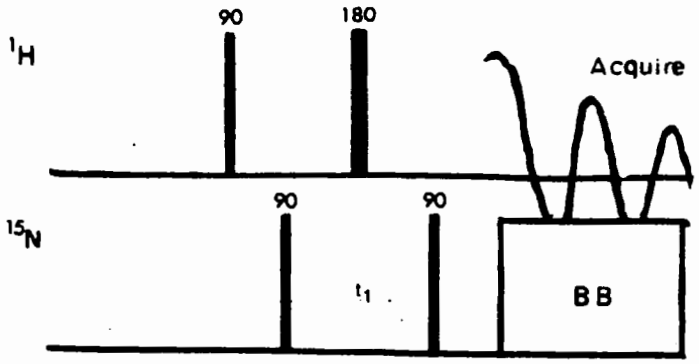


FIGURE 2
BROADBAND MODULATION CIRCUITRY

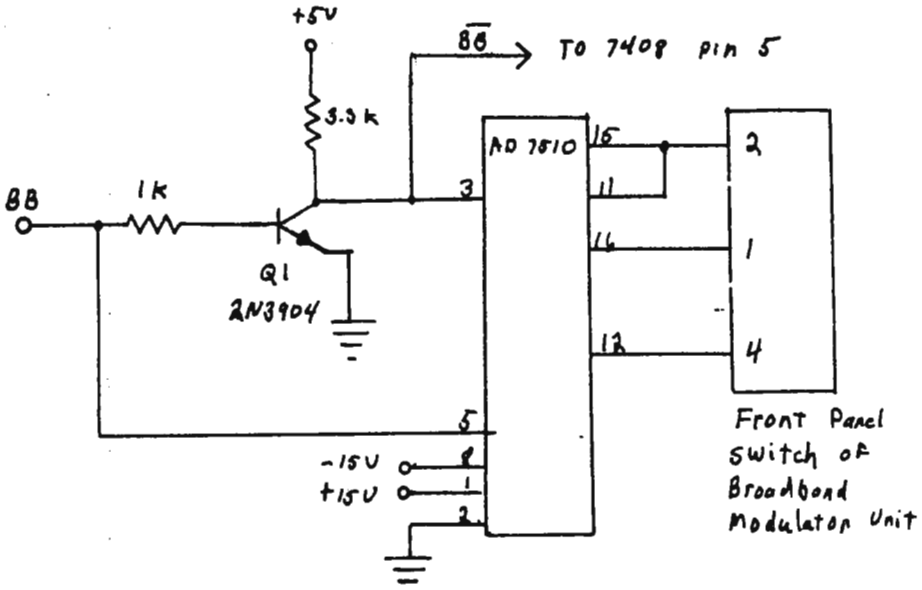


FIGURE 3
ATTENUATION CIRCUITRY

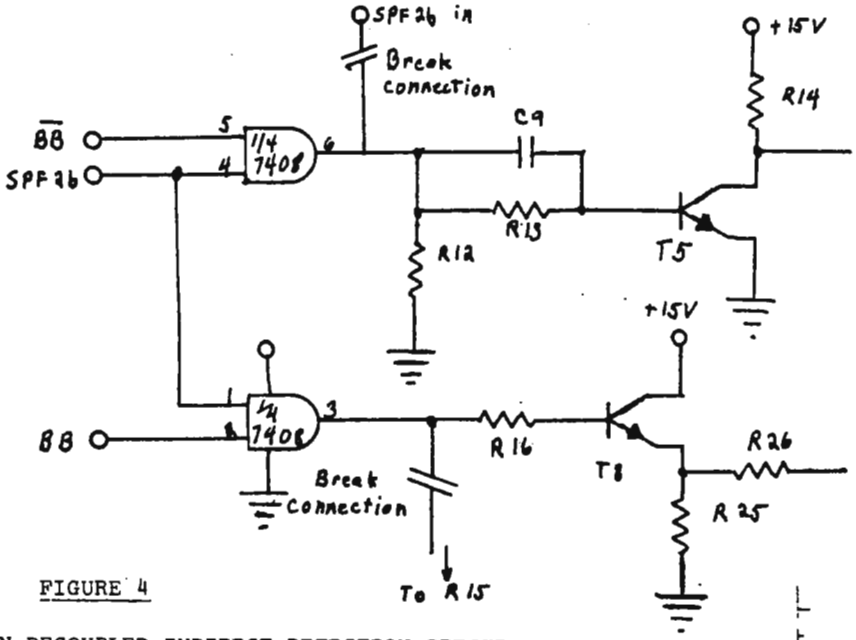
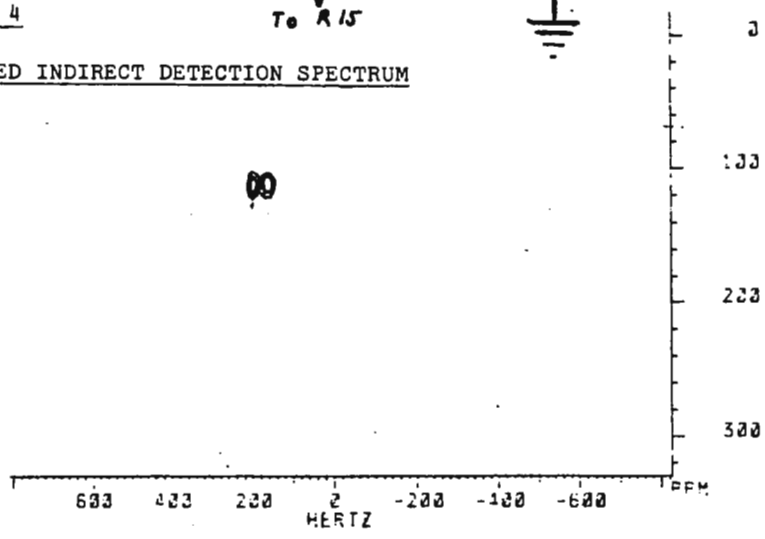


FIGURE 4
^{15}N DECOUPLED INDIRECT DETECTION SPECTRUM



FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

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NIJMEGEN
NEDERLAND

Toernooiveld
6525 ED Nijmegen
Telefoon (080) 55 88 33
Telex 4 82 28 winat nl
Telecopier (080) 553450
Afdeling

Dr. Bernard L. Shapiro
Tamu NMR Newsletter
966 Elsinore Court
PALO ALTO, California
U.S.A.

Uw kenmerk	Uw brief van	Ons kenmerk	Datum
Onderwerp		871360/CWH/bk	November 25, 1987 (received 12/1/87)

The Use of Spinlabeled Oligonucleotides for mapping the binding-groove of the DNA-binding protein of the phage IKe.

Dear Professor Shapiro,

IKe gene-5 protein is a ssDNA binding protein encoded by the filamenteous phage IKe. We have performed structural studies on this protein by means of 2D NMR in which homonuclear Hartman Hahn COSY played a crucial role. An almost complete spinsystem analysis was obtained for the residues of the so-called DNA binding wing. The wing, comprising residues 16 to 30, consists of a regular β-sheet and a four residue turn (fig. 1a). Its configuration could be derived from sequential NOEs as well as interchain NOE contacts. Its DNA binding properties were studied by applying deoxyadenylic acids with TEMPO-spinlabels covalently linked to their 3'- and/or 5'-ends (fig. 1b). After binding to the gene-5 protein these spinlabeled oligonucleotides selectively broaden those resonances which are present in the DNA-binding groove. Because bound oligodeoxyadenylic acid is rapidly exchanging with free ligand the full broadening effect can even be observed at very low oligonucleotide concentrations so that only a minor shift of the resonances occurs. The absence of shifting resonances enables visualisation of broadening effects in 1D- and 2D-difference spectroscopy. A representative example of the selectivity of these perturbations is shown in fig. 2: even the connectivities of a long side chain residue such as isoleucine are completely resolved in the 2D-difference representation. The spinlabel-induced perturbations can also be represented in relative-difference representations in which procentual effects are presented. This presentation enables direct correlation of

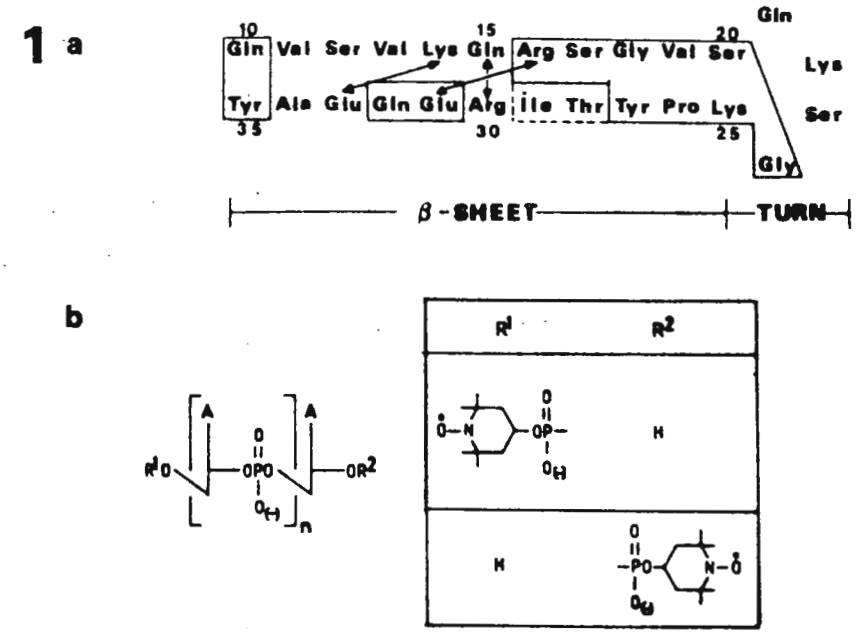

Figure 1: a) Schematic representation of the DNA binding wing of the IKe gen-5 protein as derived by means of 2D-NMR spectroscopy (see text). b) Structure of the TEMPO-spinlabel and scheme of its attachment to the oligonucleotides used in the NMR studies.

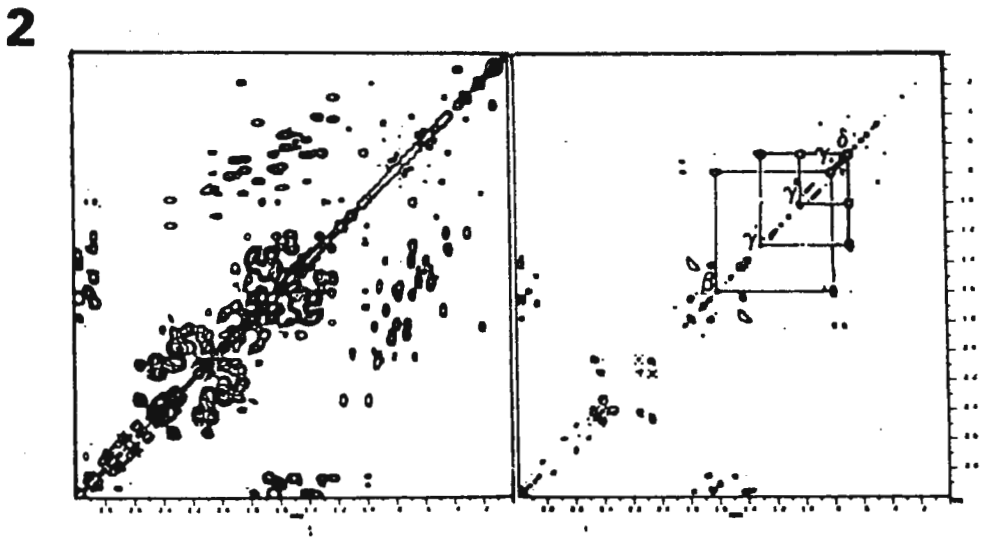

Figure 2: Part of the HOHAHA-COSY spectrum of the IKe gene-5 protein spectrum recorded at 500 MHz (left) and the corresponding difference spectrum obtained by subtracting spectra recorded without and with 1/25 equivalent of 3'- and 5'-labeled *dA3* (right). The cross peak pattern of the isoleucine-29 spin system is indicated.

FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

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Geadresseerde | Ons kenmerk | Datum | Blad No

crosspeak-intensity with distance of the corresponding proton to the spinlabel. These experiments therefore provided information about those residues in the binding-wing which are orientated towards the bound spinlabeled olinucleotide.

Sincerely yours,

Prof. Dr. C.W. Hilbers

Dr. B.J.M. Harmsen

Drs. J.P.M. van Duynhoven

Lehigh University

Department of Chemistry
telephone (215) 758-3470

Seeley G. Mudd Building 6
Bethlehem, Pennsylvania 18015

POSTDOCTORAL RESEARCH ASSOCIATE

Immediately available position involves studying the relaxation influence of paramagnetic centers with solid-state NMR techniques. Some organic/inorganic synthesis is involved, with knowledge of NMR desirable. Appointment for one year ($18,000 to $20,000) renewable by mutual consent. Send CV and arrange for two letters of reference: Dr. James E. Roberts, Department of Chemistry #6, Lehigh University, Bethlehem, PA 18015.

XEROX December 4, 1987

(received 12/10/87)

Xerox Corporation
Webster Research Center
800 Phillips Road, 0114-24D
Webster, New York 14580
(716) 422-4784

Barry L. Shapiro
966 Elsinore Court
Palo Alto, California 94303

Deuterium Lineshapes--
Some Experimental Considerations

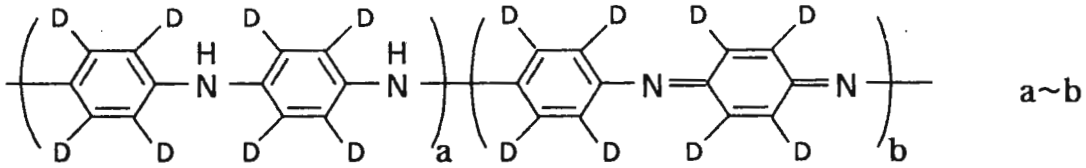
Dear Barry:

We have some practical observations to report which should be of interest to readers experiencing problems with solid-state deuterium lineshapes. Achieving high quality rigid powder patterns can be a frustrating experience, especially if painstaking adjustment of the spectrometer only leads to spectra with gross asymmetry and accoustic ringing problems as in Figs. 1 or 2. We think that we now understand and have control over the factors responsible for these artifacts on our spectrometer so that we can now reproducibly achieve spectra as in Fig. 3.

All of the spectra shown here were measured with quadrature detection on a Bruker CXP spectrometer operating at 30.7 MHz in a Cryomagnet Systems Inc. 47 KGauss widebore superconducting magnet. The probe, supplied by Cryomagnet Systems, uses an ITT Jennings model CHV1-45 gas filled variable capacitor in parallel with an ATC high voltage chip capacitor for tuning. Our probe has a Q of ~100, achieves 90 degree pulse widths of 2 μs with ~500 watts power in a 5 mm sample tube.

Spectral symmetry is known to improve sometimes by a slight detuning of the probe or by increasing the bandwidth of the preamp or transmitter. In our case we were able to improve the symmetry of the spectrum of Fig. 1 by replacing our tuned Ar^2 (Advanced Receiver Research) preamplifier or our Bruker SXP style tunable preamplifier (both of which give the same abysmal lineshape) with a broadband Anzac unit, model AM-110. The resulting spectrum in Fig. 2 has markedly better symmetry, but accoustic ringing distorts the central region of the powder pattern. The usual approaches to minimizing accoustic ringing (e.g., use of a Faraday shield or replacement of the aluminum probehead cover with a brass cover) were tried but failed to give any improvement. Finally, Dick Wittebort (Univ. of Louisville) suggested to us that there was some indication that the ATC chip capacitors exhibited piezoelectric ringing. With this in mind we removed the chip capacitor from our probe circuit and increased the number coil windings to maintain the deuterium resonance frequency. The resulting spectrum shown in Fig. 3 is devoid of accoustic ringing distortion and has good symmetry. Also, the symmetry is insensitive to probe tuning.

The sample under investigation is an insulating form of polyaniline known as polyemeraldine, which has the following structure:

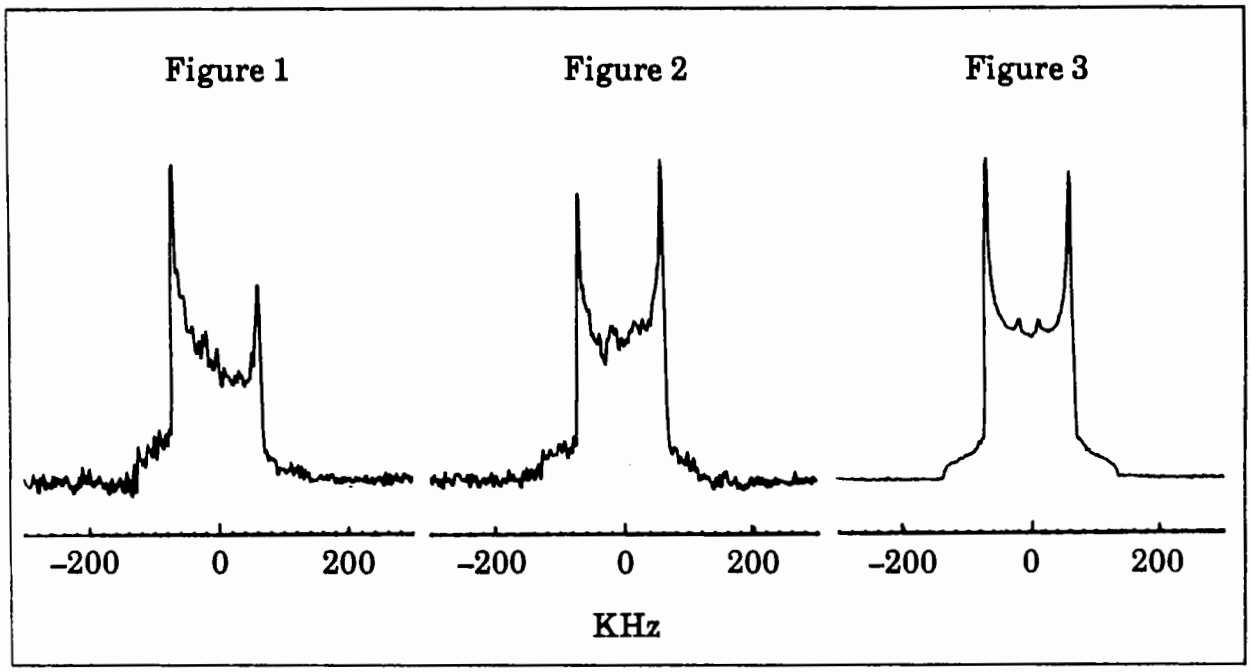


where the rings are deuterated. The central doublet is due to the small number of 1,4 π-flipping phenyl rings. A detailed study of three forms of polyaniline -- polyemeraldine, its HCl-oxidized conducting salt, and the fully reduced leucoemeraldine -- is in preparation.

Sincerely,

Sam

Sam Kaplan



Position Available

We have an opening for a technician to operate and maintain our GN-500 NMR spectrometer, a Sun3/260C workstation and future equipment to be added to the laboratory. The candidate should be capable of doing hardware repair and modification on the spectrometer, and he should be interested and capable in developing software for analysis of NMR spectra on the Sun workstation. Interest in biophysical problems is desireable. Salary would be commensurate with experience. Applications should be sent to:

Gerhard Wagner
University of Michigan
Institute of Science and Technology
Biophysics Research Division
2200 Bonisteel Boulevard
Ann Arbor, Michigan 48109
(313) 936 3858

352-64 CSIR

Council for Scientific and Industrial Research

National Chemical Research Laboratory

P O Box 395 Pretoria 0001 South Africa
Telex: 3-21312 SA Telegrams: Navorschem

Tel: National (012) 86-9211
International + 27 12 86-9211

Our file: Your file:

Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elismore Court
Palo Alto, CA 94303
USA

- 9 DEC 1987
(received 12/16/87)

^{13}C CPMAS of Oxyphenbutazone

Dear Dr. Shapiro:

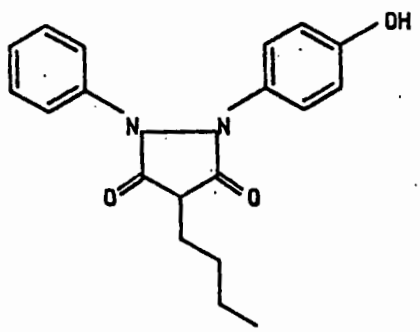
Like many other pharmaceutical compounds, oxyphenbutazone can be isolated in several forms which have very different solubilities, an important factor in clinical use. The ^{13}C CPMAS spectra of two of interest to us (Fig. 1) are quite different as are the IR spectra, powder diffraction patterns, DTA curves etc. Hopefully, with NMR we will be able, eventually, to say more than just "different forms give different spectra" and to this end we have considered the structures based on single crystal X-ray diffraction analyses[1,2].

Both structures show disorder of the butyl group but an essential difference between the two structures is that in the anhydrous material only one carbonyl per molecule is hydrogen bonded (to the phenolic OH of an adjacent molecule) whereas in the monohydrate each carbonyl group is bonded to an H_2O molecule.

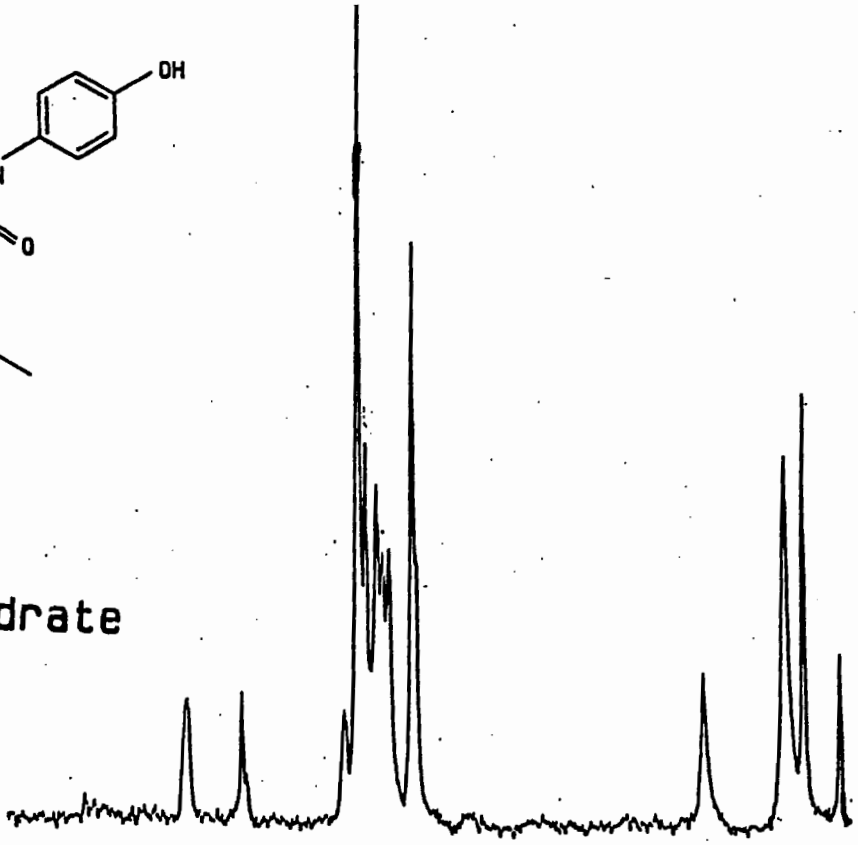
Yours sincerely

A. A. Chalmers

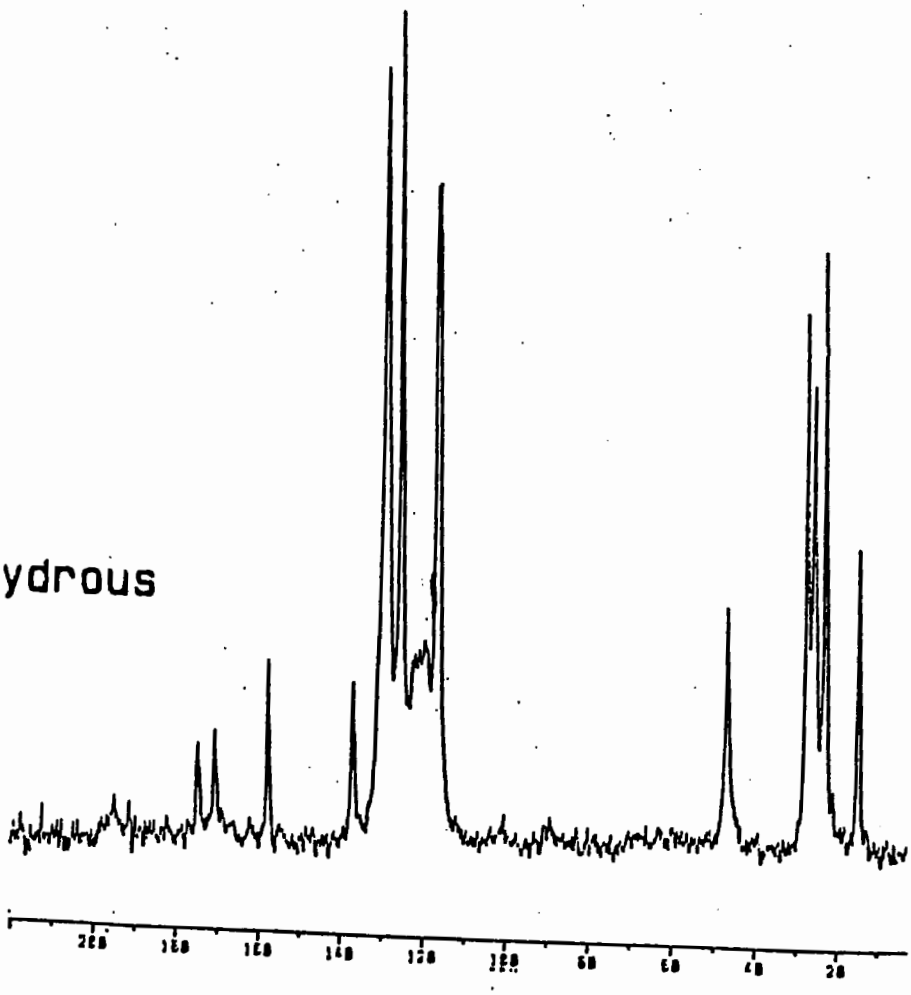
1. H.M. Krishna Murthy and M. Vijayan, Acta Cryst. (1981) B37, 210-213.
2. M. Caira, University of Port Elizabeth.



Monohydrate



Anhydrous



ROSKILDE UNIVERSITY CENTRE
MARBJERGVEJ 35
Poul Erik Hansen, Institute of Life Sciences and Chemistry
POSTBOX 260 DK-4000 ROSKILDE DENMARK TELEPHONE: 02 75 77 11 CABLES: RUCUNIV

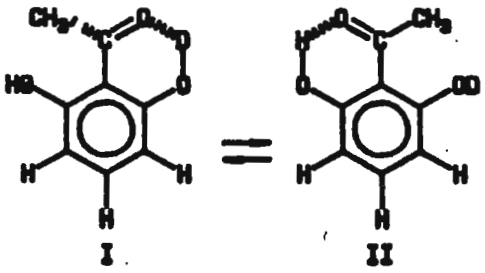
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto
CA 94303 USA

DATE: 19871210/kt (received 12/15/87) OUR REF: YOUR REF:

Dear Professor Shapiro,

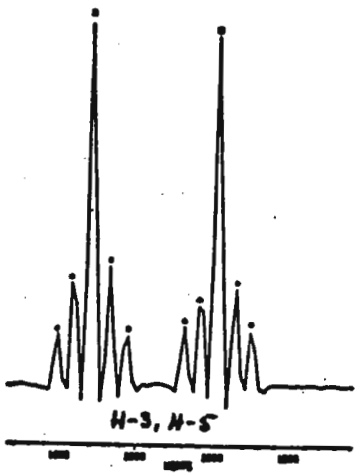
Relay Deuterium Isotope Effects

In our continued investigation of equilibrium isotope effects in 2,6 - dihydroxyacetophenone (1) and Ethyl 2,6 - dihydroxy - 4 - methyl benzoate (2) we found

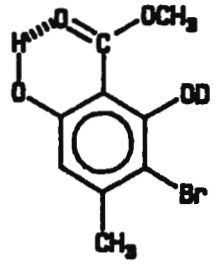


I II

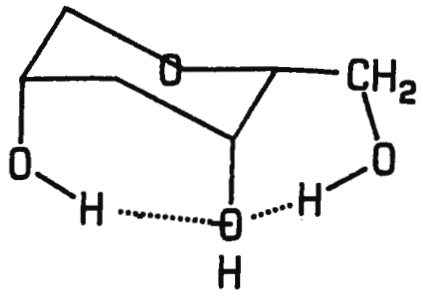
that the pertubation of equilibrium is also making H - 3 and H - 5 different in the HD isotopomer shown in Figure 1. This we have termed a relay effect as the effect depends on the fact that the C = O group on the average point more often towards the OH group (II) than towards the OD group (I). This in turn causes the OH hydrogen to point preferentially away from H(5) and C(5), which causes an equilibrium isotope effect at H - 3, H - 5 respectively C - 3, C - 5.



We have also investigated isotope perturbation of equilibrium in 3



and found that in this non-symmetrical compound both OH - 2, OH - 6, C - 2, C - 6, C - 3 and C - 5 show extra splittery due to isotopic perturbation. The effects at OH - 2 and OH - 6 are quite different from one another. We have now started to look for other similar non-symmetric situations. One suggestion is sugars. This may add some fuel to the SIMPLE discussion.[2 - 4]



In case anybody have any other suggestions or objections, please let me know.

1. P. E. Hansen, Magn. Reson. Chem. 24, 772 (1986).
2. J. Reuben, J. Am. Chem. Soc. 106, 6180 (1984).
3. J. C. Christofides and D. B. Davies, Magn. Reson. Chem. 23, 582 (1985).

Yours sincerely,

Poul Erik Hansen

PS! Recent papers dealing with NMR of olefins, carbonyl compounds and azocompounds are in demand.

352-68 The University of Akron

Department of Chemistry
Akron, OH 44325
(216) 375-7372

December 10, 1987
(received 12/15/87)

Prof. B. L. Shapiro
966 Elsinore Court
Palo Alto, California 94303

PLOTTING ROUTINES FOR VARIAN INSTRUMENTS

Dear Barry,

This past summer I left my position at Varian in Florham Park to take over the direction of the Chemistry Department Molecular Spectroscopy Laboratory here at the University of Akron. Please add me to your list of subscribers with this first contribution.

For some time, I have listened to complaints by Varian instrument owners that plots on 8 1/2 X 11 paper do not work properly on Hewlett Packard plotters. Simply by pressing a button (on HP-7475) or by swapping paper trays (on HP-7550) the plotter is supposed to take care of rotating and scaling the data to be plotted. For some types of plotted data this does not work. Specifically, when plotting scales and parameter lists, an unaccountable offset develops between successive plots of character strings. Varian attributes this problem to a bug in HP's plotter software.

I have written the enclosed two MAGICAL macro commands to get arround this problem. VPA and VSCALE MAGICAL commands are equivalent to Varian's PPA and PSCALE Pascal commands in function and usage; although they are necessarily slower than the compiled programs they do the job. Any Varian customer with version 6.1D software should be able to enter these commands in their macro library using the text editor.

Sincerely yours,

Peter L. Rinaldi
Associate Professor
Director, Molecular Spectroscopy Lab

```
:VPA(X,Y) - PLOTS PARAMETERS ON 8 1/2 X 11 PAGE OF HP PLOTTER
:$1 AND $2 ARE X AND Y POSITIONS OF START OF LIST
IF NOT($1) THEN $1=20 ENDIF
IF NOT($2) THEN $2=140 ENDIF
IF $1>180OR$1<0 THEN $1=20 ENDIF
IF ($2>140)OR($2<40) THEN $2=140 ENDIF
"GET TEXT AND WRITE TO PLOTTER"
SYSINF(EXP):R5,N1                    "LOOKS UP CURRENT EXPERIMENT"
IF AUTO=&Y THEN R5=9 N1=&EXP9 ENDIF
SYSINF(EXPLIB.@N1.ACQPAR.DATE):R1,R2,R3,R4
$3=5 "VERTICAL OFFSET BETWEEN LINES OF PARAMETER LIST"
"OBTAIN OR CALCULATE ANY NEEDED INFORMATION"
IF TN<2 THEN $4=&PROTON ELSE
 IF (TN<14)AND(TN>12.9) THEN $4=&CARBON ELSE $4=&BB ENDIF
ENDIF
IF DP=&Y THEN $5=&DOUBLE ELSE $5=&SINGLE ENDIF
IF FN>512 THEN TRUNC(@FN/1000):$6 ENDIF
"OUTPUT DATA TO PLOTTER"
WRITE(PLOT,$1,$2-$3*1,'DATE',`      `,@R2:0,'-',@R3:0,'-',@R4:0)
WRITE(PLOT,$1,$2-$3*2,'SOLVENT',`   `,@SOLVNT)
WRITE(PLOT,$1,$2-$3*3,'FILE',`      `,@FILE)
WRITE(PLOT,$1,$2-$3*5,$4,' OBSERVE') "PROTON OR CARBON OBSERVE"
WRITE(PLOT,$1+2,$2-$3*6,'FREQUENCY',` `,@SFRQ,' MHZ')
WRITE(PLOT,$1+2,$2-$3*7,'SPECTRAL WIDTH',` `,@SW,' HZ')
WRITE(PLOT,$1+2,$2-$3*8,'ACQ. TIME',` `,@AT,' SEC')
WRITE(PLOT,$1+2,$2-$3*9,'PULSE WIDTH',` `,90*PW/PW90:0,' DEGREES')
WRITE(PLOT,$1+2,$2-$3*10,'TEMPERATURE',` `,@TEMP:1,' DEG. C')
WRITE(PLOT,$1+2,$2-$3*11,'NO. REPETITIONS `,` `,@NT:0)
WRITE(PLOT,$1+2,$2-$3*12,$5,' PRECISION ACQUISITION')
WRITE(PLOT,$1,$2-$3*13,'DATA PROCESSING')
IF FN>512 THEN
 WRITE(PLOT,$1+2,$2-$3*14,'FT SIZE `,` `,$6:0,'K')
 ELSE WRITE(PLOT,$1+2,$2-$3*14,'FT SIZE `,` `,$6,'POINTS')
ENDIF
SYSINF(YN,LB):R1,R2
IF R1=1 THEN
 WRITE(PLOT,$1+2,$2-$3*15,'LINE BROADENING',`    `,@R2,'HZ')
 ELSE WRITE(PLOT,$1+2,$2-$3*15,'LINE BROADENING NOT USED')
ENDIF
SYSINF(YN,RE):R1,R2
IF R1=1 THEN
 WRITE(PLOT,$1+2,$2-$3*16,'RESOLUTION ENHANCEMENT `,@R2,'SEC')
 ELSE WRITE(PLOT,$1+2,$2-$3*16,'RESOLUTION ENHANCEMENT NOT USED')
ENDIF
SYSINF(YN,AF):R1,R2
IF R1=1 THEN
 WRITE(PLOT,$1+2,$2-$3*17,'GAUSSIAN BROADENING',` `,@R2,'SEC')
 ELSE WRITE(PLOT,$1+2,$2-$3*17,'GAUSSIAN BROADENING NOT USED')
ENDIF
WRITE(PLOT,$1,$2-$3*18,'DISPLAY')
WRITE(PLOT,$1+2,$2-$3*19,'WIDTH OF PLOT',` `,@WP/SFRQ,' PPM')
WRITE(PLOT,$1+2,$2-$3*20,'START OF PLOT',` `,@SP/SFRQ,' PPM')
```

```
:VSCALE($1) - PLOTS SCALE ACROSS AN 8 1/2 X 11 PAGE ON HP
:PLOTTER. $1 CAN BE SET TO H OR P FOR AXIS IN HZ OR PPM
:USE THIS COMMAND BEFORE A PLOT SO THAT IT WILL SET A DEFAULT
:FORMAT FOR THE PLOT IF IT S TOO BIG TO FIT ON THE PAGE AS IS
:LIMITS OF PLOT DIMENSIONS ARE 40<=WC<=220, 220>=SC>=360, AND
:SC+WC<=400
IF NOT($1) THEN SC2=0 ELSE AXIS=$1 ENDIF
SC2=0 WC2=150
IF SC<160 THEN SC=180 ENDIF
$18=@SC+WC
IF $18>400 THEN WC=400-SC ENDIF
IF WC<40 THEN WC=40 ENDIF
$18=402-SC-WC
"DRAW AXIS FOR SCALE"
WRITE(PLOT,402-SC-WC,@VP-5,'____________________') "20 DASHES"
 TRUNC(@WC/40):$17 $16=402-SC-WC+40 $15=40-(WC-$17*40)
IF $17>1.5 THEN
 REPEAT
 WRITE(PLOT,$16,@VP-5,'____________________') "20 DASHES"
 $17=$17-1 $16=$16+40
 UNTIL $17<1.5
ENDIF
 WRITE(PLOT,$16-$15,@VP-5,'____________________') "20 DASHES"
IF AXIS=&P THEN "CALCULATIONS BASED ON SFRQ"
 $12=1.1*WP/(5*SFRQ) WRITE(PLOT,(400-SC-WC/2),@VP-20,'PPM')
 $4=@SP/SFRQ $5=@WP/SFRQ
ELSE IF AXIS=&H THEN "CALCULATIONS BASED ON HZ"
 $12=1.1*WP/5 $4=@SP $5=@WP
 WRITE(PLOT,(400-SC-WC/2),@VP-20,'HZ') ENDIF
ENDIF
"CALCULATE FREQUENCY INCREMENT"
 $3=0
 IF $12>10 THEN
  REPEAT $12=$12/10 $3=1+$3 UNTIL $12<10
 ELSE IF $12<1 THEN
  REPEAT $12=$12*10 $3=$3-1 UNTIL $12>1
 ENDIF ENDIF
 TRUNC($12):$12
 IF $3>0 THEN
  REPEAT $12=10*$12 $3=$3-1 UNTIL $3<0.5
 ELSE IF $3<0 THEN
  REPEAT $12=$12/10 $3=$3+1 UNTIL $3>-0.5
 ENDIF ENDIF
$2=$12/$5*WC              "CALCULATE SPACING OF TIC MARKS"
"CALCULATE FREQUENCY ($7) AND POSITION ($8) OF FIRST TIC"
 TRUNC($4/$12):$6
 IF $6>0 THEN $6=1+$6 ENDIF
 $7=$6*$12 $8=402-SC-($7-$4)/$5*WC
"PLOT TICS AND LABELS"
REPEAT
 WRITE(PLOT,$8,@VP-7.5,'T')
 WRITE(PLOT,$8-3,@VP-10,$7)
 $8=$8-$2 $7=$12+$7
UNTIL $8<$18
```

The University of New Mexico

CENTER FOR NON-INVASIVE DIAGNOSIS
1201 Yale Blvd., N.E.
Albuquerque, NM 87131
Telephone: (505) 277-8512

December 11, 1987
(received 12/14/87)

Dr. B.L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

Dear Barry:

Interest in using NMR for the imaging of specific compounds, and their metabolites continues to grow. We have studied methods for editing normal proton images to yield images of specific compounds, using scalar couplings to 13C-enriched sites. The complications associated with this technique include the supression and/or cancellation of the larger signals from water and lipid, and maximization of the sensitivity for the proton signals. We wish to describe our initial results with 1H-13C imaging which suggest that this methodology may prove useful in a number of areas.

The NMR system was a GE 4.7 T CSI, equiped with the heteronuclear decoupling accessory. All images were obtained using the standard birdcage coil for proton excitation and reception, and a 2.5 cm two-turn surface coil for the carbon pulses. The proton and carbon 90° pulse lengths were 300 and 80 usec, respectively. The phantoms consisted of two scintillation vials containing 7.8 mL of deionized water and 10 mL of a 1.0 M solution of sodium (13C)formate.

The pulse sequence consisted of a 1331 pulse followed by phase-encode and dephasing gradients. After a delay period 1/2J, carbon 0° or 180° pulses were applied on alternate scans. The strength of the readout gradient was chosen so that the position of the gradient echo coincided with the 13C-modulated spin echo. A total of 100 scans alternately were summed and subtracted in conjuction with the magnitude of the carbon pulses. A total of 128 gradient phase-encoding steps were used to generate the image. Waltz-16 carbon decoupling was applied during the acquisition period.

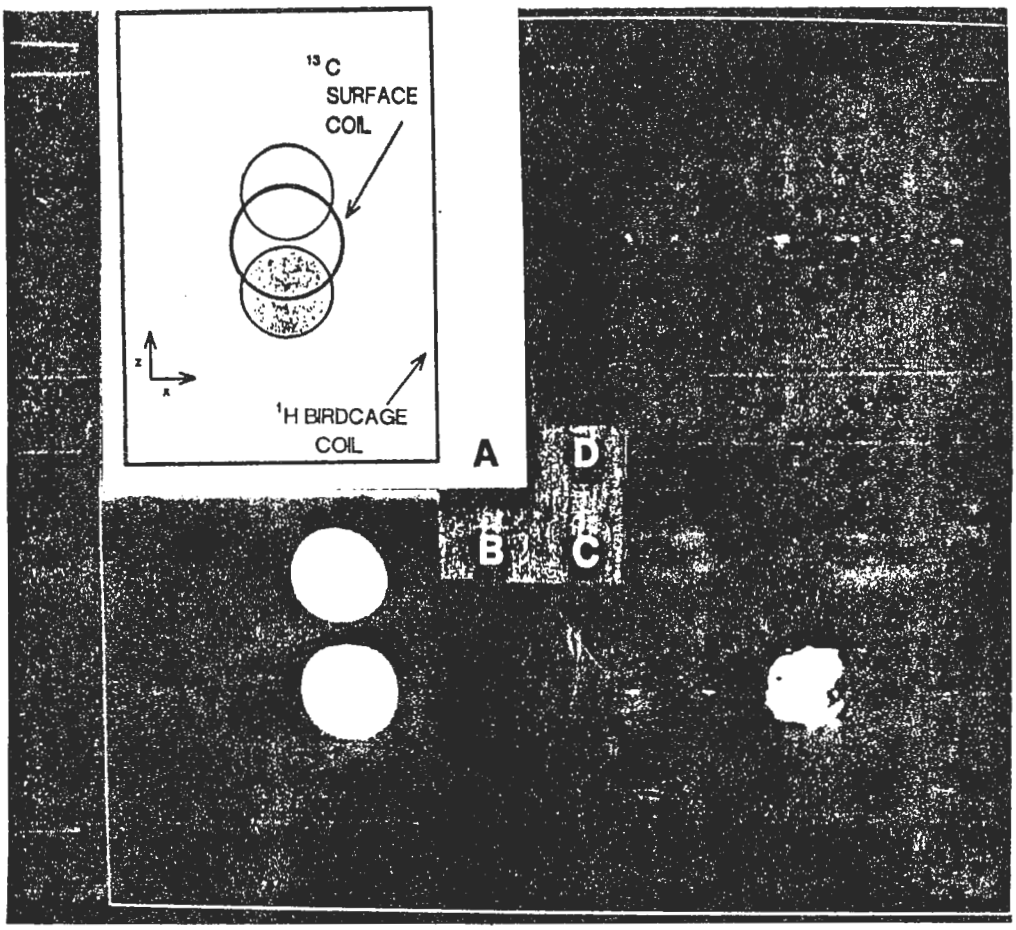
The figure below shows (a) the position of the two vials and the 13C coil, (b) the proton image of the two vials obtained using a normal gradient refocussed echo sequence, (c) the 1331 gradient echo with the carbon pulse and carbon decoupling, and

(d) the 1331 gradient echo without the carbon pulse or decoupling. As can be observed in (d), the cancellation of unlabelled spins is excellant, and inclusion of the 13C pulse and decoupling (c) generates an image of only the phantom containing the [13C]formate. Calculation of the signal to noise from single slices of the normal and 13C-modulated images shows that we are imaging 13C with the sensitivity of protons. We anticipate that this methodology will be of value in monitoring the distribution and metabolic fate of specific compounds <u>in vivo</u>.

Sincerely yours,

Richard Griffey

Richard H. Griffey Laurel O. Sillerud David van Hulsteyn



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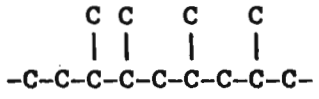
December 12, 1987.
(received 12/17/87)

Dr. B. L. Shapiro, Editor/Publisher
TAMU NMR Newsletter
466 Elsinore Court
Palo Alto, CA 94303

Dear Dr. Shapiro:

Methyl Substituted Alkanes and Ethylene/Propylene Polymers

Two classes of compounds that a substantial body of ^{13}C shift data exists are the methyl substituted alkanes and their polymeric analog, the ethylene/propylene polymers. A typical structure of these compounds usually consists of long chains punctuated at various places by methyl substituents and terminated by chain ends.



About four years ago Mark Bennett and I reviewed the data on these compounds[1] and based on our experience in NMR interpretation and borrowing some concepts from Zambelli[2], we devised very detailed ^{13}C shift rules for these compounds[1]. These are based on the empirical additive rules, but include the effects of configuration (meso/racemic). Separate equations are used for methyl, methine, and methylene carbons.

$$\delta_{CH_3} = 19.99 + \sum_i A_i + \sum_{ij} B_{ij} + \sum_{ij} C_{ij}$$

$$\delta_{CH} = 33.26 + \sum_i A_i + \sum_{ij} B_{ij} + \sum_{ij} C_{ij}$$

$$\delta_{CH_2} = 29.9 + \sum_i A_i + \sum_{ij} B_{ij} + \sum_{ij} C_{ij} + \sum_k D_k$$

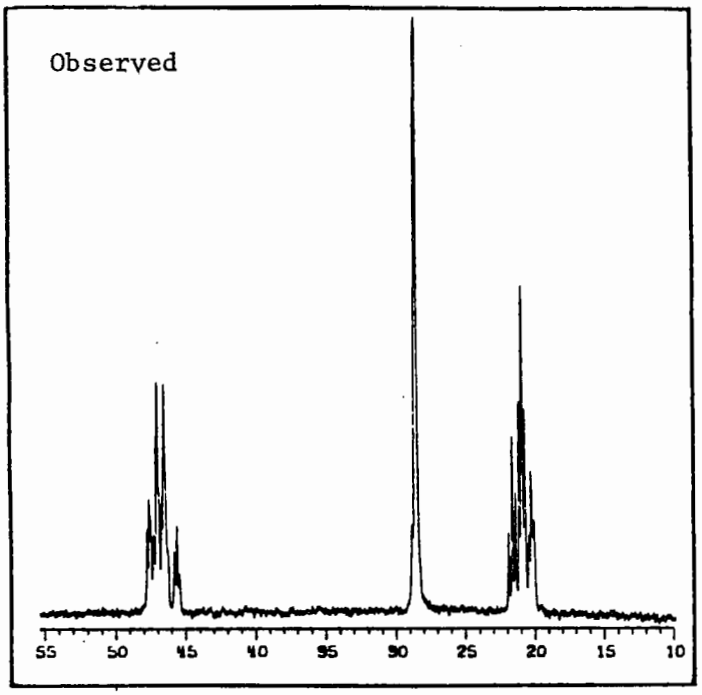
With the use of these rules, very accurate ^{13}C shifts can be predicted for a wide range of compounds[1].

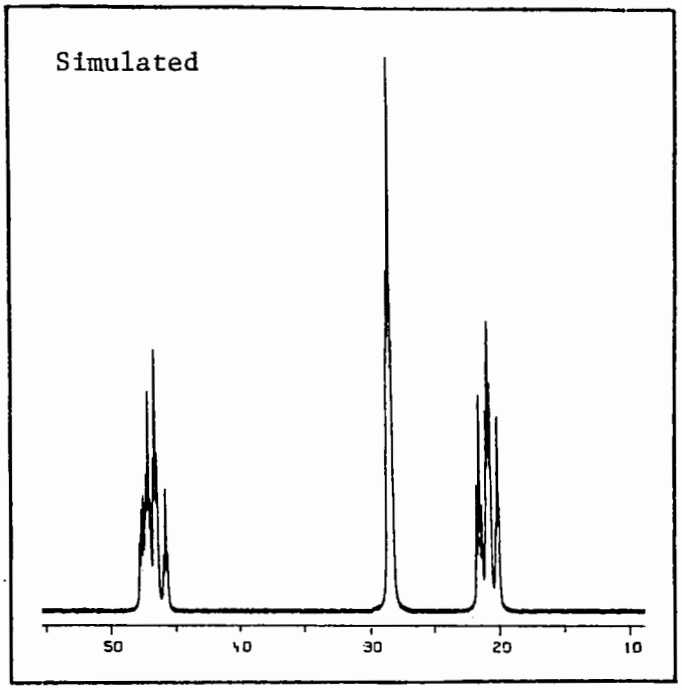
Sometime ago a synthetic (spectral simulation) approach was proposed for the visualization and analysis of ^{13}C spectra of vinyl polymers[3]. This was based on reaction probability models (e.g., Markovian statistics), Monte Carlo simulation of polymer chains, ^{13}C shift prediction, and spectral simulation. Now that detailed ^{13}C shift rules are available for polymers involving ethylene and propylene, we can use the synthetic approach to simulate any ethylene/propylene polymers. Two examples are shown in the next page. This work will soon be published[4].

Yours sincerely,

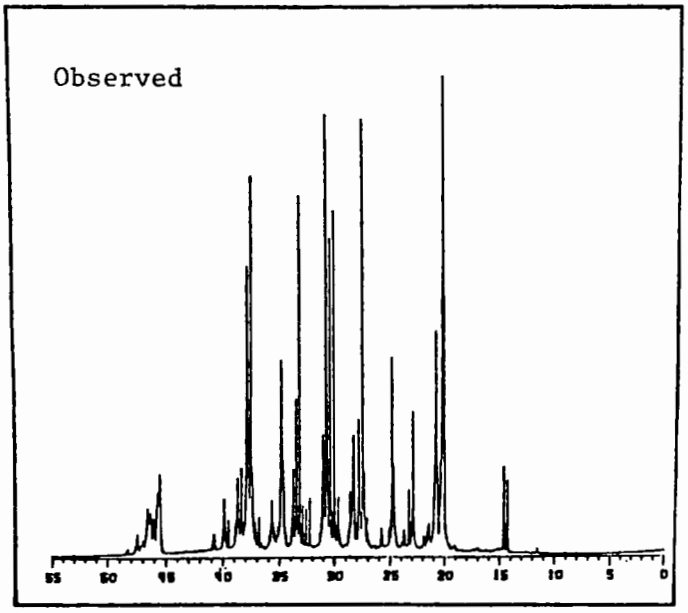
H.N. Cheng

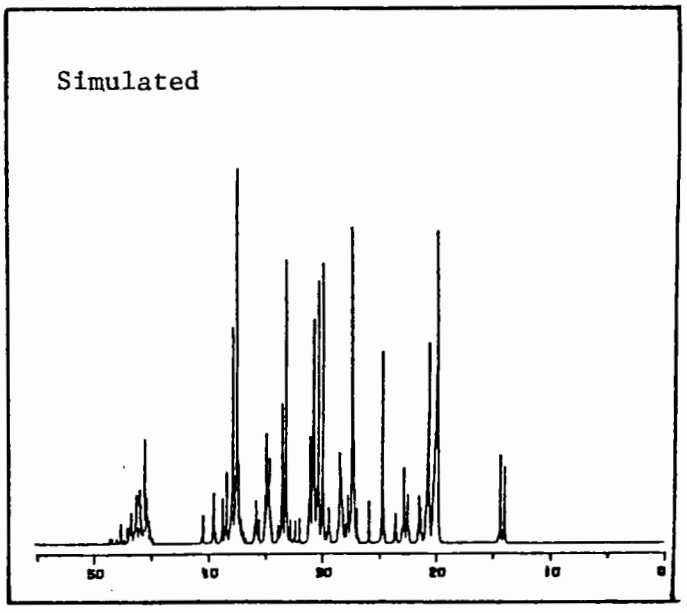
Atactic Polypropylene





Ethylene-Propylene Oil (Low MW Ethylene-Propylene Rubber)





References

1. H. N. Cheng and M. A. Bennett, Makromol. Chem., 188, 135 (1987), and references therein.
2. A. Zambelli and G. Gatti, Macromolecules, 11, 485 (1978).
3. H. N. Cheng and M. A. Bennett, Anal. Chem., 56, 2320 (1984).
4. H. N. Cheng and M. A. Bennett, Makromol. Chem., in press.

352-74

David M. Grant
Distinguished Professor

THE UNIVERSITY OF UTAH

15 December 1987
(received 12/17/87)

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

RE: "CSA Line-Shapes in Off Magic Angle Spinning"

Dear Dr. Shapiro:

Recently we have been interested in measuring ^{13}C Chemical Shift Anisotropies (CSA) by spinning the sample away from the magic angle and subsequent line-shape analysis of the spectra. This has proven to be a useful technique for obtaining CSA's in complex systems.

During the course of this work some unexpected but interesting results were obtained. It was noticed that when spinning away from the magic angle at speeds lower than the CSA in frequency units the intensity of the band at points in between the principal shielding values drops off faster than at the break points. This results in a spectrum that shows sharp lines where the scaled tensor break points ought to be. At angles close to the magic angle the appearance of the spectra may resemble multiple lines, i.e. an axially symmetric tensor becomes a doublet (see J. Mag. Res. 63, 579, 1985) and an asymmetric tensor a triplet (see figure). The interesting thing is that such multiplicity is not a consequence of different chemical species or crystalline effects but are due merely to tensor elements (scaled due to the choice of spinning angle) having break points which have sharpened to look like lines. If the spinning angle can be measured very precisely then the CSA can be obtained simply from the frequency of the lines.

In our work, however, we have always found exact line-shape simulations to be more reliable than taking a few frequency or intensity data points. A very efficient and quick algorithm has been developed to calculate such spectra which makes simulation with optimization routines affordable. These methods have been used to simulate spectra of the carbonyl part of malonic acid (see figure). Notice the triplet structure of the center band. Also, the shapes of the side-bands are not an exact replica of the center band. The tensor values obtained from this analysis were found to be in excellent agreement with reported single crystal work.

We are currently preparing the manuscript describing this approach to determining parameters from the spectral band and it should be submitted soon.

Sincerely yours,

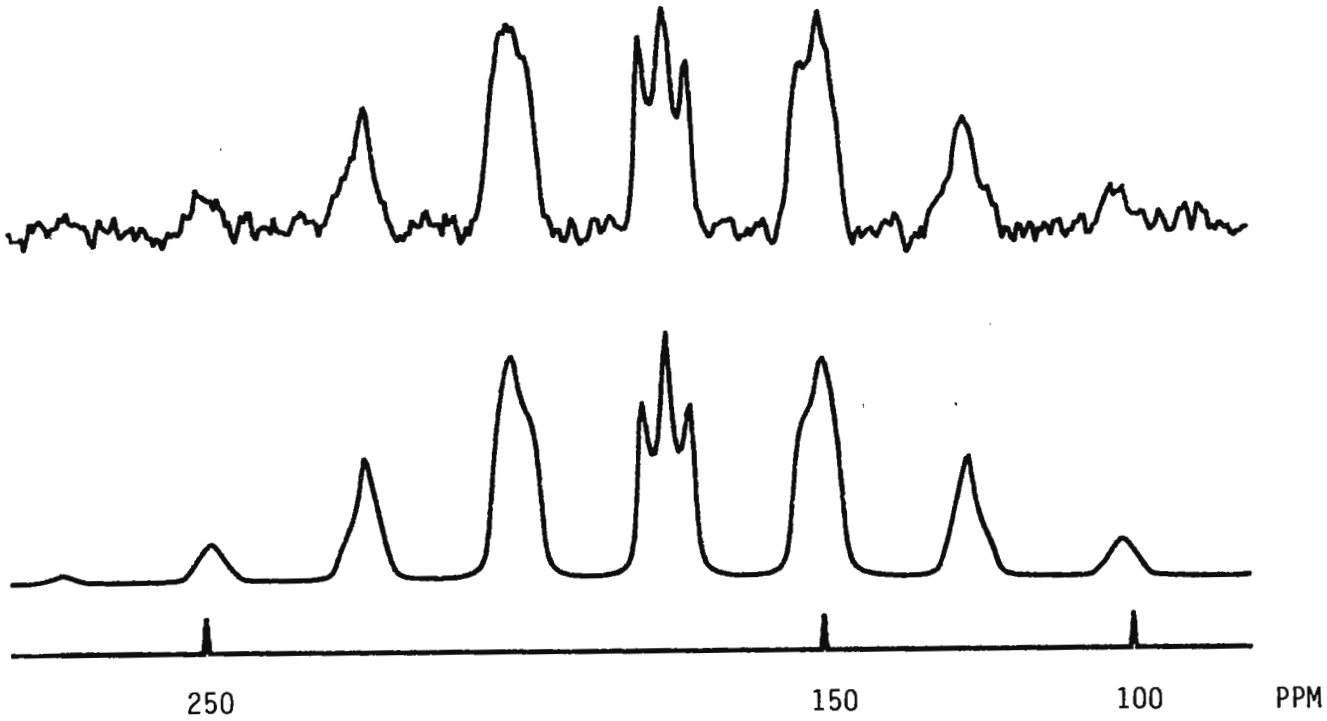
David M. Grant Donald W. Alderman Naresh K. Sethi

DMG:lt

Department of Chemistry
Henry Eyring Building
Salt Lake City, Utah 84112
(801) 581-8854

Spinning Angle 57.4°

Spinning Speed 617 Hz



Carbonyl Region of Malonic Acid $CH_2(COOH)_2$.

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INDIANA UNIVERSITY

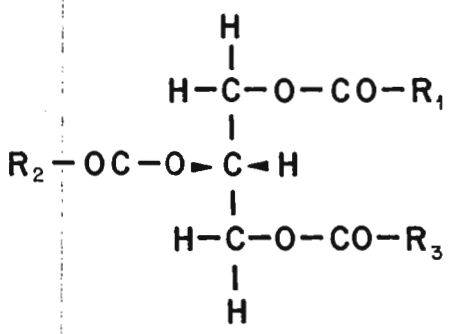
DEPARTMENT OF CHEMISTRY
Chemistry Building
Bloomington, Indiana 47405
(812) 335-5513

December 17, 1987
(received 12/18/87)

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

Dear Barry:

POSITIONAL DISTRIBUTION OF FATTY ACIDS IN TRIGLYCERIDES
BY ULTRAHIGH RESOLUTION ^{13}C NMR



Consider the general structure of a triglyceride. If R_1, R_2, and R_3 are not all identical, one faces the analytical task of identifying the positional distribution of each type of chain. This is an important problem in biochemistry, nutrition research, and industry.

The unsatisfactory state of triglyceride analysis is illustrated by the following quote from "Bailey's Industrial Oil and Fat Products", Fourth Edition, Vol. 1, published in 1979: "The great number and variety of fats and oils in nature and the effect of slight and imperceptible changes in the environment on their composition make it unlikely that the structures of oil and fat triglycerides are governed by a series of simple rules. Yet fat and oil chemists have attacked the subject of triglyceride structure with a sweeping array of generalizations. . . Today it is increasingly apparent that we will need to generate a huge amount of additional reliable data, and eliminate much of the earlier unreliable data, before a thoroughly comprehensive understanding of the structure of triglycerides is possible".

E. Wenkert et al. stated in 1976 in a review in Vol. 2 of *Topics in Carbon-13 NMR Spectroscopy* (G. Levy, ed.): ". . .cmr spectra are unable to disclose the location of specific fatty acid chains on the glycerol backbone of mixed triglycerides, such as 2-oleodistearin." P. E. Pfeffer et al. stated in 1977 in an article entitled *Analytical ^{13}C NMR: Detection, Quantitation, and Positional Analysis of Butyrate in Butter Oil*, published in Lipids 12, 869: "In additon to butyrate, the isomeric composition of acetate and propionate triglycerides can also be ascertained in the presence of longer chain esters. However, hexanoate and those of higher molecular weight cannot, due to their common C-2 resonance position."

We find that ultrahigh resolution ^{13}C NMR, even at our low resonance frequency of 50 MHz, provides the necessary resolving power to establish the

positional distribution of long-chain fatty acids of triglycerides, by taking advantage of ***resolved*** small chemical shift differences (of carbons far from the esterification point to glycerol) between fatty acid chains at the primary and secondary hydroxyl. The small spectral segment (29.89 - 30.23 ppm) in the spectra of 1,2-dipalmitoyl-3-myristoyl-rac-glycerol and 1,2-dimyristoyl-3-palmitoyl-rac-glycerol shown in Figure 1 illustrates the available resolution. Here M*n* and P*n* indicate carbon *n* of a myristoyl and palmitoyl chain, respectively. We have made specific assignments, not shown in Fig. 1, of fatty acid chains attached at C-1 and C-2 of the glycerol. Clearly, peak separations as small as 0.005 ppm are resolved in Figure 1 (see the separation of M7 and P7 in the bottom spectrum), even though these molecules are rather large and have substantial natural linewidths.

The above is one more blatant attempt on our part to convince the NMR community that ultrahigh resolution is useful not only for tiny molecules but for rather large ones as well.

Best regards,

Adam Allerhand

Steven R. Maple

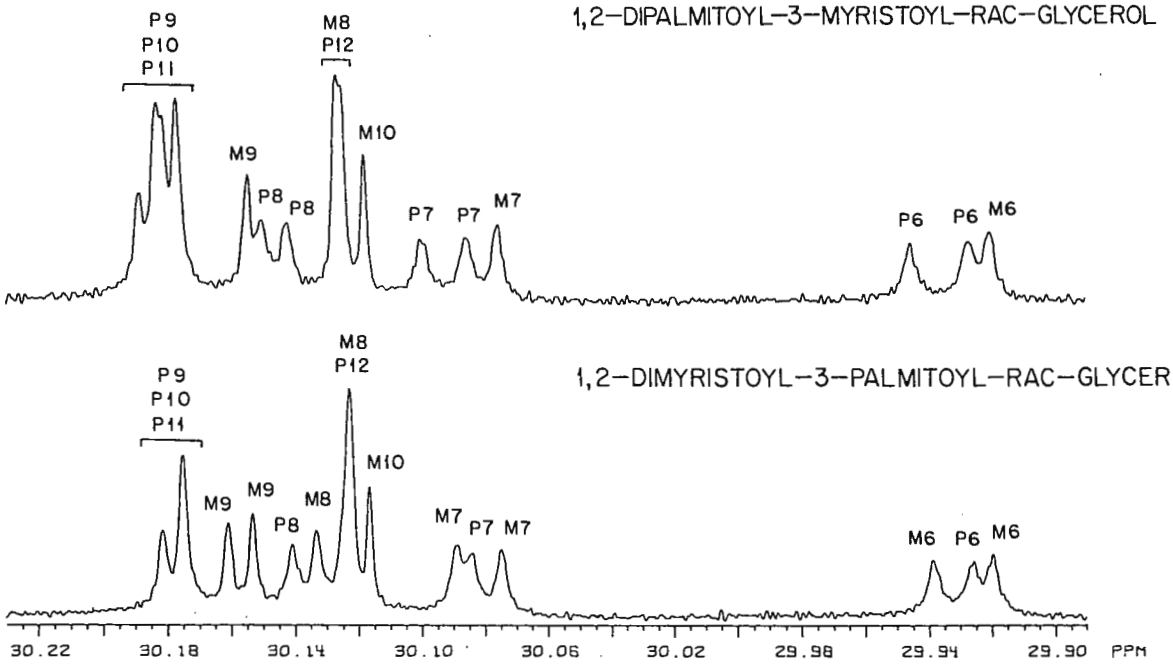


Figure 1. The 29.89 - 30.23 ppm region in the proton-decoupled ^{13}C NMR spectra of 9% 1,2-dimyristoyl-3-palmitoyl glycerol (bottom spectrum) and 9% 1,2-dipalmitoyl-3-myristoyl glycerol (top spectrum) in 79% v/v C_6H_6, 20% C_6D_6, and 1% v/v Me_4Si at 26.5 °C. Each spectrum is the result of 480 scans with an acquisition time of 29.75 s, a sweep width of ±1101.32 Hz and 128K time-domain data points. The spectra were processed with 0.15 Hz Lorentzian narrowing plus 0.18 Hz Gaussian broadening followed by Fourier transformation after adding 128K zero-fill time-domain data points, which yielded a final digital resolution of 16.8 mHz.

352-78

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Announcement of Symposium on
Quantitative NMR Spectroscopy

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

Dear Barry:

Accurate quantitation in NMR spectroscopy can be either a necessary condition for the success of certain experiments (e.g., 2-D NOE internuclear distance determinations) or a highly desirable extension of experiments not primarily designed for quantitative work (e.g., DEPT or spectroscopy of quadrupolar nuclei in solids). In either case, success usually depends on painstaking attention to details.

I would like to bring to the attention of your readers, especially those from the Western states, an NMR Symposium focusing on quantitative aspects of NMR spectroscopy on Tuesday, March 29, 1988, in Las Vegas, Nevada. It is part of the 9th Rocky Mountain Regional ACS Meeting (March 27-30) comprising 23 symposia, several general sessions, poster sessions, and short courses. The full-day NMR session will be followed by the Conference Banquet, featuring an address by Gordon Nelson, 1988 ACS President and NMR spectroscopist, and a complete Las Vegas show. The Riviera Hotel is the site of the meeting and is offering a rate of $50/night (single or double occupancy); the banquet is $37.50/person and conference preregistration is $33 (ACS members).

The Symposium agenda:

Tuesday Morning, D. M. Wilson, Presiding

"^{1}H and ^{2}H NMR Methods for Investigating the State of Water in Silicate Glasses." H. Eckert, J. P. Yesinowski

"Use of Non-Magic Angle Spinning to Measure Chemical Shift Anisotropies and Dipolar Interactions Quantitatively." N. K. Sethi, R. J. Pugmire, J. C. Sacelli, and D. M. Grant.

"Proton CRAMPS as an Analytical NMR Technique for Solids." C. E. Bronnimann, B. L. Hawkins, M. Zhang, G. E. Maciel.

"Quantitative ^{27}Al NMR in Zeolites." A. Samoson, E. Lippmaa, G. Engelhardt.

"Two-Dimensional ^{13}C NMR Powder Patterns in Rotating Solids." T. Terao, T. Nakai, J. Ashida.

"Quantitative MAS NMR of Quadrupolar Nuclei." K. Schmitt.

Tuesday Afternoon, J. P. Yesinowski, Presiding

"The Impact of Spectrometer Design on Quantitation in 1-D and 2-D NMR." G. A. Gray.

"Quantitative Analysis of ^{1}H NMR Data: Uses in Biomolecular Structure Analysis." D. E. Wemmer.

"Qualitative and Quantitative Uses of Polarization Transfer and 2-D NMR of Fossil Fuel Liquids." L. W. Dennis.

"Diffusion of Solvents and Polymers in Homo- and Heterogeneous Systems." F. D. Blum.

"Whole Body NMR Imaging: How to Make NMR More Difficult." P. J. Keller.

"The Use of Small NMR Spectrometers for On-Line Process Analysis." R. M. Pearson, L. R. Ream, J. Q. Adams, C. Job.

"Industrial Applications of Quantitative NMR Spectroscopy," S. M. Wharry, J. B. Cross, B. A. Baldwin, D. J. O'Donnell.

It is probably worthwhile pointing out also that these dates are during Easter vacation for most schools, that the desert should be in full bloom about this time, and that two of Mother Nature's most exotic attractions, Death Valley National Monument and Grand Canyon National Park, are a half-day's ride away.

Inquiries should be directed to me at (415) 620-2415 or Dan Netzel at (307) 721-2370.

Sincerely yours,

Dan Wilson

D. M. Wilson

DMW:jg

TEXAS A&M UNIVERSITY
NMR NEWSLETTER

No. 352
January 1988

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* * * * * * * * *

Concerning the Physical Format and Nature of Contributions to the Newsletter Contents - Again.

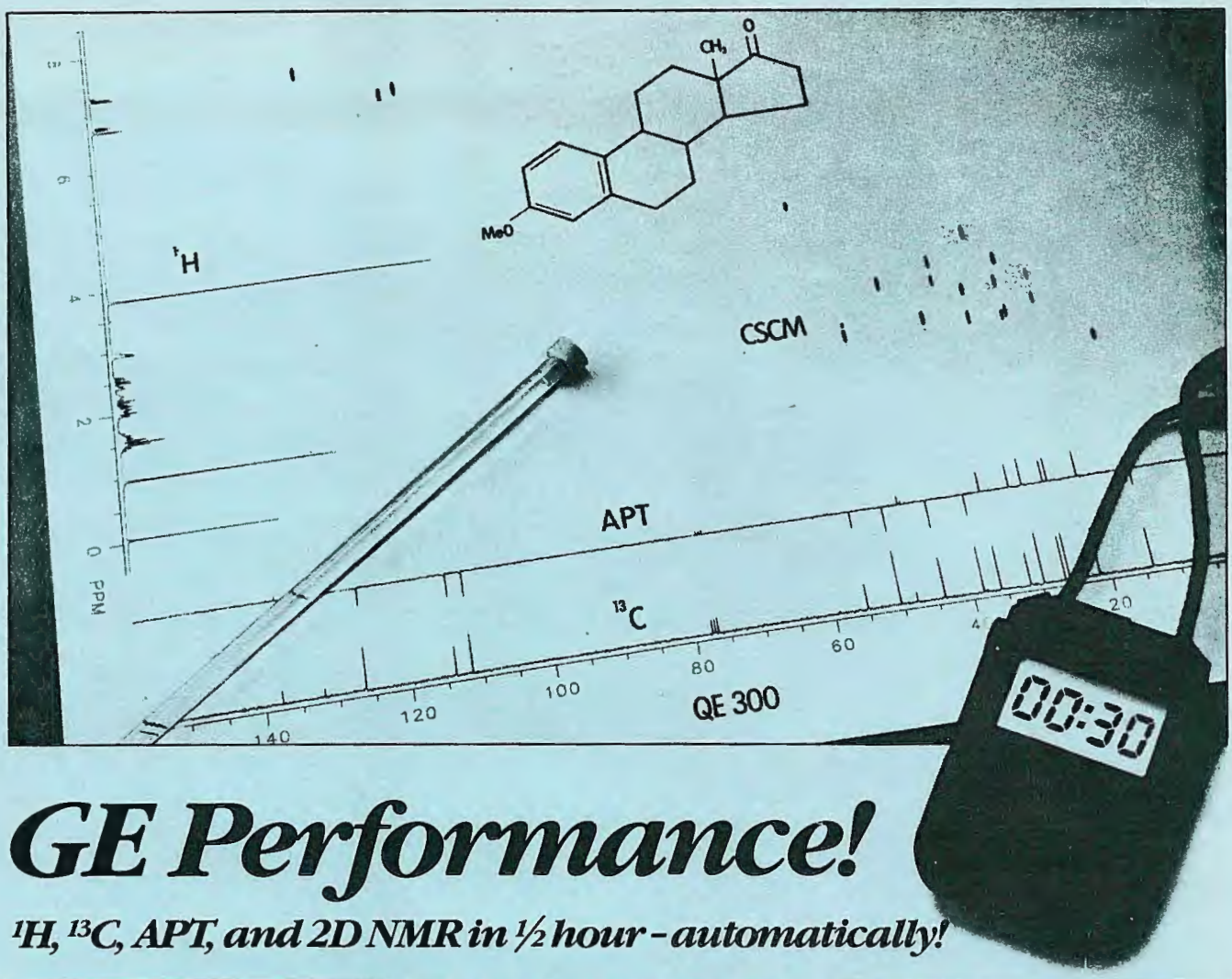
1. Please provide **short titles** for all topics of your contributions. Failure to provide titles - suitably succinct ones! - may result in my doing so, with possible attendant loss of signal. Ask Alan Marchand . . . .

2. "Positions Available", "Equipment Available", and similar notices should be formatted so as to use the *minimum vertical space*. Please do not double space such notices, or leave wide margins at the sides. I believe that such notices should rarely if ever need to exceed one-half of a page, and henceforth, such notices which exceed 4.5" (11.4 cm) in the vertical dimension, *including letterhead, address, etc.*, will be respectfully declined, and returned for condensing (This will usually result in the notice being delayed until the next Newsletter issue.). A notice which really needs to be more than 4.5" tall must be agreed to in advance.

3. Technical contributions may not exceed three pages without prior approval.

4. All contributions must be formatted so as to leave 1" (25.4 mm) margins on all four sides. This is especially important for foreign subscribers, whose paper is usually larger than that used in the U.S.A. and Canada.

B.L.S.



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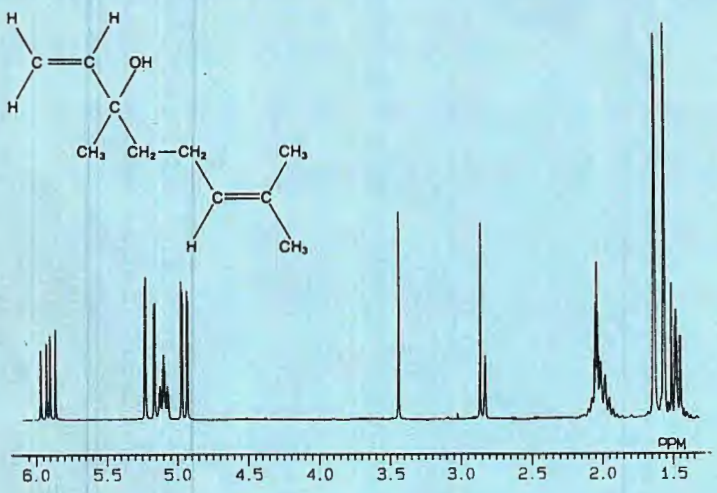

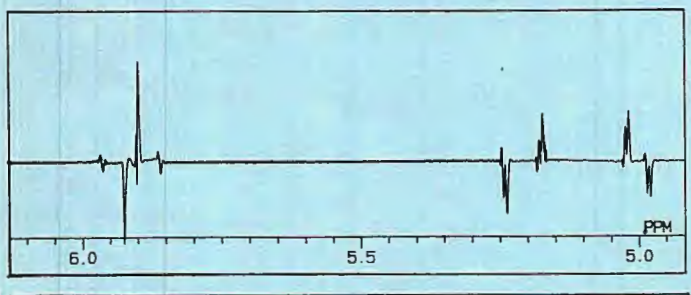

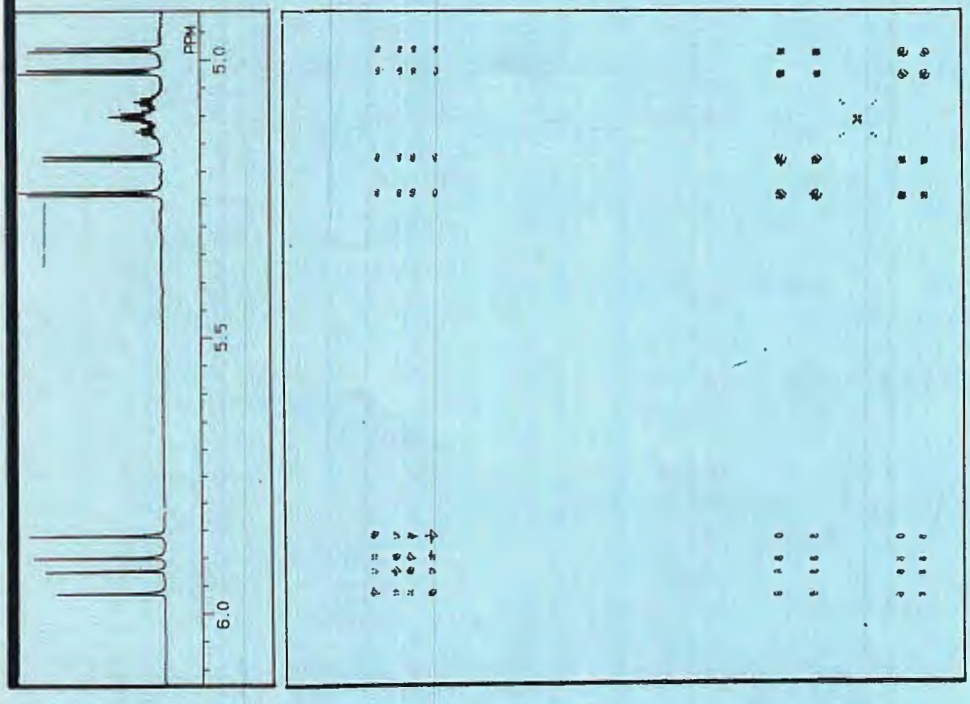

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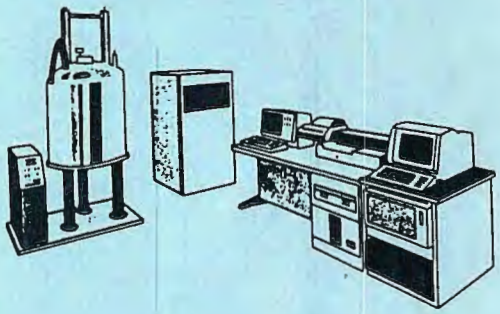

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