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NO. 328

JANUARY 1986

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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is *not* permitted, except by direct arrangement with the author of the letter, and the material quoted *must* be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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#### FORTHCOMING NMR MEETINGS (Additional listings are solicited)

British Radiofrequency Spectroscopy Group - April 9-11, 1986; Oxford University, Oxford OX1 3QR England; see Newsletter No. 323, p. 23.

27th ENC - April 13-17, 1986; Hilton Hotel, Baltimore, Maryland; see page 8 and Newsletter No. 323, p. 31.

8th Rocky Mountain Regional Meeting - June 8-12, 1986; Denver Convention Complex, Denver, Colorado; Meeting Chairman: William E. Beard, USDA-ARS, P.O. Box E, Ft. Collins, Colorado 80522.

International Society of Magnetic Resonance (ISMAR), 9th Meeting - June 29-July 5, 1986; Hotel Gloria; Rio de Janeiro, Brazil. Chairman: N.V. Vugman, Federal University of Rio de Janeiro, Rio de Janeiro, 8razil.

U.S.-Latin American Workshop on Recent Developments in Organic and Bioorganic NMR - July 7-11, 1986; Campinas, Brazil; see Newsletter No. 323, p. 59.

Federation of Analytical Chemistry and Spectroscopy Societies (FACSS XIII) - September 28-October 3, 1986;
St. Louis, Missouri; Program Manager: Dr. Sydney Fleming, FACSS (Titles), 24 Crestfield Road, Wilmington, Delaware 19810.

1986 Eastern Analytical Symposium - October 6=10, 1986; Hilton Hotel, New York; see Newsletter No. 325, p. 27. ⊕20-⊋H

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

All Newsletter Correspondence Should be Addressed to:

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

#### DEADLINE DATES

No. 330 (March) ----- 28 February 1986 No. 331 (April) ----- 28 March 1986



Department of Physical & Inorganic Chemistry THE UNIVERSITY OF ADELAIDE GPO Box 498, Adelaide SOUTH AUSTRALIA 5001

19 November 1985

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

#### THE LOCATION OF WATER IN POLY(METHYLMETHACRYLATE)

OR

#### NEW USES FOR OLD MAS ROTORS

Dear Professor Shapiro,

Poly(methylmethacrylate) in the glassy state can absorb significant amounts of water. Uptakes of approximately 1% by weight occur when a dried sample is immersed in liquid water at ambient temperatures (D.T. Turner, Polymer 1982, 23, 197).

The presence of water affects the properties of the solid polymer. It acts as a plasticizer, easing restrictions on cooperative motion of segments of the polymer chain causing a decrease in the glass-transition temperature  $T_g$  - the temperature at which the material passes from the glassy to the rubbery state. Water is believed to be responsible directly for another transition at much lower temperatures. This is observed around 200K in dynamic-mechanical measurements at frequencies of 1 Hz.

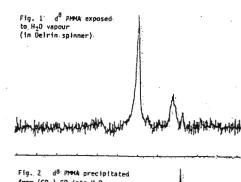
The response of a sample to an applied load at a particular temperature depends on whether the load has frequency components which compensate transitions which are active at that temperature. The presence or absence of water is therefore directly relevant to the mechanical performance of poly(methylmethacrylate).

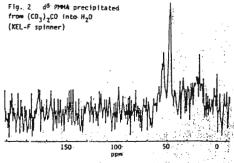
Water uptake by PMMA is reported to occur by two processes: accommodation in pre-existing microvoids, proceeding with an increase in density and no change in dimensions, and swelling with relatively little change in density. In samples examined by Turner, microvoids (i.e. the non-swelling component) accounted for about 50% of the uptake by weight in the early stages, declining to around 40% as the slower swelling process became predominant.

The availability of good  $d^8$  PMMA in the form of superannuated MAS rotors suggested to us that a PE/MAS spectrum of this material swollen with  $^1{\rm H}_2{\rm O}$  could tell us the location of water in PMMA at the molecular level.

After one of our d<sup>8</sup> PMMA MAS rotors suffered during a software failure, rendering it useless for further work, we dissolved

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the remains in  $CDCl_3$  and cast them in a thin sheet. After removing residual solvent, some of the  $d^8$  PMMA was equilibrated with water vapour for 3 months.

Conventional PE/MAS and TOSS and difference spectra were obtained of "wet" and "dry" samples. Only the quaternary, methylene and to a lesser extent,  $\alpha\text{-methyl}$  resonances are visible in the "wet" sample (Fig. 1). The  $\alpha\text{-methyl}$  resonance is present in the "dry" sample and absent from the difference spectrum. It probably arises from proton impurity at this group in the sample of d $^{8}$  PMMA used. Quaternary and methylene resonances are absent from the "dry" sample spectrum and prominent in the difference spectrum.

A further sample of  $d^8$  PMMA was dissolved in  $d^8$ -acetone and carefully precipitated with  $H_2O$ . This yielded (Fig. 2) the same result.

At first sight the result is surprising. One would have expected that dipole-dipole interactions would have an important role in the swollen phase. Yet the experiment shows that the  $^{13}\text{CO}$  and  $^{13}\text{CD}_3\text{O}$  groups are not close enough to  $^{1}\text{H}_2\text{O}$  to show proton-enhanced  $^{13}\text{C}$  resonances. The close contact occurs between  $^{1}\text{H}_2\text{O}$  and the chain backbone carbons  $^{13}\text{CD}_2$  and the quaternary  $^{13}\text{C}$ . The  $\alpha^{13}\text{CD}_3$  is unaffected.

Second thoughts remind us that the structure of condensed phase solutions must be sought in 1:1 and 2:2 as well as 1:2 interaction. In this case component 1 is a preformed glassy phase into which component 2 diffuses. The  $^{13}\text{CO}$  and  $^{13}\text{CD}_3\text{O}$  of the side chain will be largely responsible for chain-chain attractive forces in the glass and it is possible, and in fact likely, in view of our results, that these are not greatly perturbed by the absorption of water, at least in the initial stages.

The detailed structure of the amorphous glassy state of PMMA is unknown, and formally unknowable with available techniques. Our material was atactic with about 60% syndiotactic triad content. Highly syndiotactic PMMA can be crystallized and a detailed structure has been determined. As expected the chains (a loose slow turning helical conformation) are packed to accommodate the non-bonded forces between side chains (both repulsive and attractive). The COOCH3 groups point out from the helix as does the  $\alpha \text{CH}_3$ . Inside the helix there is sufficient space to accommodate solvent molecules in a non-bonded state (H. Tadokoro, *Polymer* 1984 23 148).

If the factors that induce st-PMMA to crystallize in such a form also operate in s-rich at-PMMA, it could be that a loose helical conformation may also occur, not to the extent of perfection to permit crystallization, but sufficient to accommodate water molecules in a molecular mixture with PMMA. This water lies within the coil in intimate contact with the chain backbone carbons remote from the COOCH3 and  $\alpha CH_3$ .

Yours sincerely,

E.H. WILLIAMS, P.E.M. ALLEN & D.R.G. WILLIAMS

P.S. Evan Williams is now with Varian Associates Inc., Palo Alto.

## DEPARTMENT OF CHEMISTRY TELEPHONE 902-424-3305



DALHOUSIE UNIVERSITY HALIFAX, CANADA B3H 4J3

November 19, 1985

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

Dear Barry:

Re: Scalar Coupling Constants in CO and  $N_2$ 

Because the only isotope of oxygen with spin is a quadrupolar nucleus ( $^{1}$ 0, I=5/2) direct measurements of scalar coupling constants involving oxygen are rare (1). For small molecules such as CO, CO, and N\_0 oxygen-17 relaxation times are relatively long thus permitting direct measurement of J(C,0) (2) and J(N,0) (3). In the case of dinitrogen ( $^{1}$ N,  $^{1}$ N) we were unable to measure J( $^{1}$ N,  $^{1}$ N) directly because the coupling constant is small and nitrogen-14 (I=1) relaxation is extremely efficient, however an indirect measurement is possible (4). Experimental results on CO and N\_2 are important because they are the simplest molecules for which one expects both the orbital and spin-dipolar mechanisms to make significant contributions to the observed J. Unfortunately, we do not have the sign of any of these coupling constants; hopefully future MO calculations will shed some light on this problem (5).

Molecule	<u>Scalar Coupling Constant</u> (magnitude)
· CO .	$J(^{13}C,^{17}0) = 16.4 \pm 0.1 \text{ Hz}$
000	$J(^{13}C,^{17}0) = 16.1 \pm 0.1$
NNO	$^{1}$ J( $^{15}$ N, $^{17}$ 0) = 50.8 $\pm$ 2.8
	$^{1}$ J( $^{15}$ N, $^{15}$ N) = 8.6 $\pm$ 0.2
NN	$J(^{15}N,^{14}N) = 1.8 \pm 0.6$

A point which may not be obvious to readers unfamiliar with gas phase nuclear relaxation is that nmr line widths in the gas phase are generally much broader than those in solution (6). The above data was obtained from measurements of each gas dissolved in CDCl<sub>3</sub>.

Our next contribution will deal with recent results obtained on our new MSL-200.

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Yours sincerely,

Rod

Rod Wasylishen

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NE-M10 513-5PP	Compatible with vortex plugs and coaxial inner cells.	203	13.00	12.50	11.75	
NE-H10 513-7PP	100 MHz and up: Research, FT applications. Compatible with vortex plugs and coaxial inner cells.	178	14.25	13.75	13.00	
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#### **DEPARTMENT OF HEALTH & HUMAN SERVICES**

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Locating a Spectrometer for In Vivo Spectroscopic and Imaging Studies.

November 19, 1985

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

Dear Barry:

We have recently installed a Bruker Biospec 1.9 T/310 mm NMR spectrometer for in vivo spectroscopic and imaging studies. The placement of such an instrument obviously constitutes a lesser problem than the installation of whole body instruments, which are frequently housed in specially constructed buildings. Nevertheless, there are a variety of safety considerations - e.g., restricting those with pacemakers beyond the 5-gauss limit, keeping metal objects from the magnet, and last and perhaps least, the protection of credit and other magnetic cards - which require that the NMR laboratory be carefully designed. Our solution to these problems may be of interest to others who are comtemplating the installation of such a system.

The magnet-containing "inner sanctum" (Figure 1, A), has non-functional doors, and can only be entered through a "court-yard" (B). A warning about the potential dangers is attached to the door to B, and that door, C, is generally locked, with keys available only to knowledgeable personnel. At the entrance to B there is a cabinet, D, with lockable compartments into which credit cards and magnetic objects carried in people's clothing can be placed. B is used for work with animals and various studies complementary to the work carried out in A. Access to A is through a set of swinging doors, E, which are also provided with warning signs. Our building contains a core facility that provides services to the laboratories and is attached to the rear walls of the laboratories. Only authorized personnel are permitted in the core; and, since part of the core is within the >5-gauss region, the door to the core (F) is also provided with a warning against entry by those with pacemakers.

Gunther L. Eichhorn

Rajasekharan P. Pillai

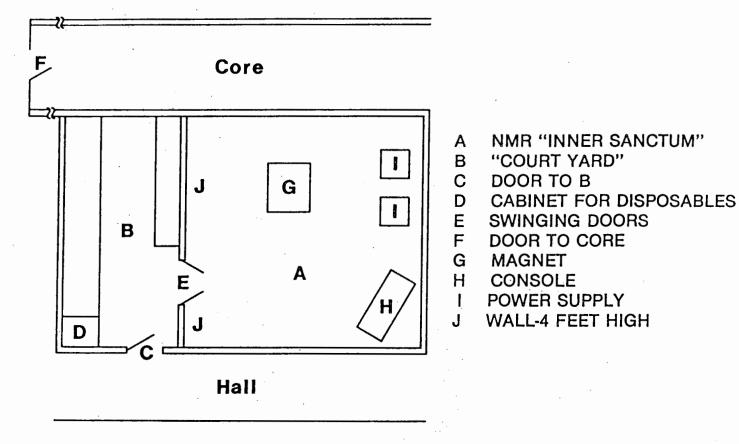


Fig. 1

ENC Inc.

Twenty-seventh Nuclear Magnetic Resonance Spectroscopy Conference Baltimore, Maryland, April 12-17, 1986

December 11, 1985

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

Dear Barry:

Re: 27th Experimental NMR Conference

I wish to bring to the attention of the NMR community a small error in the mailing for the 27th ENC. The dates on the letterhead were indicated as April 12th through the 17th. The 12th is a Saturday and there are no scheduled events for Saturday the 12th. The conference will begin with registration as usual Sunday afternoon with the first session being Monday morning. People not receiving registration materials by this time may request them from Dr. P.M. Henrichs, Eastman Kodak Company Research Laboratories, Rochester, NY 14650, telephone 716-477-6229.

Sincerely,

Robert G. Bryant Dean's Professor

RGB/an enc.

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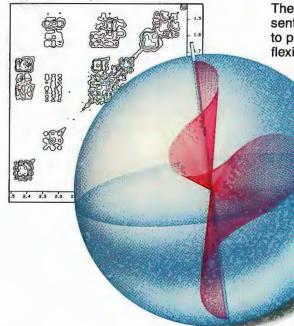
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Professor BERNARD SHAPIRO

Dept of Chemistry

TEXAS A & M University

College Station - Tx 77843 - U.S.A.

26 November 1985
MONTEDIPE/PM/CER
Stab. Petrolchimico
Via della Chimica
30175 Porto Marghera
(Venezia) Italy

Dear Professor SHAPIRO,

1H NMR spectra of bisglycidylether of bisphenol A and their interpretation as a function of temperature.

We report the structure of the bisglycidylether of bisphenol (A).

The  $^1\text{H}$  NMR spectra of (I) were obtained from 7.3  $^{10^{-2}}$  M CDCl $_3$  solutions using a WP 80 sy BRUKER FT spectrometer at 80 MHz, in the temperature range -50° to 50°C. Examining the spectra, the resonance groups are found in the following spectral range.

Table 1

T/°C = 29.1

<sup>1</sup>H c.s. (ppm)

TMS = 0

$$\delta$$
 CH<sub>3</sub> = 1.63

 $-C$  (CH<sub>3</sub>)  $\frac{1}{2}$ 
 $\delta$  CH<sub>2</sub> = 2.67 ÷ 2.93

 $\frac{H}{H}$ 
 $C = \frac{H}{O}$ 
 $C = \frac{H}{H}$ 
 $C = \frac{H}{O}$ 
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FOGLIO N.

From the spectral analysis of the 5 spin system we obtained tha data reported in Table 2.

		Table 2	(Hz)			
T/°C	$\boldsymbol{\nu}$ (1)	<b>v</b> (2)	$\boldsymbol{v}$ (3)	$\boldsymbol{\nu}$ (4)	$\boldsymbol{\nu}$ (5)	
- 50.2	240.945	227.953	276.685	310.682	343.533	
- 27.5	237.980	225.226	273.685	312,479	340.236	•
29.1	230.001	218.149	265.890	315.590	333.546	
50.0	228.997	217.187	264.532	317.635	332.149	
	<b>⊿ v</b> (1)	<b>△v</b> (2)	$\Delta v(3)$	<b>△V</b> (4)	<b>△v</b> (5)	•
	- 11.95	- 10.77	- 12.15	6.95	- 11.38	
T/°C	J (1.2)	J (1.3)	J (2.3)	J (3.4)	J (3.5)	J (4.5)
- 50.2	4.700	4.296	2.674	6.250	2.756	- 10.802
- 27.5	4.818	4.189	2.737	6.033	2.959	- 10.833
29.1	4.956	4.050	2.576	5.549	3.438	- 11.074
50.0	5.005	3.998	2.645	5.431	3.499	- 11.134
	<b>∆</b> J (1.2)	<b>∆</b> J (1.3)	<b>∆</b> J (2.3)	<b>∆</b> J (3.4)	$\Delta$ J (3.5)	<b>∆</b> J (4.5)
	+ 0.305	- 0.298	- 0.029	- 0.819	+ 0.743	- 0.332

As it can be seen in table 2, the resonance frequencies  $\nu(1)$ ,  $\nu(2)$ ,  $\nu(3)$  and  $\nu(5)$  shift towards high fields with the temperature, while the frequency  $\nu(4)$  shifts to low fields.

All the coupling constants change very little with temperature except J (3.4) and J (3.5) which change (in opposite directions) by about 1 Hz, because of the free rotation of the  $CH_2O$  group with respect to the oxyrane rigid group.

The frequencies and the J constants obtained from the spectral analysis of the aromatic part of the molecule are independent of temperature changes (being rigid systems). By using the equation of KARPLUS-CONROY (1):

 $J^3$  = A+B cos  $\Phi$  + C cos 2  $\Phi$  for the vicinal coupling constants, at the dihedral angles related to the constants J (1.3) and J (2.3) versus temperature can be obtained. Table 3 reports the values of the dihedral angles thus calculated.

In view of possible band deformations, only the dihedral angles lower than  $90^{\circ}$  have been selected for each value of J and temperature.

		Table 3
T/°C	$\Phi_{13}$	$\Phi_{23}$
- 50.2	57.88°	71.68°
- 27.5	58.63°	70.97°
29.1	59.64°	72.84°
50.0	60.02°	72.01°

The spacial configuration of the epoxy group can be obtained from these data. The vicinal coupling constants J (3.4) and J (3.5) should be considered average values because of the free rotation around the bond  $C \longrightarrow C \longrightarrow C$ 



FOGLIO N.

The populations  $p_A$ ,  $p_B$ ,  $p_C$  of the different rotamers have been calculated by means of the equation system:

$$J(3.4) = J_G(p_A + p_B) + J_T p_C$$

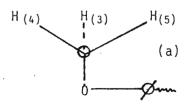
$$J (3.5) = J_G (p_A + p_C) + J_T \cdot p_B$$

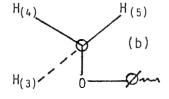
$$p_A + p_B + p_C = 1$$

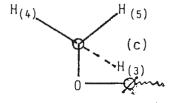
where

$$J_T = 13$$
 and  $J_G = 4.0$  (1;2)

The rotamers labelled with (letters) a, b, c are:







From calculations related to this system it results that  $p_B \simeq 0$ , and table 4 is obtained.

Table 4

$T^{-1} \times 10^{3} (K^{-1})$	РА	РС	$log_{10} p_A/p_C$
4.485	0.750	0.250	0.4771
4.071	0.774	0.226	0.5346
3.308	0.828	0.172	0.6825
3.094	0.841	0.159	0.7234

By applying the Arrhenius plot to  $\log_{10}~p_A/p_C$  versus 1/T, it has been found that the thermodynamic  $\Delta H$  is equal to 0.82 Kcal mole<sup>-1</sup>.

#### References: .

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#### Sincerely yours

G. GURATO Cy. Gurato R. PERNICE

M.F. COLETTA \*
W.P. Lolette

\* Centro di studio sugli stati molecolari radicalici ed eccitati, (presso DIPARTIMENTO DI CHIMICA FISICA dell'Università) via Loredan 2, PADOVA.



#### ISTITUTO SUPERIORE DI SANITA' VIALE REGINA ELENA, 299 - 00161 ROMA

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

Roma, 19 Novembre 1985 Telegrammi: ISTISAN - ROMA Telex RM071 ISTISAN

Uptake and metabolism of glucose 6-phosphate in experimental tumors. A 31-P NMR study.

Dear Prof. Shapiro,

Friend erythroleukemia cells (FLC) - derived from committed erythroid stem cells rendered leukemic by infection with Friend virus - form solid tumors when injected s.c. in syngeneic mice.

These tumors, indistinguishable from undifferentiated reticulosarcomas, represent an interesting experimental system, thanks to the histopatological homogeneity of the tumor mass (1).

<sup>31</sup>P NMR spectra of these tumors, freshly excised from mice, exhibit resonances in the phosphodiesters (glycerophosphorylcholine and glycerophosphorylethanolamine), as well as in the frequency range of phosphomonoesters signals (2,3). Analysis of either ethanolic or PCA tissue extracts indicated that the latter signals are essentially due to phosphorylethanolamine (PEtn), phosphorylcholine (PCho) and AMP. Sugar phosphates are instead practically below detection or give only minor contributions to the spectral profile in this region.

In order to assess the feasibility of  $^{31}\text{P}$  NMR in monitoring pool sizes of glycolytic intermediates (4) in experimental tumors, 0.2 ml of glucose 6-phosphate (G-6-P, 2% w/v) were injected in vivo in FLC tumors. The latter were then isolated from the animals at various times (5-30 min) after injection of the substrate.

Analyses of ethanolic tissue extracts indicated that:

a) G-6P was taken up by the tumor cells in vivo and converted into products of the Embden-Meyerhoff pathway, mainly fructose 6-phosphate (F-6-P), and fructose 1,6-bisphosphate (F-1,6-P).

b) 10 minutes after injection, the peak areas of F-6-P and F-1,6P signals amounted altogether to about 85% of the total area of G-6-P peaks ( $\beta$  and  $\alpha$ anomers).

c) The pool sizes of G-6-P and its glycolytic products all decreased below detection levels 30 minutes after G-6-P injection.

This work is partially supported by CNR Special Projects Biomedical and Clinical Engineering n. 84.02129.57 and Oncology n. 84.00730.44. Thanks are due to M. Giannini and B. Santurbano, for their technical assistance.

Yours sincerely,

Franca Podo fule Carpuell' Nuemo Di beto

F. Podo, G. Carpinelli, M. Di Vito, G. D'Agnolo,

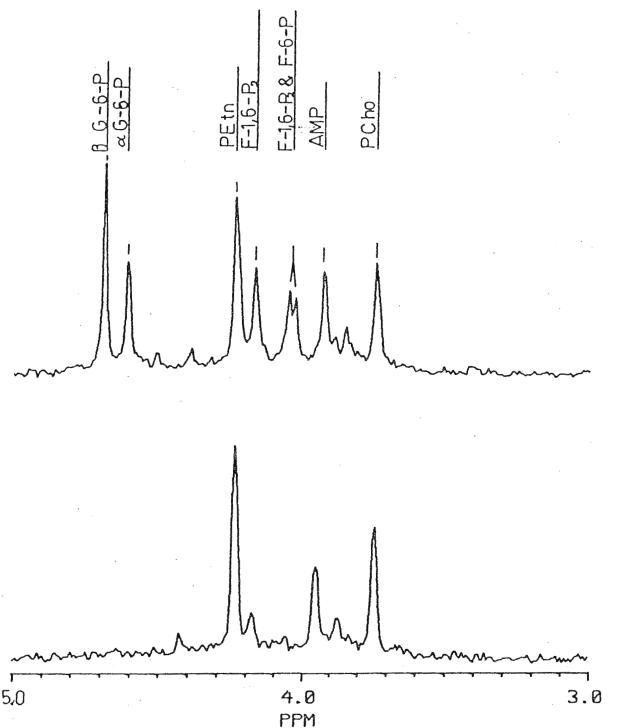
L'Proietti, F. Belardelli,

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Pigure 1. <sup>31</sup>P NMR spectra (161.9 MHz) of a) ethanolic extract (pH=7.0) of FLC solid tumors freshly excised from DBA/2 mice, 12 days after implantation; b) ethanolic extract (pH=6.9) of tumors grown as in a) 10 minutes after intratumoral injection of glucose 6-phosphate.

Professor Adam Allerhand Department of Chemistry Indiana University Bloomington, Indiana 47405

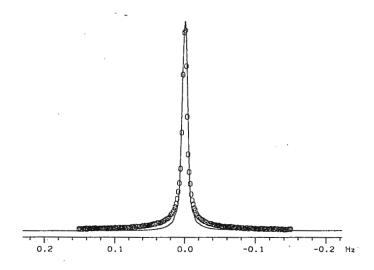
Professor Bernard L. Shapiro TAMU NMR Newsletter Department of Chemistry Texas A & M University College Station, Texas 77843

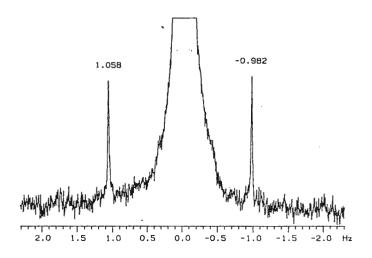
#### RESOLUTION PERFORMANCE OF 200 MHz and 500 MHz SYSTEMS

Dear Barry:

This contribution is evidence of my desire to renew my subscription to TAMU NMR Newsletter.

I have recently reported the development (1-3) and applications (4) of "ultra-high" resolution NMR. Specifically, I have obtained an instrumental linewidth at half-height (W, ) of as little as 7 mHz in <sup>13</sup>C NMR at 50 MHz ("200 MHz" instrument), in a standard old 12-mm probe with a sample volume of 4.2 mL. Here I wish to point out that my recently published results at "200 MHz" are already obsolete, because the newest results in a 10-mm probe from Cryomagnet





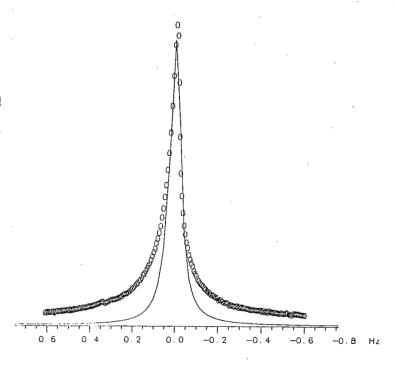
Systems, Inc. yield  $W_i = 3$  mHz, and greatly improved linewidths at 0.55% and 0.11% of maximum peak height (5). Also, I'd like to report some very preliminary and promising results about resolution on 500 MHz systems.

The top spectrum on the preceding page shows the proton decoupled C-1 resonance of air-free toluene (with 20% v/v CD<sub>3</sub>OD), 3mL sample, under argon at 21.2 °C and 50.3 MHz, in a 10-mm probe, after one scan with a spectral width of  $\pm 50$  Hz (quadrature detection), and 64K total data points. No digital line broadening or narrowing was applied. Fourier transformation was done with an additional 64K of "zero fill" data points, resulting in a simulated acquisition time of 655.36 s, which yielded a digital resolution of 1.526 mHz. The hexagons are experimental points, and the curve is the best-fit Lorentzian to the top 8 points. The best-fit width at half-height is 7.7 mHz. However,  $T_1$  measurements yield  $1/\pi T_1$  = 4.6 mHz, so that the upper limit to  $W_1$  is 3.1 mHz.

From the standpoint of practical applications, a W<sub>in</sub> of 3 mHz is probably not much more useful than 10 or 20 mHz. However, the new 10-mm probe also exhibits impressive performance at 0.55% and 0.11% of peak height, and this will have practical applications in detection and study of minor components. The bottom spectrum on the preceding page also shows the proton-decoupled C-1 resonance of air-free toluene, under the same sample and spectral conditions as the top spectrum, except that 4 scans were used, and 4.0 mHz Lorentzian digital line broadening was applied. The main peak is truncated at 1.1% of its peak height. The satellite peaks at about ±1 Hz are long-range J satellites (4). The observed linewidth at 0.55% peak height is 0.58 Hz, out of which 0.46 Hz is contributed by the instrument (5). The observed linewidth at 0.11% peak height is 1.3 Hz, out of which 1.0 Hz is contributed by the instrument (5). These instrumental contributions are an order of magnitude smaller than typical specifications of instrument manufacturers.

I believe that the above performance is readily achievable on most "200 MHz" and "300 MHz" NMR spectrometers, after minor instrument modifications (1-3).

However, it is also of interest these days to establish the resolution performance of "500 MHz" systems, which are becoming increasingly available in many organizations. Recently I had the opportunity to spend a day at the controls of a GN-500 at General Electric NMR. One day is certainly not enough time to climb up the "learning curve" of an unfamiliar new apparatus. However, the results are most encouraging. The spectrum shown on this page is the 13C resonance of the carbonyl of acetone (with 20% v/v cyclohexane- $d_{12}$ ), recorded in a 10-mm probe at 30 °C. The observed line



-width at half-height is 61 mHz. The value of  $1/\pi T_1$  is about 15 mHz, so that we have here an instrumental contribution of about 45 mHz. Actually, another spectrum (not shown) yielded W<sub>1</sub>  $\lesssim$  40 mHz. Manufacturers specify 200 mHz. The observed widths at 0.55% and 0.11% were 4.5 and 9 Hz, respectively, which compare favorably (but not impressively so) with manufacturers' specifications of 6 and 15 Hz, respectively (GE-NMR), or 7 and 12 Hz, respectively (Bruker).

The above results were obtained on an unmodified GN-500. I have reason to believe that, with slight changes, instrumental contributions can be lowered to 20 mHz or less at half-height (10-mm <sup>13</sup>C), 1.5 Hz at 0.55%, and 3 Hz at 0.11%. If this prediction becomes reality, "500 MHz" systems can become "ultra-high" resolution NMR spectrometers. Please stay tuned.

Sincerely,

Adam Allerhand Professor of Chemistry

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Los Alamos

Los Alamos National Laboratory Los Alamos New Mexico 87545 December 13, 1985

Off-Line Processing of NMR Spectra

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

Dear Prof. Shapiro,

We have been interested in off line processing of NMR spectra for a while. We have acquired the software from George Levy, et al at Syracuse Univ. for data manipulation on a VAX which works quite well once some local problems were solved. Our problem was we have three Bruker spectrometers and until recently, the software for data transfer from an ASPECT to a VAX was inelegant or nonexistent. We finally got transfer programs from Syracuse which were supposed to work and after some local debugging, thought that we might really be able to transfer data. We then encountered some strange difficulties related to the transfer protocols.

First, we are located approximately 3 miles from our VAX 11-780 as the crow flies but probably closer to 10 miles as the telephone cables run. We would like to have multiple ports to the VAX for transfering data, processing data, scientific computations, and some other computer graphics. Our solution to the communication problem was to install a single two-pair "leased line" between our building and the VAX. (We actually had to have the telephone company check several pairs until we got a line which was relatively noise free.) We use a "Codex" synchronous modem running at 9600 baud at either end for data transmission. We have installed a Micom Micro 800/2 multiplexer/data concentrator at either end, this accomplishes the asychronous to syncronous conversion, gives us 8 lines multiplexed on the single physical line, and presumably concentrates data such that we get faster transmission when there are multiple users. This all sounds great but we found that some FID's would hang the transmission up. We think that the problem is in the Syracuse transfer protocol. The 24 bit ASPECT word is broken into three eight bit bytes which are transmitted to the VAX and then reassembled. Occasionally in a data set we were encountering a control character which was stopping either the multiplexer or the VAX. We thought that we had defeated all of the XON/XOFF protocols so were quite frustrated by the problem. Finally, we decided to rewrite portions of the software such that we break the ASPECT 24 bit word into four 6 bit units rather than the three 8 bit ones. To each 6 bit word, we add 100 (octal). This assures that all characters are in eight bit printable ASCII code. These characters are then transmitted to the VAX, the two most significant bits are masked off, the 4 "words" are recombined into a 24 bit word which then happily goes into the NMR1 software. The main disadvantage is that we have to transmit 4 bytes per ASPECT word rather than 3. In principle, this slows down the data transmission by 33%, but a slow data transmission is lots better than a flakey one.

The transfer software does not allow the use of "wildcard" characters so the transfer of multiple files can be quite cumbersome and wasteful of operator time. ASPECT Pascal and ADAKOS make it difficult to implement wildcards so we have figured out how to use an IBM-PC as an intelligent terminal to supervise the transfer of multiple one dimensional files.

Finally, we have attempted to compile and run the transfer programs on an ASPECT 3000 computer. Unfortunately, we get runtime errors in the compilation of the Pascal routines and the documentation of the ASPECT Pascal routines is insufficient to allow us to easily decipher the problem. Since we are able to easily transfer spectra or FID's from our two ASPECT 2000A computers, and we can move disk packs from the 3000 to the 2000A, we decided that it was not worth spending any more time rewriting software.

Unfortunately, the transfer software is proprietary to Syracuse University so we cannot pass the code on to other users.

Sincerely,

Beat H. Meier

William L. Earl.

Bed Mare

Bill

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE,
CB2 1EW
TELEPHONE (0223) 66499

13 December 1985

Professor B L Shapiro Department of Chemistry Texas A and M University College Station Texas U S A

Dear Barry

#### NMR of Asparagine in Potatoes

The antiquarian booksellers of Cambridge have presented me with a petition. They ask that all future NMR meetings which you attend should be relocated here ......

Seriously though, let us turn to food. The flavour and keeping qualities of crisps (chips to you) depend, among other things, on the concentration of free asparagine. There are tedious GC/MS assays of asparagine, but we have stumbled on a neat NMR trick which enables us to see asparagine in pieces of raw potato tissue.

We have been using NMR to monitor the metabolic response of a variety of tissues to \$^{13}\$C-formaldehyde. In the course of this work, my graduate student Ralph Mason carefully sliced some potatoes into the spectrometer and obtained the spectra opposite. The top spectrum demonstrates that formaldehyde is metabolised to formate and methanol [an almost ubiquitous pair of reactions] and gives an extra compound resonating at 55 ppm. It soon became apparent that this is the cyclic adduct of asparagine, as shown. Glutamine is present in similar concentrations (i.e. several mM) but the adduct, being a seven membered ring, is less stable and is not formed to any significant extent. So, we have an in situ asparagine assay, although I make no claims for great precision.

The most important lesson from this is that it demonstrates that one can infiltrate a labelled reagent into plant cells and make a specific labelled adduct with an unlabelled naturally-occurring compound of

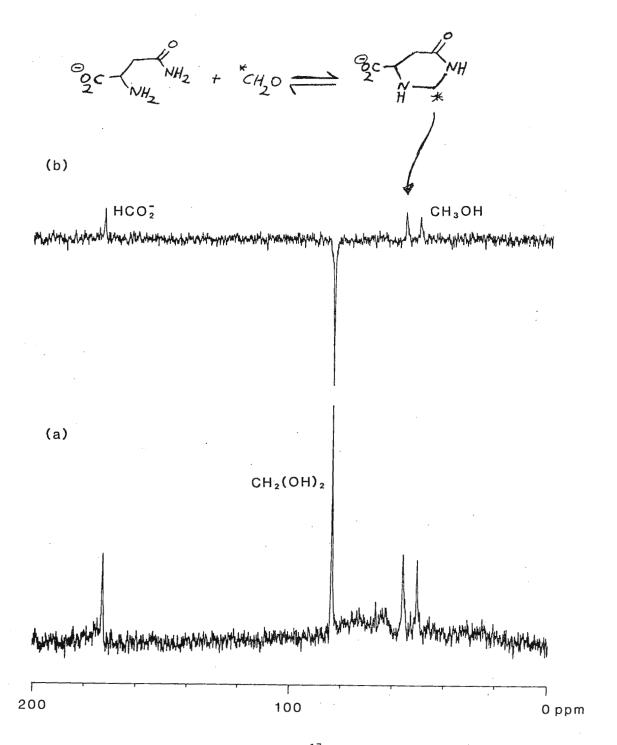


Figure: (a) 100.6 MHz proton decoupled <sup>13</sup>C spectrum of a core of potato tissue (Maris Bard) after 8 hours exposure to 10 mM [<sup>13</sup>C] formaldehyde at pH 7. 1000 transients were acquired during 35 minutes, and 10 Hz exponential line broadening was applied. The broad background signals arise from potato components. (b) Difference spectrum obtained by subtracting a spectrum acquired during the first hour of formaldehyde exposure from the '8 hr' spectrum. The potato background has disappeared and it is clear that growth of signals is accompanied by loss of formaldehyde.

interest. The adduct, with its characteristic spectroscopic properties can then report on the concentration of the species of interest. This concept is widely used in radioimmunoassay, and has been applied to the NMR assay of  $\text{Ca}^{2+}$  in animal cells. Our crisp and dry report on this potato work will be published in Phytochemistry in mid-86.

With best wishes

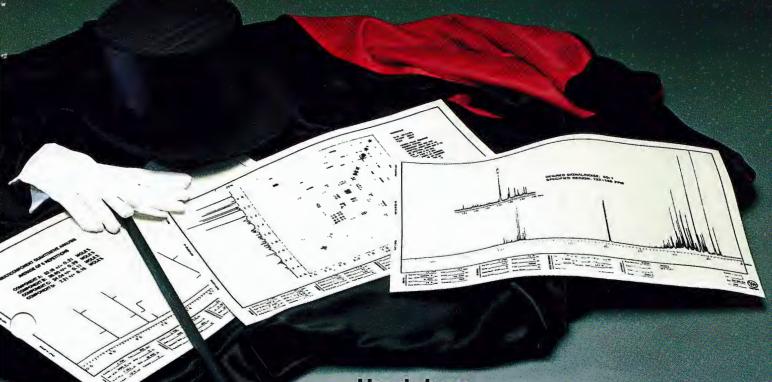


#### Dr J K M Sanders

- 1. R.L.M. Synge, Potato Research, 1977, 20, 1.
- 2. G.A. Smith et al., P.N.A.S., 1983, 80, 7178.
- 1. Please go forward with this splendid idea; 2. Arrange for me to stay in the Master's Lodge at Queens'.

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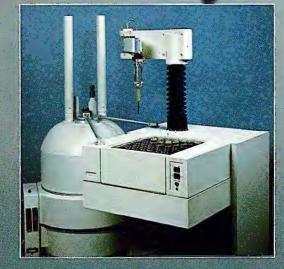


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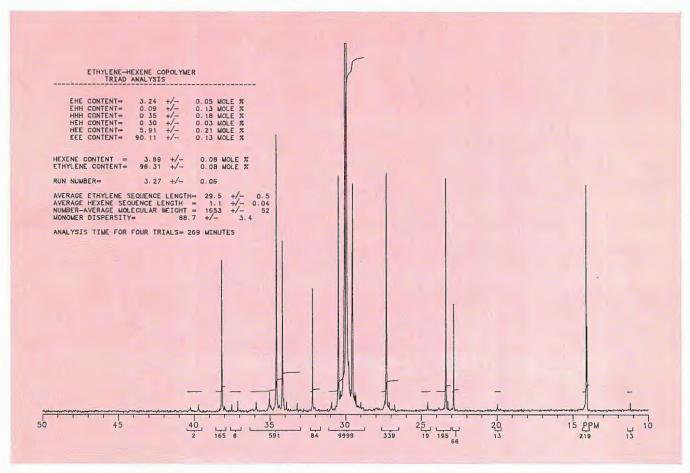


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Telephone 401-863-2587. If you don't have spare probes, but know someone who might, please send the name, address, etc.

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Professor Bernard L. Shapiro
TEXAS A&M UNIVERSITY
Department of Chemistry
COLLEGE STATION, TEXAS 77843-3255
U.S.A.

Uw kenmerk

Uw brief van

Ons kenmerk 851000/CWH/nk

Datum November 20, 1985

Onderwerp

Spinlabeled oligonucleotides and gene-5 protein

Dear Professor Shapiro,

For some years we have been interested in the interaction between double helix destabilizing proteins and DNA in particular in the interaction between the gene-5 protein encoded by the M13 phage and DNA.

In our earlier NMR studies we have shown by means of NOE experiments that aromatic residues of the protein, i.e. a tyrosyl and a phenylalanyl residue are involved in the interaction with DNA (1). To be able to give a further description of the DNA binding groove of the protein we have performed NMR experiments on the protein combined with a spinlabeled oligonucleotide. Upon binding of this spinlabeled oligonucleotide to the protein, broadening of resonances from residues in the DNA binding groove is expected. A neat example demonstrating the selectivity of the linebroadening induced by the spinlabel is shown in the Figure below.

In Figure A and B the aromatic part of the protein spectrum before and after addition of 1/50 equivalent of 5' spinlabeled d(A)<sub>3</sub> is presented. As a result of the addition of the spinlabel the signals from Tyrosine I are bleached out of the spectrum to a significant extent, while the resonances of Phenylalanine I are only marginally affected. They do however exhibit the shifts expected upon oligonucleotide binding (1). The difference spectrum presented in Figure C demonstrates that no other resonances are affected. Interesting conclusions can also be drawn for the aliphatic part of the spectrum (not shown).

It is often assumed that DNA binding proteins bind with a fixed orientation to DNA. In general this assumption is hard to prove. By means of spinlabeled oligonucleotide polar binding can be demonstrated, because 3' and 5' spinlabeled oligonucleotide.



#### FACULTEIT DER WISKUNDE EN NATUURWETENSCHAPPEN

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KATHOLIEKE UNIVERSITEIT NIIMEGEN

Geadresseerde

Prof. B.L. Shapiro

Ons kenmerk

851000/CWH/nk

Datum

November 20, 1985

Blad No

-2-

nucleotides are expected to exhibit reversed broadening in case of polarity of the binding.

(1). N.C.M. Alma, B.J.M. Harmsen, J.H. van Boom, G.A. van der Marel and C.W. Hilbers (1983). Biochemistry 22, 204. 2104

C.W. Juli

Prof. Dr. C.W. Hilbers

Sincerely Yours,

Dr. B.J.M. Harmsen

Drs. E.A.M. de Jong

The effect of 5' spinlabeled d(A), upon the aromatic resonances of the M13 gene-5 protein. spinlabel: 4-hydroxy TEMPO, coupled to the oligonucleotides via a phosphodiester bond. (for further explanation see text)

Phonylalanine I

C

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December 5, 1985

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

Title: Use of 2D NMR for Chemical Shift Assignments in Benzoxazine Derivatives

Dear Barry,

In the course of some studies of benzoxazine derivatives with Professor Harold Heine of Bucknell University we obtained the C NMR spectrum of the compound shown in the Figure. Carbon atoms c and d had chemical shifts between 80 and 90ppm with two peaks for each arising from the presence of amide isomers. In order to unequivocally assign the H and C spectra we obtained the 2D correlated spectra (H,H and H,C) shown. We assumed the proton resonances at highest field (5ppm) were due to the vinyl ether protons b and b'. From these assignments, the resonances for a, c and d (and the other isomers a', c' and d') could be identified. All coupling constants were consistent with the assignments.

Examination of the C-H correlation spectrum (B) enabled us to determine that the lowfield pair of peaks between 80 and 90ppm (d,d') are due to the carbon atom between nitrogen and oxygen whereas the resonances labelled c and c' belong to the carbon between oxygen and the vinyl carbon.

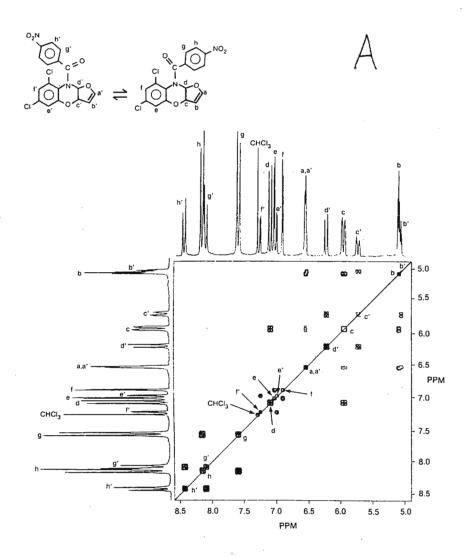
Both spectra were obtained on our XL-200. We would like to acknowledge the participation in this work by Helen Feng, a summer student on leave from New York University School of Medicine.

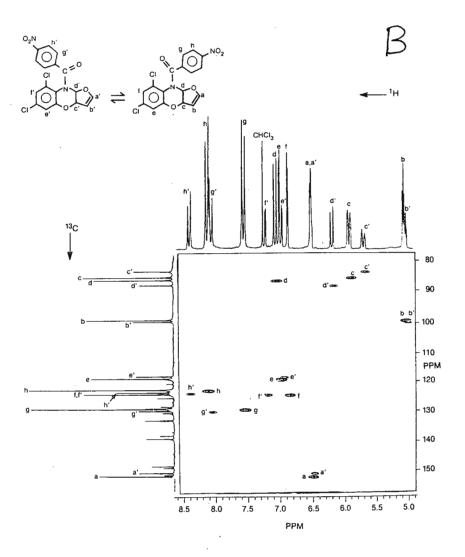
Sincerely,

Paul Donahue

Johnne Smith

Liz Williams







Deift University of Technology

#### Department of Chemical Engineering and Chemistry

P.O. Box 5045 2600 GA Delft, The Netherlands Julianalaan 136 2628 BL Delft, The Netherlands University switch board: (015) 789111 Telex 38151 bhthd nl

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

Your reference and date

Our reference

Office telephone

Date

JAP/mk

(015) 78 5892

November 21, 1985

Subject

Sub-division

A structure elucidation with the use of lanthanide induced shifts

Laboratory of Organic Chemistry

Dear Professor Shapiro,

Recently, we isolated a compound of which the structure is either 1 or 2. As a result of their great similarity, it was impossible to

discriminate unambiguously between these structures on the basis of coupling constants. Moreover, in both structures the nitro group is in the proximity of a bulky group and, consequently, it is not lying in the plane of the benzene ring. Therefore, a prediction of chemical shifts using the increments documented in literature was impossible.

We have spent quite a lot of spectrometer-time with unsuccessful attempts to solve this problem with the use of INADEQUATE. The one dimensional version gave C-C coupling constants, but the C-C connectivity could not be determined since the differences between some of the coupling constants were not large enough. The 2D version failed because the signal-to-noise ratio was still too low after an accumulation time of a weekend.

Finally, we could solve the problem in just one hour with the use of <sup>1</sup>H NMR and a lanthanide shift reagent. Upon addition of Eu(fod)<sub>3</sub> two of the aromatic protons show about equal (large) downfield induced shifts, whereas the induced shift of the remaining aromatic proton is relatively small (Figure 1). The association constants of Eu(fod)<sub>3</sub>-adducts of alcohols are much higher than those of nitro compounds. Therefore, in this case Eu(fod)<sub>3</sub> coordinates preferentially to the OH-function. The induced shifts thus show that the structure of the isolated compound is 1. A comparison of the Eu(fod)<sub>3</sub> induced shifts of this compound with those of compound 3 (Figure 2) supports this conclusion.

Sincerely yours,

A.J. Hoefnagel

J.A. Peters

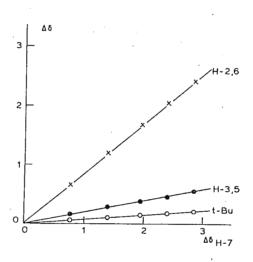


Fig. 1. The effect of addition of Eu(fod)<sub>3</sub> to a sample of 1 or 2 in CDCl<sub>3</sub>; the lanthanide induced shifts of H<sub>7</sub> versus those of the other protons.

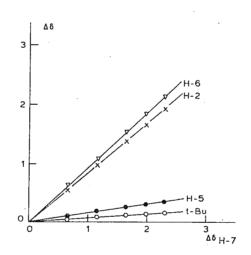


Fig. 2. The effect of addition of Eu(fod)<sub>3</sub> to a sample of 3 in CdCl<sub>3</sub>; the lanthanide induced shifts of H<sub>7</sub> versus those of the other protons.

Orchard Park PO Box 332 Danbury CT 06810 Telephone: 203 796 2500

November 22, 1985

#### "Cimarron"

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

Dear Barry:

The importance of molecular motions to NMR relaxation has been known since the early days of NMR, and for some time relaxation rates and their field dependence have been used to characterize motions. Often, being able to predict the value of  $T_1$  may yield valuable insights as to motional sensitivity or optimum acquisition parameters.

I have written a PASCAL program ("Cimarron") that may be of some interest to fellow resonators, which calculates liquid state  $T_1$ ,  $T_2$ , NOE and cross relaxation rates for dipolar relaxation, and  $T_1$  rates and linewidths for quadrupole relaxation. The user is prompted for the field, tumbling rate, relevant X-H bond length or QCC, and motional models. The program currently supports 6 internal motional models, including two, three, and four site exchanges, free and restricted diffusion, and the immobilized case. The spectral densities are based on the work of Attila Szabo and Bob London and their co-workers, and the relevant references are included in the source code. A listing of the program will be provided by request, of all but the graphics part of it, which uses an IBM software product (GRAPHICS, P/N 6273648). Cimarron is not that user friendly, and as usual, the results are only as good as the model assumed, but it still may serve as an unuseful tool.

Attached is a sample output. Please credit this account to Tom Mattone.

Sincerely,

3

Robert D. Johnson

/ejk

(continued on page 35.)

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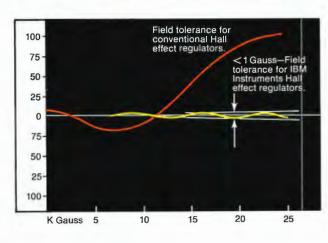
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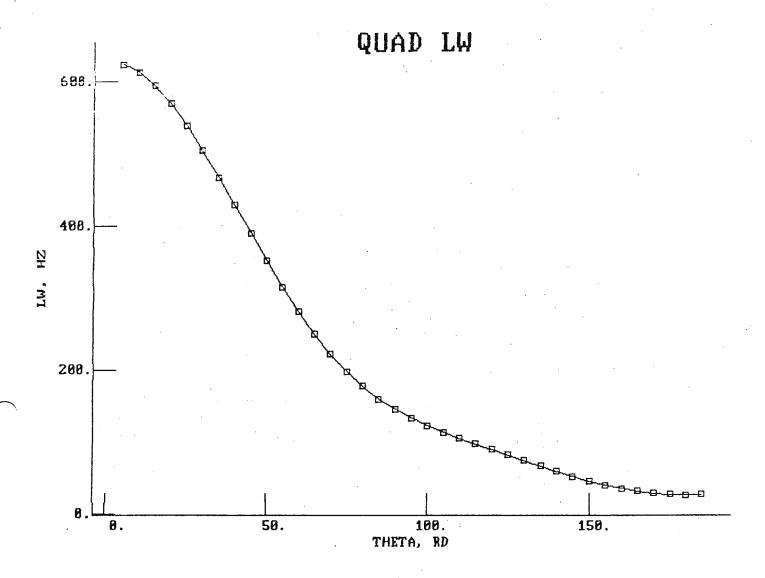
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(continued from page 32.)



Deuterium Quadrupolar Linewidth  $T_{m}=\ 11 ns,\ QCC=\ 190\ kHz,\ v_{D}^{}=\ 55\ MHz$  Restricted Diffusion Model, with the angle between the axis of internal motion and the CD bond = 116 degrees.



#### The University of Arizona

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

1985

November 22, 1985

A Proud Beginning

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

Dear Barry:

13C NMR STUDIES OF SEQUENCE DISTRIBUTIONS IN 1-SUBSTITUTED POLY-1,3-(BICYCLOBUTANES)

Last year we had a paper dealing with the stereochemistry of poly(bicyclobutane-1-carbonitrile). It was of interest that the 13C chemical shifts of nitrile functions provide a general probe of cis/trans

stereochemistry in cyclobutanecarbonitriles, but we could not provide a quantitative explanation of the nitrile and backbone resonances. More recently, we (Mr. Y. H. Mou and Dr. Ray Chan) examined the spectra of some other poly-1,3-(bicyclobutanes) and found "text-book" examples

**PBBC** 

of triad and tetrad sequences which were consistent with Bernoulli statistics. Re-examination of PBBC (Fig. 1) removed all of the ambiguities. The quaternary carbon exhibited partial tetrad structure, and removed the anomalous integral of the nitrile resonance at 121.79 ppm. For brevity we include only the CN results in the attached table. The dyad ratio 0.32:0.68 is obtained from the quaternary 13C resonances.

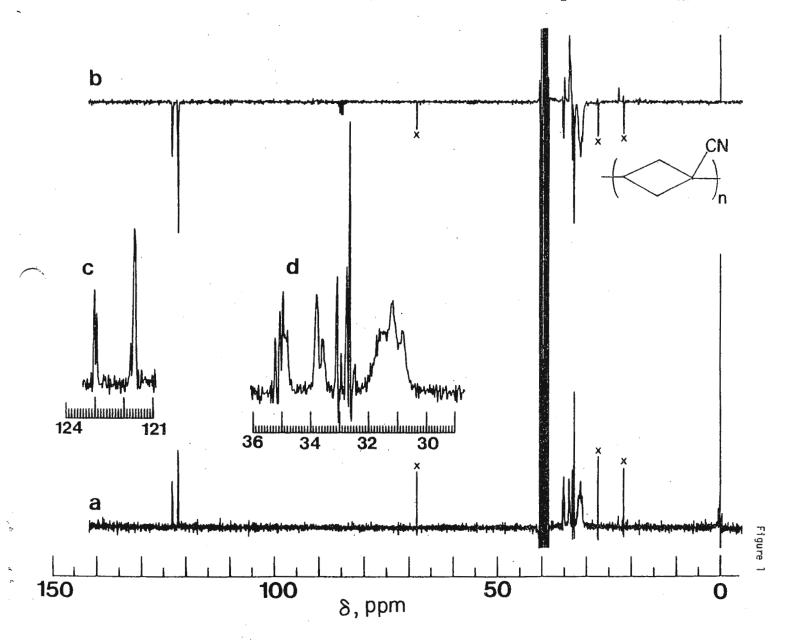
Sincerely yours,

Mike Barfield

Table I. Carbon-13 NMR Chemical Shifts of PBBC Compared with those of the Four Trimers, and Fractions of Tetrad, Triad and Dyad Sequences

Carbon C <sub>i</sub>	δ(trimer) ppm	Sequence (tetrad)Triad	δ <sub>i</sub> (PBBC)	PBBC Integrals		Ring-Enchai Triad	nment Dyad
CN	123.32 (123.12)	(t) <u>tt</u>	122.95	0.31	(0.03) (0.07)	0.10(0.10)	
	123.11 (123.02)	(t)ct } (c)ct	123.04	0.74	(0.03) (0.07) (0.07) (0.15)	0.23(0.22)	0.32
	121.93	(t) <u>tc</u> (c) <u>tc</u> }	121.79	0.26	0.08(0.07)	•	
	121.79	(t) <u>cc</u> (c) <u>cc</u>	121.66	1.96	(0.15) (0.15) (0.31)	0.60(0.61)	0.68

Figure 1. (a) The 62.90 MHz <sup>13</sup>C NMR spectrum of free-radical initiated poly(bicyclobutane-1-carbonitrile) PBBC in Me<sub>2</sub>SO-<u>d</u><sub>6</sub>. (b) A pseudo-INEPT spectrum of the ring carbon resonances. (c) An expansion of the nitrile resonances, (d) Expansion of the ring carbon resonances. The scales below the spectra are in ppm down-field of internal Me<sub>4</sub>Si. Impurities are designated with an x.



 M. Barfield, L.-F. Kao, H. K. Hall, Jr., and L. G. Snow. <u>Macromolecules</u>, 17, 240 (1984).



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November 19, 1985

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

Dear Barry:

Fourier transforms are now routinely done in both NMR and IR spectroscopy (to cite the most everyday examples). Much of what is done in this routine work is to simply convert from a time-domain program or an interferogram into a more readable frequency-domain spectrum--without actually knowing what is going on during the calculation.

For pedagogical purposes, I have written an easy-to-use program which allows one to take Fourier transforms of a large number of functions (both built-in and user-supplied). The functions studied can be either ordinary FID's, frequency spectra, or any of a large number of things such as square waves, ramps, triangular waves, etc.

In using this program, one can also combine functions via addition, subtraction, multiplication, and/or division.

All results can be plotted or stored on disk in numerical form. A sample plot is enclosed. System requirements are an IBM PC (256K minimum) or compatible, a color monitor, and a dot matrix plotter such as an Epson.

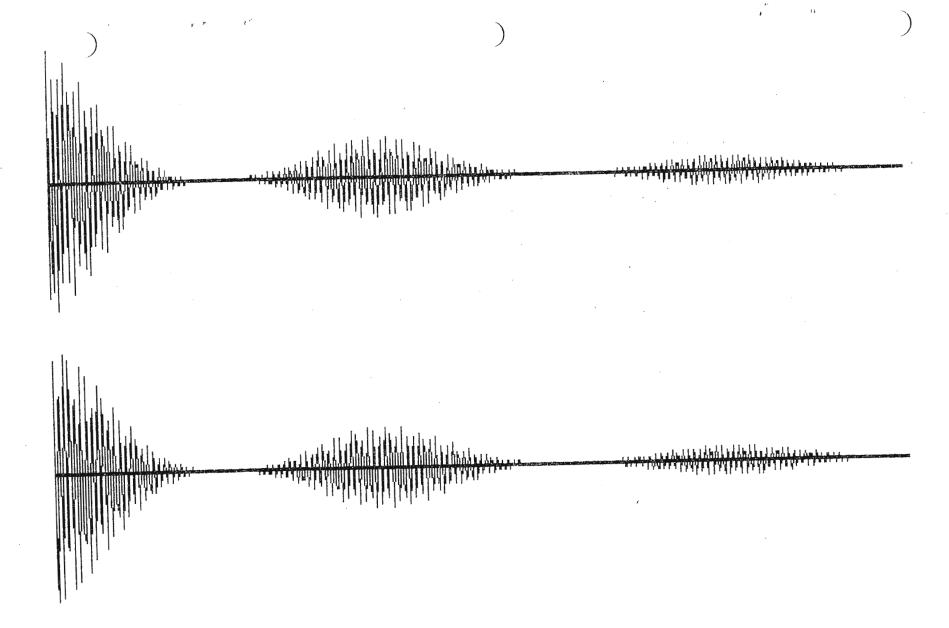
Anyone desiring this program is welcome to a copy provided <u>I receive a DS/DD disk and a self-addressed disk mailer along with sufficient postage to send the disk back!</u> Documentation is included on this disk.

Sincerely yours,

Milton D. Johnston, Jr.

Associate Professor

Suggested title: FFTUTOR



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DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING GATES AND CRELLIN LABORATORIES OF CHEMISTRY JOHN O. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

November 20, 1985

Dr. Barry Shapiro, Editor/Publisher TAMU NMR Newsletter Department of Chemistry Texas A&M University College Station, Texas 77843-3255

Dear Barry:

Solid-State Carbon-13 NMR of Ascorbic Acid

For a number of reasons, we have been interested in the NMR of ascorbic acid but much of what we have been doing has already been anticipated by the elegant work of Stefan Berger.

One very pleasing development has been the coming-on line of the solidstate NMR in the Southern California Regional Facility which utilizes a Bruker 200-MHz solid-state spectrometer operating at 50.3 MHz for carbon-13.

The carbon-13 cross-polarization spectrum of crystalline ascorbic acid taken with this spectrometer at a spinning rate of 4.65 KHz is shown in Figure 1.

The resolution is seen to be excellent and the shifts generally close to those of ascorbic acid dissolved in water. Of particular interest is the fact that there is a doubling of several peaks notably that of C3, but also discernible of C4 and C6.

The explanation of the doubling is simple, there are two molecules in the unit cell of ascorbic acid (cf. Hvaslef, <u>J. Acta Cryst.</u>, **B24**, 23 and 1431 (1968)) which differ mostly in differences in the rotational angle around the C3-C4 bond.

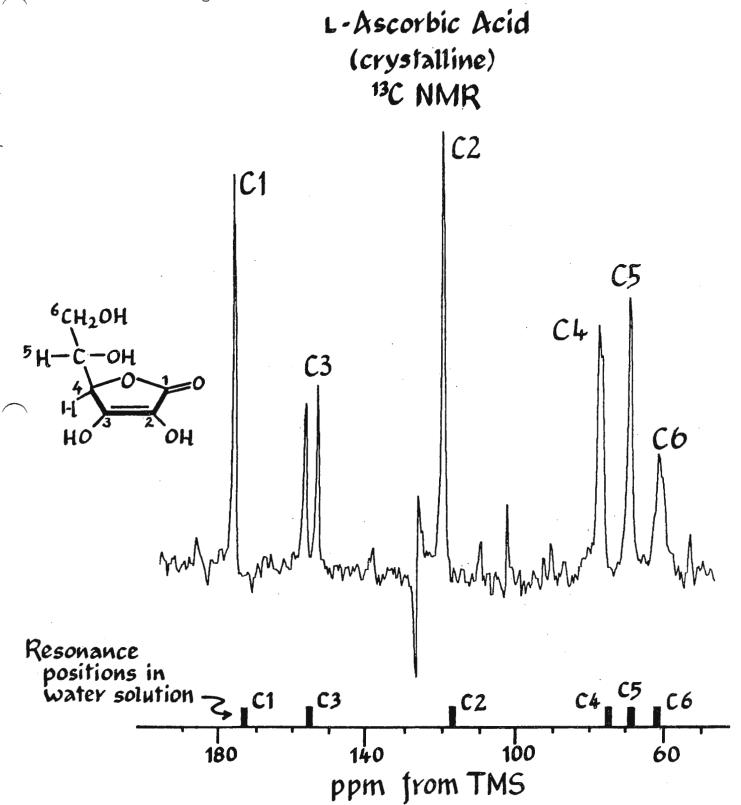
With all good wishes,

Very truly yours,

ames P. Yesinowski

John D. Pohents

Figure 1



#### UNIVERSITY OF GUELPH

COLLEGE OF PHYSICAL SCIENCE Department of Chemistry and Biochemistry

GUELPH, ONTARIO, CANADA - N1G 2W1 Telephone (519) 824-4120



November 28, 1985

Dr. Barry Shapiro
Texas A & M University NMR Newsletter
Department of Chemistry
Texas A & M University
COLLEGE STATION Texas 77843
U.S.A.

Title: 13C NMR Studies of Scandium and Yttrium Binding to Adriamycin

Dear Barry:

We have been investigating the binding of lanthanides to the antitumor antibiotic adriamycin (c.f. I) in water and in methanol. From our analysis of the lanthanide perturbations in the Yb(III) and Pr(III) complexes of adriamycin by 1H NMR, we have determined that Pr(III) and Yb(III) bind to the C12, C11 oxygen atoms, (J. Amer. Chem. Soc. (1984) 106, 6905). In a continuation of this study, we investigated the binding of S (III) and Y(III) to adriamycin by  $^1$ H and  $^{1.3}$ C NMR. Yttrium has one magnetically active isotope of spin  $\frac{1}{2}$  (100%) although direct observation of the nucleus is difficult in dilute solutions owing to the long T<sub>1</sub> value. <sup>1</sup>H 2DJ resolved experiments of the Y(III)-adriamycin complex in methanol indicated that more than one type of metal complex had formed. We also observed 89Y-1H scalar couplings in the 'H spectrum to the aromatic protons of adriamycin (H1, H2). In order to further characterize the binding of yttrium and scandium to adriamycin, we looked for perturbations in the 13C spectrum of adriamaycin, particularly in the aromatic region. Figure 1 shows a series of 13C spectra of adriamycin in DMSO with varying amounts of Y(NO3)3 or  $S_{1}(NO_{3})_{3}$  added. It can be clearly seen that the pair of peaks assigned to the C11 and C6 carbons of adriamycin split into doublets. These probably represent diamagnetic shifts in the complex (B,C,D). It is interesting to note that the doublet at 188 ppm (C12, C5) does not undergo any perturbation. Spectra E and F are 13C spectra in which different amounts of  $S_0(NO_3)_3$  were added. It is clear that  $S_0(NO_3)_3$  produces large perturbations in the aromatic region which are distinct from those produced by  $Y(NO_3)_3$ . We are in the process of analyzing these perturbations in more detail.

Yours truly,

T.IM: bb

R.E. Lenkinski

I.J. McLennan

(continued on page 45.)

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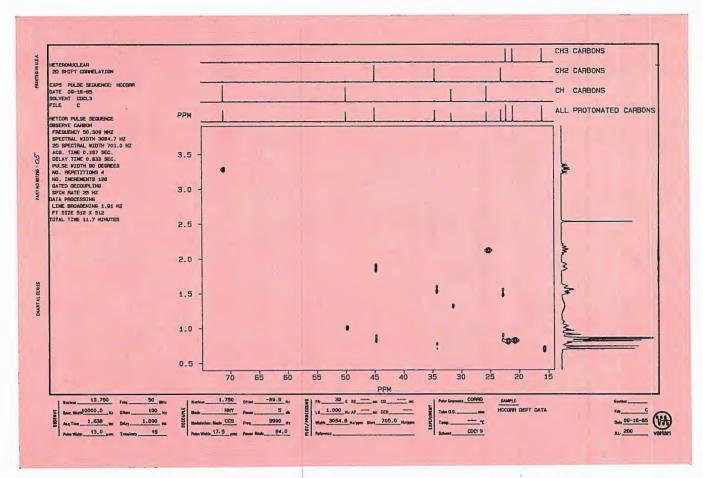


Varian Instrument Group, 220 Humboldt Court,

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For the carbon experiment, where sensitivity is more of a problem, the signal-to-noise ratio was checked periodically during the course of the experiment, and the acquisition terminated when a preselected signal-to-noise ratio was reached. Using this number of scans as a guide, conditions were then chosen for the DEPTGL experiment, and that series of spectra was then acquired and automatically combined (spectral editing) to produce subspectra containing, respectively, protonated carbons, CH carbons, CH<sub>2</sub> carbons, and CH<sub>3</sub> carbons.

With 1D spectral information in hand, MAGICAL next determined the minimum spectral width for the heteronuclear correlation experiment for both protons and carbons (using protonated carbons only, as determined from the DEPTGL experiment). The rest of the 2D parameters were also optimized based on the 1D experiments, and the 2D experiment was then acquired, processed, scaled, and plotted. From start to finish, the entire series of experiments required only 22 minutes. This time will, of course, vary from sample to sample, because the MAGICAL analysis is not "canned," but adapts to the requirements of each particular sample.

Write or call Varian today to learn how you can achieve these results. Write **MAGICAL NMR**, Varian MarCom, 220 Humboldt Court, Sunnyvale, CA 94089 or call **800-231-5772**.

#### (continued from page 42.)

Figure 1. <sup>13</sup>C NMR spectra of adriamycin in DMSO obtained at 100.62 MHz with two level broad band <sup>1</sup>H decoupling, (pulse repetition rate 3 seconds), number of acquisitions 6000. The peaks denoted by "X" are Quad Images. The pair of peaks denoted by "O" are resonances corresponding to the C11 and C6 carbons of adriamycin.

A. 50 mM adriamycin;

B. 50 mM adriamycin with 11 mM Y(NO,), added;

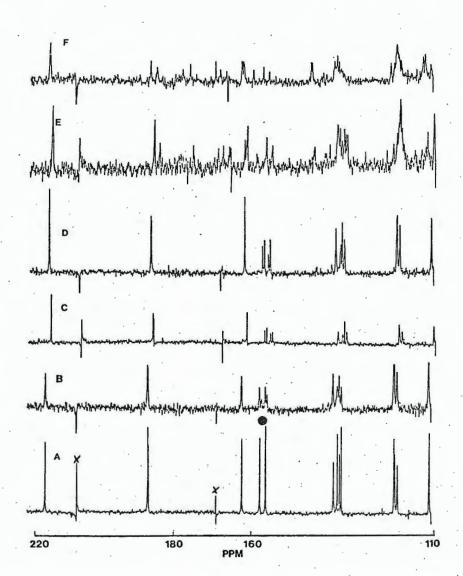
C. 50 mM adriamycin with 24 mM Y(NO,), added;

D. 50 mM adriamycin with 41 mM Y(NO,), added;

E. 72 mM adriamycin with 20 mM  $S_c(NO_3)$ , added;

F. 50 mM adriamycin withh 20 mM  $S_c(NO_s)$ , added.

The spectra are not all plotted with the same vertical display.





VRIJE UNIVERSITEIT

VAKGROEP FYSISCHE EN THEORETISCHE CHEMIE Sectie Fysische Chemie

SUBFACULTEIT SCHEIKUNDE

1081 hv amsterdam de boelelaan 1083

telefoon 020 - 548

Professor Dr. B.L. Shapiro Department of Chemistry Texas A & M University College station TEXAS 77843 U.S.A.

uw kenmerk

uw brief van

ons kenmerk

datum

bijlage(n)

December 11, 1985

onderwerp

A Caveat Concerning "Super High Resolution" Spectroscopy. The NMR Spectrum of Indene Revisited.

Dear Dr. Shapiro,

An "extremely high resolved" <sup>1</sup>H NMR spectrum of Indene (fig. 1) at 270 MHz has been published in the literature <sup>1</sup>). The NMR parameters (chemical shifts and indirect coupling constants) were communicated with 3decimal places and the stated accuracy of the J couplings was 0.001 - 0.003 Hz.

It is the purpose of this letter to draw attention to the fact that partial orientation of the molecules by the magnetic field of the spectrometer may occur and that, if this happens, the experimental line positions can be modified substantially. Corrections should then be applied to the J couplings, which, in the present example, may be much larger than the quoted accuracy. These corrections depend on the interproton distances as  $r^{-3}$ ; hence, J couplings between neighbouring nuclei are particularly subject to errors.

The partial orientation mentioned above results from the interaction of the anisotropic magnetic susceptibility with the external magnetic field. An order of magnitude estimate of the corrections to be made, can readily be given. For this purpose, consider a molecule giving rise to an AX-spectrum. If the molecule is partially aligned, the apparent doublet splitting in the AX-spectrum is no longer given by J, but by J + D. Here D is the dipolar coupling due to incomplete averaging. It can be shown that<sup>2</sup>)

$$D = -\frac{\gamma_A \gamma_x h}{2\pi^2 r^3} \left[ (3/2 \cos^2 \alpha - 1/2) < 3/2 \cos^2 \theta - 1/2 >_{B_0} + 3/4 (\sin^2 \alpha \cos 2\beta) < \sin^2 \theta \cos 2\phi >_{B_0} \right]$$

In this expression r is the internuclear distance,  $(\theta,\phi)$  are the polar angles of the laboratory z'-axis with respect to the molecular axes system;  $(\alpha,\beta)$  are the polar angles which the internuclear vector  $\vec{r}$  makes with the molecular frame (fig. 2). The other symbols have their usual meaning.

In the above formula it is assumed that the magnetic field  $B_0$  is along the laboratory z'-axis and that the molecular frame coincides with the principal axes system of the magnetic susceptibility. The angles  $\theta$  and  $\phi$  are, of course, time dependent on account of the Brownian motion. The corresponding angular functions should therefore be averaged, thereby taking into account the interaction of the susceptibility with the field  $B_0$ . This is denoted by angular brackets <.....> $B_0$ . From Boltzmann statistics it follows: $\frac{2}{\theta}$ 

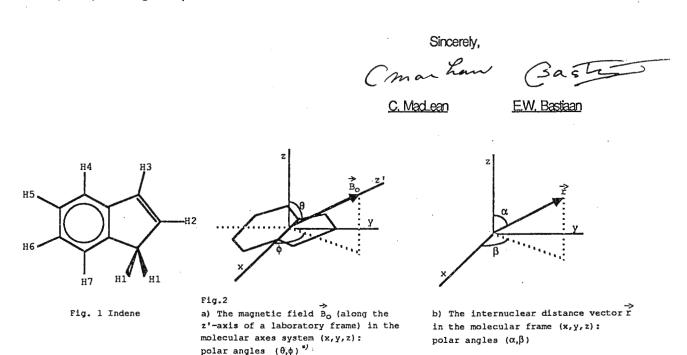
$$<3/2 \cos^2 \theta - 1/2 >_{B_0} = \Delta \chi B_0^2 / 15 kT$$
  
 $<\sin^2 \theta \cos 2 \phi >_{B_0} = \delta \chi B_0^2 / 15 k$ 

The quantities  $\Delta\chi = \chi_{ZZ}$  - 1/2  $(\chi_{XX} + \chi_{YY})$  and  $\delta\chi = \chi_{XX}$  -  $\chi_{YY}$  are called the anisotropy and the asymmetry of the magnetic susceptibility, respectively. Usually the molecular axes are chosen such that  $|\Delta\chi| > |\delta\chi|$ . Returning to Indene now, an estimate of the magnetic field induced dipolar couplings requires susceptibility data. Unfortunately these are not available for Indene, but for Naphthalene<sup>2)</sup>  $\Delta\chi = -2.0 \times 10^{-28}$  emu,  $\delta\chi = 0.0 \times 10^{-28}$  emu and for Benzene<sup>3)</sup>  $\Delta\chi = -1.0 \times 10^{-28}$  emu (here  $\delta\chi = 0$  because of axial symmetry). As an approximation, assume  $\Delta\chi = -1.5 \times 10^{-28}$  emu and  $\delta\chi = 0.0$ , making <3/2  $\cos^2\theta - 1/2 >_{B_0} \approx 10^{-6}$ . Since in planar molecules  $\alpha = 1/2 \pi$ , the order of magnitude of D is given by

$$D = \frac{\gamma_A \gamma_X h B_o^2 \Delta \chi}{60\pi^2 r^3 kT}$$

Substituting  $B_0 = 6.35 \times 10^4$  gauss (spectrometer frequency of 270 MHz for protons),  $r = 2.5 \, \text{Å}$  (e.g. protons 5 and 6; see fig. 1) and the above value of  $\Delta \chi$ , one finds D = -0.008 Hz. This result illustrates that apparent J couplings are prone to substantial errors. The corrections to the quoted 1) J couplings thus far exceed the accuracies stated, except for long-range couplings between protons that are widely separated.

The effects mentioned above can be circumvented by measuring the spectra at different fields (note that D varies with the square of B<sub>0</sub>). Alternatively, dipolar line splittings can be measured, from which the susceptibility anisotropy and asymmetry can be obtained. The limitations discussed above thus open up exciting new possibilities<sup>2</sup>).



\*) N.B. For simplicity the x and y principal axes of  $\chi$  are assumed as indicated in the diagram.

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## UNIVERSITÀ DI MILANO ISTITUTO DI BIOCHIMICAE DI CHIMICA

VIA CELORIA, 2 20133 MILANO TEL. (02) 293.662 Wilano, December 12, 1985

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

Transient NOEs and Conformational Properties of 2-Phenylbenzodioxanes

Dear Barry,

Both NOE and relaxation time measurements can in principle be used to determine interproton distances for organic compounds in solution. The use of steady-state NOE to obtain quantitative results becomes often difficult, when the number of the interacting spins is high, because not all the necessary NOE effects can be measured with a sufficient accuracy. On the other hand T measurements are too much affected by other than dipolar relaxation contributions, arising for instance from chemical exchange, paramagnetic substances, etc. In addition the complete elimination of oxygen from the solutions is always difficult. For transient NOEs all these problems are less severe. Thus we applied this method to the 2-phenylbenzodioxanes in solution.

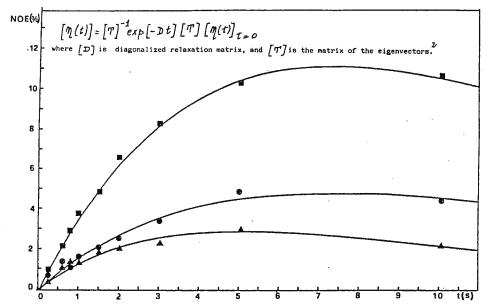
I 
$$R = R' = R'' = Me$$

II  $R = Me$   $R' = R'' = H$ 

III  $R = i-Pr$   $R' = R'' = H$ 
 $R''' = OMe$ 
 $R''' = OMe$ 
 $R''' = OMe$ 

I, II and III are model compounds for some sweet substances, one of which (450 times sweeter than saccharose) was synthesized in our laboratories. The importance of the three-dimentional shape of biologically active substances is well known. In this particular case, the internal motions defining the molecular geometry in solution are the inversion of dioxane ring and the rotation of phenyl group around C(2)-C(1') bond. For the three compounds the preferred conformation (85-90%) of dioxane ring is the half chair  $H_2$  with equatorial substituents (calculated from  $J_2$ , and model dioxanes). The motion of the phenyl group in I is strongly hindered, but in the case of II and III free rotation is apparently possible. In addition the simmetry of the phenyl group implies equal populations for the rotamers with torsion angles  $\mathcal{Y}=H(2)-C(2)-C(1')-C(6')$  and  $\mathcal{Y}+180^{\circ}$ .

NOE experiments were carried out by selective inversion of single resonances. The experimental points were fitted to the biexponential equation reported on the figure, through a non-linear least-squares procedure by using a "two-spin approximation". This method was shown to give a good estimate of the cross-relaxation rates  $\delta$  (reported in the table), which carry the structure information, but a less satisfactory values of the relaxation rates  $\rho$ . The



Experimental transient NOEs on H-2 ( • ), H-3 ( • ) and 5'-Me ( • ) following inversion of H-6' for I in acetone-d<sub>6</sub>. The selective inversion was obtained with a 25 ms decoupling pulse. Relaxation delay 30-40 s, average duration of an experiment of 8 to 10 data points about 10 hours.

I			II		
irr.	obs.	ر <sub>ij</sub> (s <sup>-1</sup> )	irr.	obs.	$\sigma_{ij}^{\prime}$ (s <sup>-1</sup> )
2'-Me	H-2	0.0388 <u>+</u> 0.0004	H-6'	H2	$0.0190 \pm 0.0010$
2'-Me	H-3	0.0035 <u>+</u> 0.0010	H-6'	H-3	0.0095 <u>+</u> 0.0007
2'-Me 5'-Me	H-3' H-6'	$\begin{array}{cccc} 0.0297 & \pm & 0.0009 \\ 0.019 & \pm & 0.001 \end{array}$		•	III
H-6'	H-2	0.0090 <u>+</u> 0.0005	H-6'	H-2	0.0317 <u>+</u> 0.0011
H-6'	H-3	0.0209 <u>+</u> 0.0003	H-6'	H-3	$0.0179 \pm 0.0009$
H-6'	5'-Me	$0.0079 \pm 0.0005$			

ratios of  $\delta$  parameters gave the ratio of the averaged interproton distances  $\langle t_{ij}^{-6} \rangle / \langle t_{ij}^{-6} \rangle$ , from which the preferred orientation of the phenyl group was calculated, by using a geometrical simple program developed in our laboratory which takes into account the ring inversion.

In the case of I a preference for rotamers with torsion angles  $\mathcal{V}=145^{\circ}\pm20^{\circ}$  was found. Actually a conformational analysis performed with the geometrical program and with the aid of Dreiding models showed that the less hindered structures lie in the range  $140^{\circ}\pm\mathcal{V} \leq 170^{\circ}$ . In both dioxanes II and III the free rotation has been excluded, and rotamers with angles  $120^{\circ}\pm\mathcal{V} \leq 170^{\circ}$  are preferred.

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Evro Ragg

Profy Rosanna Mondelli

## BRISTOL-MYERS COMPANY PHARMACEUTICAL RÉSEARCH AND DEVELOPMENT DIVISION P.O. Box 4755 • Syracuse, N.Y. 13221-4755

December 6, 1985

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

Dear Professor Shapiro:

#### INTERFERENCE BETWEEN 360 MHz CONSOLES

To initiate our subscription to the TAMUNMR Newsletter, I would like to describe our facility and discuss a (temporary) solution to an interference problem between two consoles operating at the identical frequency.

At Bristol-Myers' Syracuse Pharmaceutical Research and Development facility we have two high field 360 MHz instruments; a Bruker WM360 wide-bore (about 4 years old) and a newer Bruker AM360. The WM360 is equipped for Pt  $^{9}$ 5 {N $^{14}$ 8} experiments. The AM360 is set up for maximum throughout, having a Satellite station for simultaneous processing and plotting, and a sample changer.

The initial interference problem was due to the close proximity of the two instruments (in adjacent rooms) and either poor shielding on the WM360 decoupler The acquisition of normal proton spectra on the AM or on the AM360 preamp. console is not possible during BB proton decoupling on the WM360. Indeed, even homonuclear decoupling on the WM console resulted in observing "birdies" in the spectra on the other console. High power (6H or less attenuation) decoupling will completely swamp the receiver on the AM console. The same conditions in the opposite direction result in similar but much less intense effects. discussions with Bruker, we concluded that our situation was far from unique. When effective operation of the laboratory was hindered by this interference and attempts to achieve a solution to the problem were initiated, it became apparent that several possibilities were available. The most direct solution seemed to be to change the 10 MHz clock frequency by a small increment thereby changing all derived frequencies. In our particular system, the master 10 MHz oscillator is located within the PTS synthesizer. Upon consideration, it was concluded that this solution would seriously complicate the frequency calculations. experimentation a much simpler and, in hindsight, more obvious solution presented itself. The lock'frequency was shifted to the next lower sideband. The lock receiver sensitivity is about 30% less on the lower sideband but is still quite sufficient for CDCl2. The offset frequency is 43430 Hz greater at the proton frequency and is sufficiently offset to eliminate any interference from the other console. Sensitivity has not suffered due to the weaker lock signal.

We have found this to be an adequate solution in the short term. Because one of our instruments is scheduled to be relocated within six months, we left the "fix" at this stage. However, by modifying the lock receiver board for more sensitivity at the lower sideband a more acceptable and permanent solution could be attained.

Sincerely,

James H. Medley, Ph.D.

James H. M. D.

jmr

cc: R. H. Erlich

S. A. Hanna

B. S. Krishnan

jmr

RESEARCH AND DEVELOPMENT

November 25, 1985 C10 TOSS in Al-27 NMR Wha-6-85

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

Dear Professor Shapiro:

After installing a new Chemagnetics probe in our IBM WP-200, we first examined the Al-27 NMR spectrum of AlCl3.6H20. It was not surprising that the spectrum showed spinning sidebands since Al-27 is a quadrupolar nucleus. However, it was a little surprising to see how many sidebands appeared and their intensity. Since we were spinning at 3.5 KHz already and the spinning system of this probe is only rated for 3-5 KHz, the TOSS sequence quickly came to mind for suppression of these sidebands (1-4). Although this sequence was originally developed for suppression of spinning sidebands in CP/MAS C-13 NMR, this approach is still valid using direct polarization. So with references in hand, we proceeded to the spectrometer.

The spectra obtained (Figure 1) pretty much tell the whole story. Although the TOSS sequence did indeed suppress the spinning sidebands, the necessary delay times employed allowed significant decay of the signal. Relaxation measurements on this sample gave a  $T_1$  of 13.7 s, a  $T_2$  of 1.3 ms and a  $T_1 \rho$  of 7.0 ms. Since one revolution is 0.3 ms, the assumption of  $T_2$  being many revolutions no longer applies (3). From these data it is easy to see the loss of signal from  $T_2$  decay severely limits the application of the multi-pulse sequences to Al-27 NMR. The signal loss for TOSS and other pulse sequences are listed in Table I.

Two other pulse sequences were also examined, TOSS with eight refocussing pulses (4) and a sequence suggested by Hemminga and DeJager which involves two refocussing pulses (5). With the TOSS-8 sequence, we ran into the limitation of the ASPECT 2000 pulse programmer. Using the delays suggested in the reference, this sequence contains over 16 durations all less than 0.2 ms which exceeds the limitations of the pulse programmer. Increasing one of the center delays by 3 revolutions alleviates this problem. However, the necessary increase in acquisition time of 6 revolutions meant waiting until over 95% of the signal decays before turning on the ADC. The resulting spectrum had very poor signal-to-noise and cannot be used to evaluate this TOSS-8 sequence.

The third sequence examined (suggested by Hemminga and DeJager) did not stress any instrument limitations, just that of the researcher. The authors indicate there are only two delay times that need to be determined,  $t_1$  and  $t_2$ . They give the equations necessary to determine these two values; and

although in radians, the equations work very nicely and yield unequivocally  $t_1$  and  $t_2$  for a given spinning speed. However, there is no mention of the delay prior to acquisition. Calculation of this delay following Dixon's method (3) gives a value less than  $t_2$ , meaning the ADC should be activated BEFORE the final pulse. In order for the delay before acquisition to have any meaning, it is necessary to add one revolution to  $t_2$ . This then gives the two pulse values first reported by Dixon, TOSS-2 (3).

Just for fun, we decided to try this sequence with two sets of delays, the first set used a minimum delay between the last 180 and the start of acquisition. As can be seen, the signal is not significantly attenuated and the first order sidebands are indeed suppressed. The second set of delays used the values suggested by Dixon, and the resulting spectrum is similar to the full TOSS spectrum.

This exercise clearly indicates the TOSS sequences have little application in QUANTITATIVE A1-27 NMR, however, they can be used for qualitative information as shown in Figure 2. The spinning sidebands from the tetrahedral component in this zeolite mask the octahedral signal. Use of the DPHJ sequence gives a spectrum with two signals and no spinning sidebands.

Sincerely, Attiplen Whaver

Stephen M. Wharry 144 Petroleum Laboratory

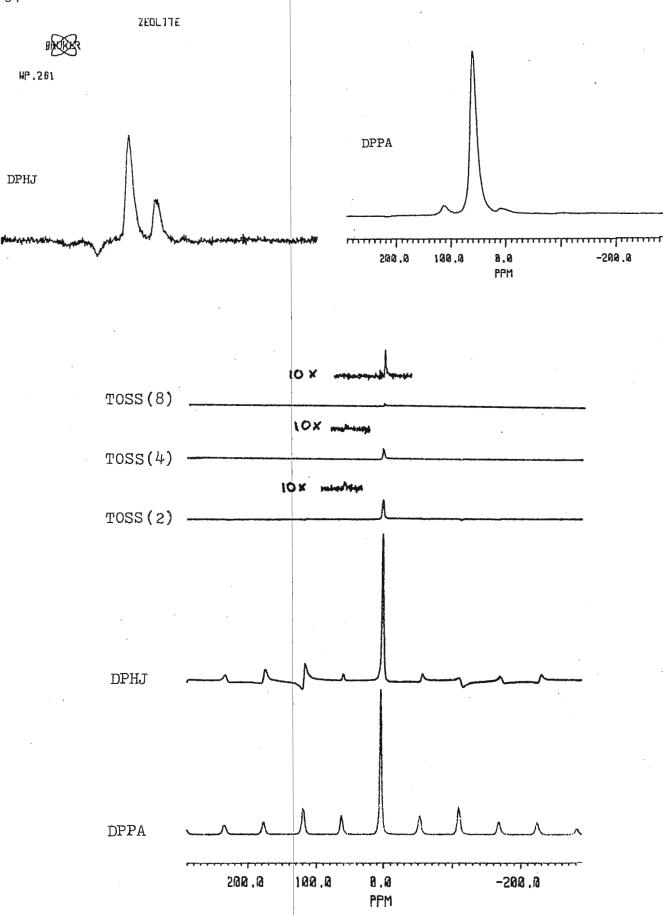
**(918) 661-9793** 

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#### TABLE I

	Signal	Signal/1st ssb
Normal	1,.0	0.13
(DPHJ) <sup>5</sup>	1.0	0.05
(TOSS-2)3	0.13	0.03
(TOSS-4)3	0.08	0.05
(TOSS-8)4*	0.02	<0.1

<sup>\*</sup>Extra revolutions added to relieve pulse programmer indigestion.



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SCHOOL OF PHARMACY DEPARTMENT OF PHARMACEUTICAL CHEMISTRY SAN FRANCISCO, CALIFORNIA 94143

#### A Convenient Book-keeping of peaks in 2D-NMR Spectral Analysis

December 6, 1985

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

#### Dear Barry:

In the process of developing an automatic assignment program for the peaks in protein 2D-NMR spectra, it became necessary to have a list of peaks along with their chemical shifts which can be easily matched with the peaks in the contour plot. The representation of peaks as a 'number plot' is widely used in our department and we like to share this simple idea with other NMR users.

2D data are collected on a Nicolet GN-500 NMR spectrometer and processed on a VAX750 computer and the resulting spectrum is presented as a contour plot in the usual way. A peak search is done with the lowest contour level as the minimum height. (In the case of negative peaks, highest contour level is used as the maximum height). A peak is defined at (i,j) if the intensity at (i,j) is greater than (in the case of negative peaks, less than) or equal to those at  $(i\pm 1,j)$ ,  $(i\pm 1,j\pm 1)$ ,  $(i,j\pm 1)$ . The points  $(i\pm 1,j)$ , (i,j),  $(i,j\pm 1)$  are fitted to a paraboloid of or each peak to get its chemical shifts and intensity, which are then stored in a 'peakfile'.

The 'number plot' is obtained by plotting the peak numbers at the proper chemical shifts so that each number will match to the corresponding peak in the contour plot. By superimposing the 'number plot' on the contour plot, the chemical shifts of any peak can be read from the 'peak file' easily.

A sample of the contour plot, number plot and the peakfile are given in the figure.

S.Manogaran

R.M.Scheek

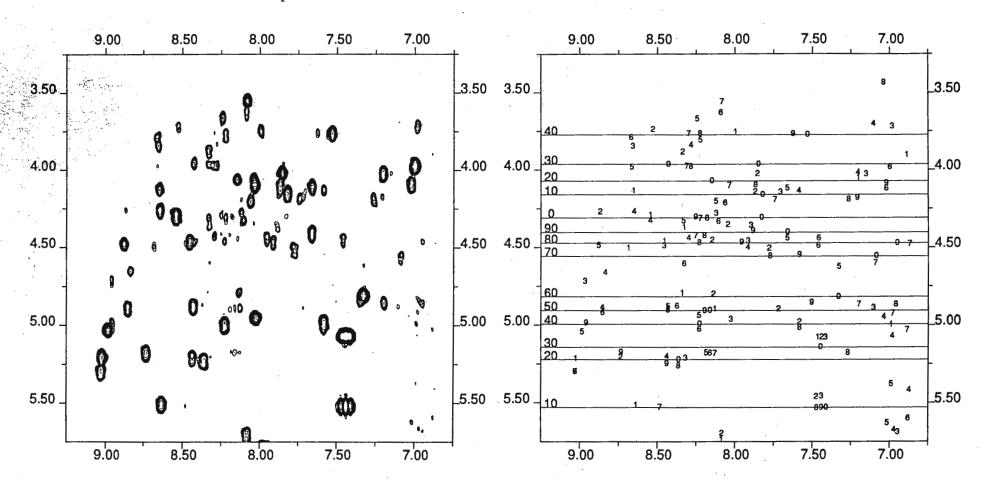
I.D.Kuntz

<sup>&</sup>lt;sup>1</sup>A.Spitzbart, Analytic Geometry, Scott, Foresman and Co., p.280 (1969)

Number plot

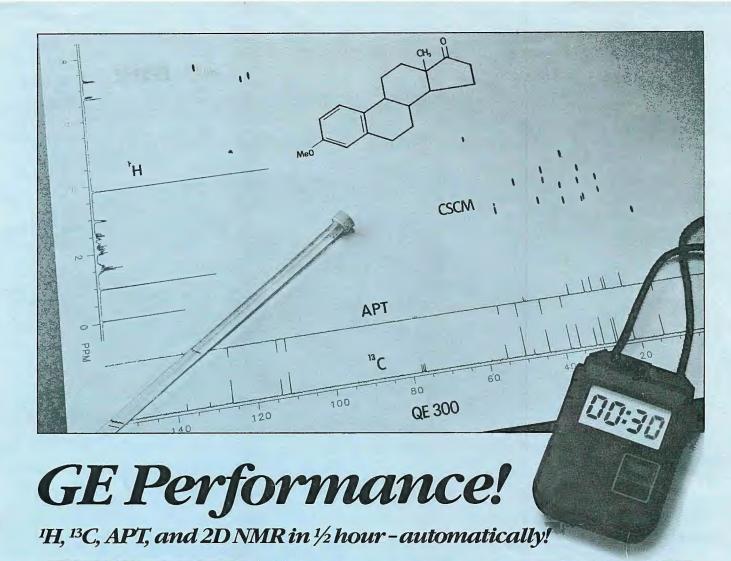
 $r_{i_1}$ 

 $\mathcal{F}_{i}^{j}$ 



Peak file

peakno	wl (Hz)	w1 (ppm)	w2 (Hz)	w2 (ppm)	peak height
1	431.681	5.738	520.816	8.087	90976.602
2	434.643	5.698	521.156	8.085	88482.109
3	435.269	5.689	686.529	6.947	18269.973
4	436.297	5.675	683.046	6.971	22866.162
5	439.468	5.631	676.437	7.017	27225.871
6	441.500	5.603	696.088	6.882	18806.002
7	446.903	5.529	462.918	8.485	16834.365
8	446.556	5.534	610.120	7.473	381863.656
			/		



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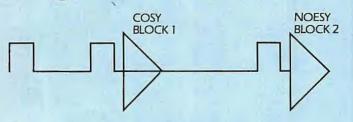
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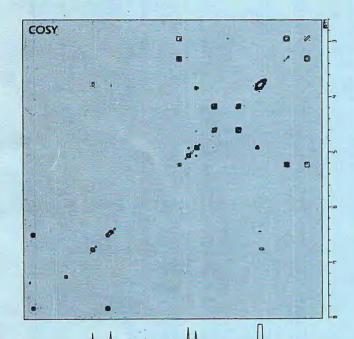
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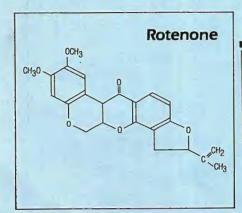
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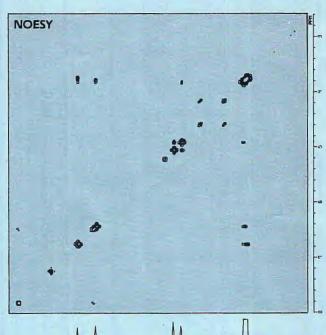


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\*COCONOSY (Haasnoot, et. al., J. Magn. Reson., 56,343 [1984])





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