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XXIII Congress Ampere on Magnetic Resonance - September 15-19, 1986; Rome, Italy; XXIII Congress Ampere, Dipartimento di Fisica, Universita de Roma, "La Sapienza," P. le Aldo Moro 5, I-00185 Roma, Italy.

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 20-24, 1986; Hilton Hotel, New York; see Newsletter No. 329, p. 23 and Newsletter No. 325, p. 27.

An International Meeting Sponsored by the British Radiofrequency Spectroscopy Group on New Methods in Magnetic Resonance -September 6-8, 1986; York, U.K.; Dr. T.K. Halstead, Department of Chemistry, University of York, York YO1 5DD, U.K.

Third Congress of the European Society for Magnetic Resonance in Medicine and Biology - September 21-24, 1986; Aberdeen, U.K.; Dr. M.A. Foster, Department of Bio-Medical Physics, University of Aberdeen, Foresterhill, Aberdeen AB9 2ZD, U.K.

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. 336 (September) ---- 26 August 1986 No. 337 (October) --- 26 September 1986

Prof. Dr. GERHARD HÄGELE Institut für Anorganische Chemie und Strukturchemie I der Universität Düsseldorf Dipl.-Chem. W. Kückelhaus 4000 Düsseldorf, den 25.5.1986 Universitätsstr. 1/26.42.U1.32 Telefon 0211 - 311-2288/2287 Telex 8 587 348 uni d

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

Subject: JOBO and HAMA Programs for Calculation of Aromatic Ring Current Effects

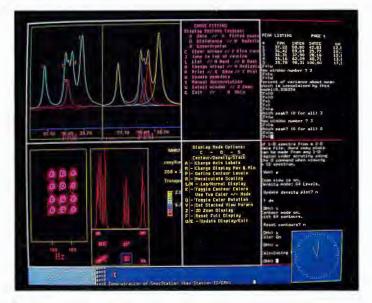
Dear Professor Shapiro,

we want to report about two new computer programs which we have developed to predict shielding contributions for protons being influenced by the magnetic anisotropy of aromatic ring systems. JOBO, the first program, is based on the semi-classical theory of JOHNSON and BOVEY<sup>1)</sup>. The required data tables which have been compiled by EMSLEY, FEENEY and SUTCLIFFE<sup>2)</sup> are implemented in the software. For HAMA, the second program, we employed the quantum mechanical ring current model of HAIGH and MALLION<sup>3,4)</sup>. Both programs were designed for consistent data input containing the molecular structure in form of cartesian coordinates. The molecular geometry can be obtained by molecular mechanics or MNDO calculations. If only x-ray data are available, JOBO and HAMA convert them to cartesian data sets. A detailed input description is given at the head of the programs. (See program listings enclosed to this letter). The final output of JOBO and HAMA yields dia- or paramagnetic shielding contributions  $\Delta_{\delta H}$  (ppm) where a negative sign implies high field shift and vice versa. Note that shielding contributions for methyl protons may be obtained optionally as averaged values for rigid or rotating CH<sub>2</sub>-groups. Our experience has shown that JOBO and HAMA are suitable tools for NMRstudies and the correlation of NMR-parameters with molecular structures.For example we have investigated the P-epimeric menthyl- and neomenthyl-substituted methylphenylphosphineoxides<sup>5)</sup> shown in Fig. 1. Results from x-ray analysis<sup>6)</sup> of this compounds were used as data input for computing with JOBO and HAMA. The estimated values  $\Delta_{SH}$  (I-IV) are summerized in Tab. 1 and compared with the observed ones. As we expected the calculations confirmed that the molecular structures of I-IV in solution state must be very similar to those in solid state. Furthermore we were able to differentiate between highand lowfield form  $(\delta_p)$  of pairwise P-epimeric phosphineoxides and could

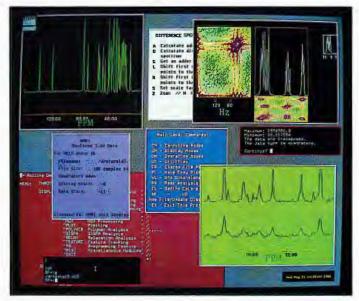
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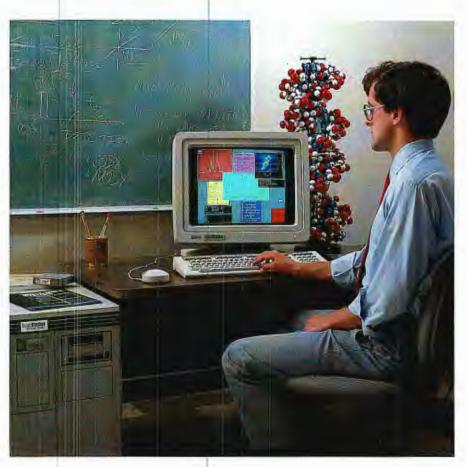
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- Maximum entropy Fourier self-deconvolution allows simultaneous optimization of spectral signal-to-noise and resolution (through narrowing of resonance lines).
- Maximum entropy processing increases experimental efficiency by minimizing truncation errors where FID acquisition is restricted, as in 2-dimensional FT NMR experiments.



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New Methods Research, Inc. 719 East Genesee St., Syracuse, NY 13210 (315) 424-0329 assign the corresponding <sup>1</sup>H-resonance signals. A detailed interpretation of calculated values will be described in a separate publication in preparation. Also we hope that both programs will appear in the QCPE-series as soon as possible. Software and application notes for successful use of JOBO and HAMA are available on request from the authors.

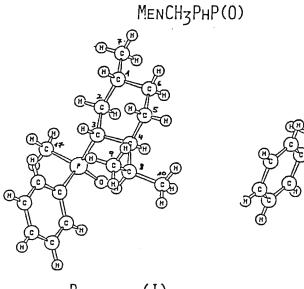
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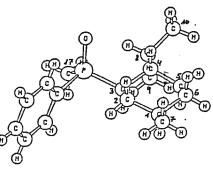
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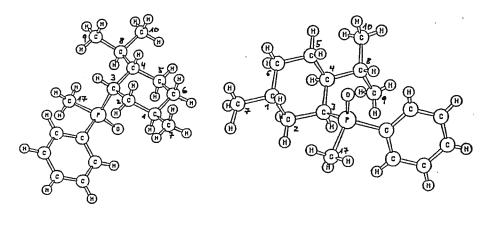




R<sub>(P)</sub> (I)

S<sub>(P)</sub> (II)

NEOMENCH<sub>3</sub>PHP(0)



S(P)

(IV)

Fig. 1: Molecular structures of model compounds I - IV

([]])

 $R_{(P)}$ 

334-	-6
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Н <sub>і</sub>		∆ <sub>δH</sub> (،	JOBO)			∆ <sub>δH</sub> (I	HAMA)		∆ <sub>δΗ</sub> (	I)-∆ <sub>ðH</sub>	(11)	Δ <sub>δΗ</sub> (	111)-4	<sub>δH</sub> (IV)
	I	II	III	IV	I	II	III	IV	JOBO	HAMA	obs.	JOBO	НАМА	obs.
н <sub>1</sub>	_	-0.18	0.18	-	0.02	-0.07	0.05	0.05	0.18	0.09	0.00	0.18	0.00	0.25
H <sub>2ax</sub>	-	-0.86	-0.16	0.07	0.06	-0.33	-0.07	0.03	0.86	0.39	0.16	-0.23	-0.10	-0.34
H <sub>2eq</sub>	-	-0.09	-0.71	-	0.05	-0.06	-0.29	0.06	0.09	0.11	0.16	-0.71	-0.35	-0.53
H <sub>3</sub>	0.25	0.15	0.20	0.18	0.08	0.05	0.06	0.04	0.10	0.03	0.01	0.02	0.02	-0.10
н <sub>4</sub>	0.03	0.10	0.05	-0.03	0.01	0.04	0.02	-0.02	-0.07	-0.03	0.38	0.08	0.04	0.13
H <sub>5ax</sub>	-0.06	0.01	-	0.12	-0.02	0.00	0.02	0.05	-0.07	-0.02	0.12	-0.12	-0.03	0.03
H <sub>5eq</sub>	-0.07	-	• _	0.02	-0.03	0.01	0.05	0.01	-0.07	-0.04	0.15	-0.02	0.04	-0.08
H <sub>6ax</sub>	-	-0.05		-	0.01	-0.02	0.00	0.01	0.05	0.03	0.09	-	-0.01	-0.06
H <sub>6eq</sub>	-	-0.03	-	-	0.00	-0.01	0.01	0.02	0.03	0.01	0.04	-	-0.01	-0.10
H <sub>7a-c</sub>	-	-0.18	-0.14	-		-0.06	-0.05	·-	0.18	0.06	0.07	-0.14	-0.05	-0.29
H <sub>8</sub>	-0.71	-	-	-0.11	-0.29	0.05	0.05	-0.09	-0.71	-0.34	-0.37	0.11	0.14	0.25
в Н <sub>9а-с</sub>	-0.62	-	-	-0.80	-0.22	0.01	0.04	-0.28	-0.62	-0.23	÷0.45	0.80	0.32	0.66
H <sub>10a-c</sub>	-0.19	-	-	-0.10	-0.07	0.03	-	-0.04	-0.19	-0.10	0.02	0.10	0.04	0.14
10а-с <sup>Н</sup> 17а-с	0.15	0.22	0.20	0.21	0.05	0.08	0.07	0.07	-0.07	-0.03	0.01	-0.01	0.00	0.18

Tab. 1: Calculated and observed shielding contributions  $\Delta_{\widetilde{\delta}H}$  (ppm)

#### References

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June 13, 1986

Sealable MAS Rotor for Air-Sensitive Materials

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

Dear Professor Shapiro:

We wish to report the use of a sealable MAS rotor for obtaining CP/MAS spectra of air-sensitive materials and/or liquids and gels. As opposed to either heat sealing glass inserts (1,2) or matching Kel-F inserts that require heat fusing a machined cap to the rotor top (3), our design does not require heat to seal.

Figure 1 diagrams the pyrex MAS rotor insert for the double bearing Kel-F (Chemagnetics, Inc.) rotors used in a M-100S 13C CP/MAS probe and magnet (Chemagnetics, Inc.) retrofit to a JEOL FX-60QS spectrometer. The glass inserts were made to specification by Wilmad Glass Company (Part No. SK-2133).

To seal the insert, a small amount of epoxy resin (EPO-KWIK resin and hardener, Buehler) was placed at the constriction to form the seal. Once set, the rotor was cut at the constriction using a Buehler Isomet Low Speed saw equipped with a high concentration diamond wafering blade. Careful placement of the sample and epoxy, and, careful cutting afford a well balanced rotor for MAS.

Figure 2 shows the resultant 25 MHz 13C CP/MAS spectrum of hexamethylbenzene adsorbed onto silica gel (10% w/w) used as a calibration standard to determine MAS speed of the sealed insert. Spinning speeds of 3KHz were routinely obtained. We have also prepared aqueous gels, placed them in the rotors and have spun these at 3 KHz with no solvent loss. Previous attempts to spin these materials in conventional Kel-F rotors resulted in spinning off of the solvent and difficulties in obtaining balanced spinning. We are currently working on optimizing experimental conditions to obtain NMR spectra on these gels as these materials lie in the region between the true liquid and solid states.

In conclusion, the advantages of epoxy sealing glass rotor inserts are:

- No damage to the sample and/or solvent loss due to heat sealing.
- Sealing with epoxy resin is easier in a glove box environment when handling air-sensitive materials.
- 3. Sealed pyrex inserts are better adapted to variable temperature CP/MAS experiments.

#### REFERENCES

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- D. Geschke and E. Quillfeldt, J. Magn. Reson. 65, 326 (1985).
- 3. W. T. Ford, S. Mohanraj, H. Hall and D. J. O'Donnell, J. Magn. Reson. 65, 156 (1985).

Very truly yours,

PAUL J./GIAMMATTEO W. W. Hellmuth F. G. Ticehurst Texaco Inc. Beacon, NY 12508

Paul W. Cope Wilmad Glass Company, Inc. Buena, NJ 08310

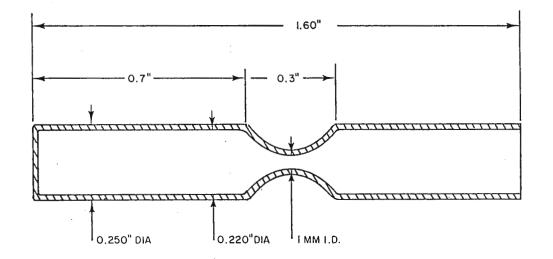
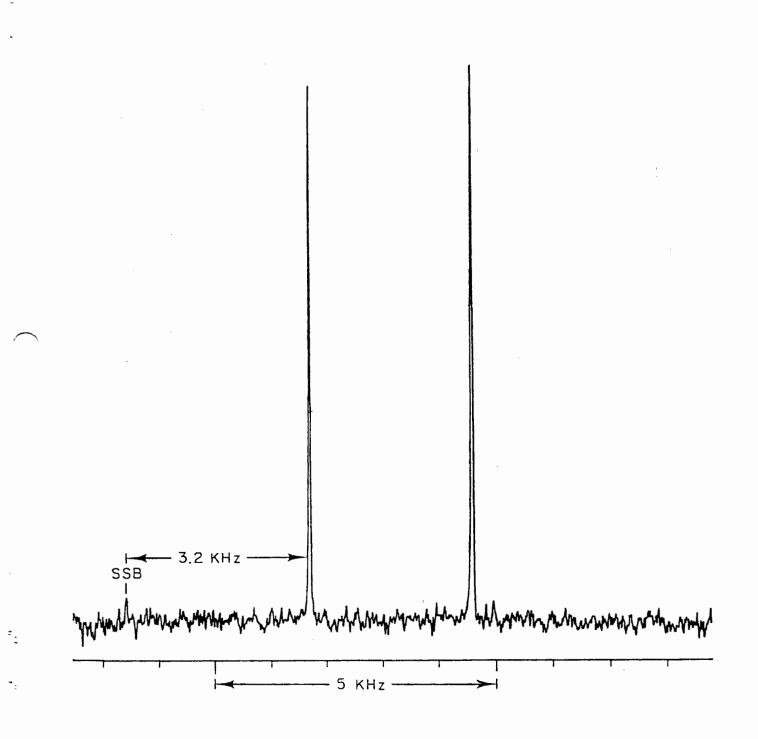


FIG. 1. Diagram of Wilmad Glass Co. sealable pyrex MAS rotor insert (part no. SK-2133) for Chemagnetics. Inc. Kel-F rotors.

334-8

FIG. 2. CP/MAS spectrum of hexamethylbenzene on silica gel (10% w/w) obtained using the sealed glass insert. 3.2 KHz side band is shown.





#### Brock University

Department of Chemistry St. Catharines, Ontario, Canada L2S 3A1 Telephone (416) 688-5550 Extension 3406 2

May 26, 1986.

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

#### Industrial Silicon carbide: MAS Nmr of Surface Impurities

Dear Barry:

We are continuing our MAS nmr studies of silicon carbide (TAMU-NMR 312-33 (1984); J.Chem. Soc., Chem. Commun. 159 (1985)) with emphasis on industrial samples. Abrasive grade silicon carbide, unlike the high-purity samples emphasized in our earlier work, gives silicon-29 peaks from a number of minor silicon environments with short  $T_1$ 's. Since crystalline silicon carbide has inefficient spin diffusion and very long  $T_1$ 's, spectra of the short- $T_1$  components can be obtained merely by rapid pulsing that saturates the abundant crystalline component. As the relaxation delay decreases, in addition to new peaks appearing the crystalline-SiC peaks broaden; apparently we selectively see the silicons near paramagnetic centres, which shorten  $T_2$  as well as  $T_1$ .

With industrial samples a very short delay between pulses is instructive. Figure 1 shows a silicon-29 spectrum of abrasive grade silicon carbide (6H polytype) obtained with a 0.1 sec relaxation delay between 30° pulses. The three peaks at lowest field are the residual peaks of the "bulk" crystalline SiC; only these are detectable when a "normal" relaxation delay of 5 minutes or more is used. The peaks that appear only at very short relaxation delays must correspond to a very small fraction of the total silicon in the sample. Not all our industrial samples give the same minor-component peaks, not surprisingly since the sources and preparation conditions vary. However peaks at -32.4, -44, -49, -56, and -97 ppm recur in many samples.

If silicon carbide has a surface oxide layer with Si-O bonds, as does elemental silicon, then extra nmr signals are expected. The -97 ppm chemical shift is consistent with silicate, and the peaks with intermediate chemical shift might correspond to surface silicons bonded to both carbon and oxygen. Evidence that the extra signals do arise primarily from surface material comes from hydrofluoric acid washing experiments. Figure 2 shows silicon-29 MAS nmr spectra of a typical sample before and after washing with 3% HF, which breaks Si-O bonds but leaves Si-C bonds unaffected. Most of the extra nmr signals disappear; however an underlying hump survives which might arise from amorphous silicon carbide. (Amorphous silicon carbide gives rise to a broad signal centered at -15 ppm, with a peak width at half height of about 15 ppm.) Carbon-13 MAS nmr spectra of silicon carbide are analogous to silicon-29 spectra, with a "mirror image" relationship of chemical shifts. However at short carbon-13 relaxation delays we have had problems due to severe rotor signal interference, which has delayed our carbon-13 work. To get around his problem we are working with boron nitride and PSZ spinners (TAMU-NMR, 315-7 (1984)).

The spectra were obtained on the Bruker WH-400 instrument of the South Western Ontario High Field Nmr Centre with assistance from Bob Lenkinski and Bill Klimstra. At Brock University we have recently taken delivery of a Bruker AC-200 system and plan to obtain in-house MAS nmr spectra to supplement those from the Regional Centre.

J. S. Hartman

Yours sincerely,

Steve Beatro Minderio

B. G. Winsborrow

-100

PPM

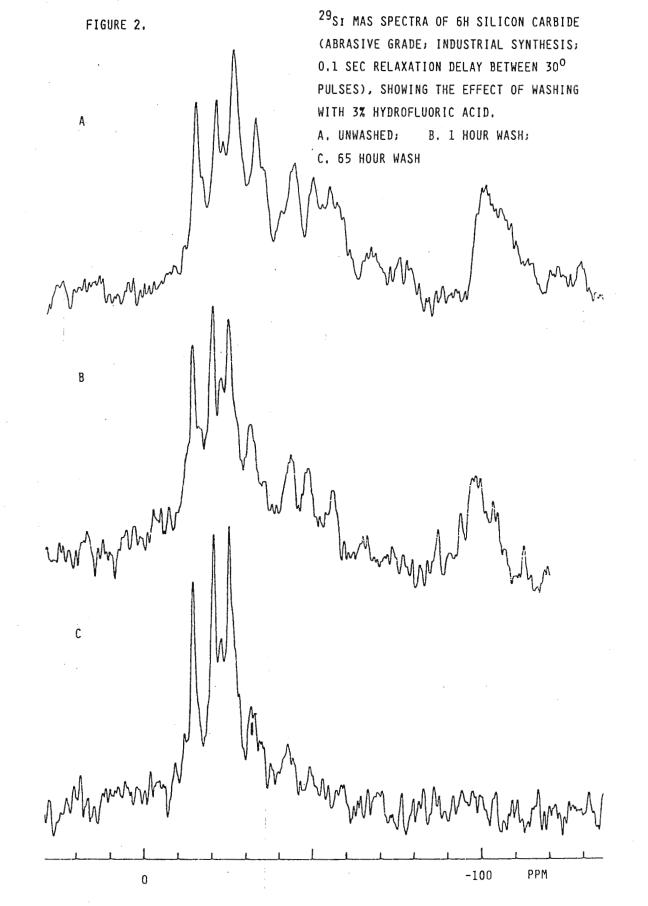
FIGURE 1.

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29<sub>SI</sub> MAS NMR SPECTRUM OF 6H SILICON CARBIDE, WITH SHORT-T<sub>1</sub> COMPONENTS FAVOURED. (90,700 SCANS; 0.1 SEC RELAXATION DELAY BETWEEN 30<sup>O</sup> PULSES)

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31P spectra at 90 MHz on a 9 cm<sup>3</sup> selected volume in a human brain. Acknowledgement: Obtained in cooperation with the Department of Molecular Biophysics and Biochemistry, Yale University.

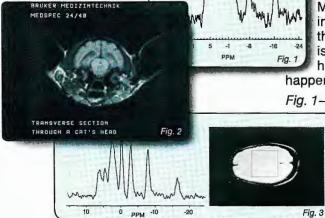


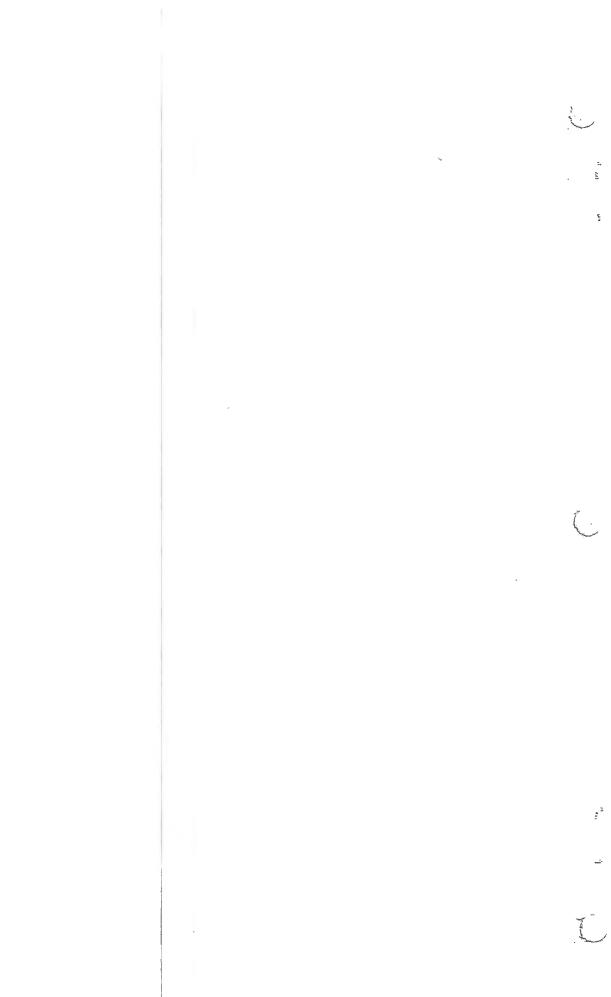
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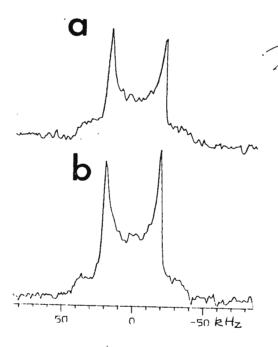
May 31, 1986

#### Dear Professor Shapiro:

#### Solid Deuterium Probe with 4mm ID coil

One usually needs 70 mg to 100mg of sample to fill a 5mm ID solenoid coil (5 mm OD NMR tube) for solid state NMR work. Obtaining such a large amount of labeled material is not always easy. This letter gives information about a 4mm ID coil which provides higher sensitivity on a limited amount of sample (less than 40mg) and requires less transmitter power ( which also means fewer probe arcing problems). Shown below are 38.45 MHz H spectra of  $(CH_3-d_3)$ -L-alanine (8 mg). The smaller coil gave 40% better S/N than the 5mm coil, as expected. 90° pulses were 2.2 us on both coils, but the 4mm coil required only about one-half the transmitter power.

Sincerely,



Yukio Hiyama and Dennis A. Torchia

Zuchio Hiyama & Jenni O. Torchin

160 aquisitions, 1 kHz line broadening a) with 5mm coil (11mm long) Transmitter output 350 V b) with 4mm coil (7mm long) Transmitter output 250 V p-p

#### CHEMICAL CENTER



UNIVERSITY OF LUND PHYSICAL CHEMISTRY 2 PROFESSOR STURE FORSEN

Lund, June 3, 1986

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

Subject: <sup>25</sup>Mg NMR of Mg<sup>2+</sup> Binding to Calmodulin

Dear Professor Shapiro,

Having demonstrated the usefulness of  ${}^{43}$ Ca NMR (I = 7/2, Q = 0.05 x  $10^{-24}$  cm<sup>2</sup>) in studying Ca<sup>2+</sup> interactions with calmodulin (CaM) and with other calcium-binding proteins (1), we are now extending our studies to  ${}^{25}$ Mg NMR (I = 5/2, Q = 0.20 x  $10^{-24}$  cm<sup>2</sup>).

The affinity of calmodulin to  $Mg^{2+}$  has been under debate recently. Results ranging from no binding to  $K_d = 0.1 - 1.0$  mM have been reported (see ref. 2 and 3 for a summary). Since the intracellular concentration of  $Mg^{2+}$  is higher than that of  $Ca^{2+}$  by a factor of ca.  $10^4$ , a  $K_d$  in the mM range could mean a serious competition between  $Mg^{2+}$  and  $Ca^{2+}$  for calmodulin. Our initial results show that this is indeed a valid concern.

The <sup>25</sup>Mg line width ( $\Delta\nu$ ) is significantly broadened in a CaM-Mg<sup>2+</sup> solution due to exchange of free and bound <sup>25</sup>Mg<sup>2+</sup>. The Ca<sup>2+/25</sup>Mg<sup>2+</sup> competition experiments indicate that Mg<sup>2+</sup> binds to all of the four calcium sites of CaM. To simplify the system, we then studied the binding of Mg<sup>2+</sup> to sites I and II of CaM by adding two equivalents of Ca<sup>2+</sup> to block sites III and IV. The plot of  $\Delta\nu$  as a function of [Mg<sup>2+</sup>]/[CaM·Ca<sub>2</sub>] is shown in Fig. 1, and the temperature dependence of  $\Delta\nu$  is shown in Fig. 2. The experimental points were treated with the total bandshape analysis described previously for <sup>43</sup>Ca (4). The following results gave the best fit: K<sub>d</sub> = 0.5 mM, k<sub>off</sub> = 2250 s<sup>-1</sup> at 25<sup>o</sup>C,  $\Delta$ H<sup>#</sup> = 8.7 kcal/mol,  $\Delta$ G<sup>#</sup> = 12.9 kcal/mol, and quadrupole coupling constant = 1.8 MHz.

Further studies on the  $Mg^{2+}$  binding to sites III and IV of CaM and to its proteolytic fragments are in progress.

Address

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- 4. Drakenberg, T., and Forsén, S., and Lilja, H. (1983) J. Magn. Reson. 53, 412-422.

Isan Anthe

Torbjörn Drakenberg

Ming-Daw Tsai (on leave from the Ohio State Univ.)

Eva Thulin

Sture Forsén

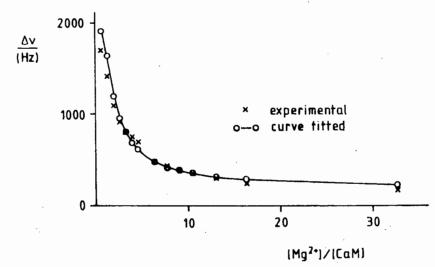


Figure 1. Titration curve

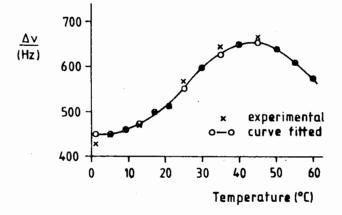


Figure 2. [Mg<sup>2+</sup>]/[CaM]=5.24



Professor Bernard L. Shapiro Texas A&M University NMR Newsletter Department of Chemistry Texas A&M University College Station, Texas 77843 Department of Chemistry State University of New York at Stony Brook Stony Brook, New York 11794 telephone: (516) 246-5050

June 18, 1986

Bulk Magnetic Susceptibility (BMS) Forever

Dear Barry:

We would like to comment on a letter by Brown, Ribeiro, and Spicer which appeared in the April Newsletter (331-36). They have also recently published the same results in the refereed literature (Magn. Res. Med., 3, 289 (1986)). The authors state that, "surprisingly", the Gd(III) complexes they studied (GdEDTA<sup>-</sup>, Gd(PPP)<sup>7-</sup><sub>2</sub>, and GdDTPA<sup>2-</sup>; see abbreviations below) induced downfield shifts of the <sup>23</sup>Na NMR signal. Unfortunately, surprise is not really called for: the authors have apparently failed to consider BMS effects. These are unavoidable in the coaxial tube system employed by Brown, et al.; the classic configuration of Evans (D.F. Evans, J. Chem. Soc., 2003 (1959)), with the paramagnetic species in the annular space. For a coaxial tube system aligned with the direction of 8, one can easily derive the expression giving the downfield shift,  $\Delta_{m{X}}$  (in ppm), caused by the difference in BMS,  $\Delta m{k}$ , between the phases in the two tubes to be:  $\Delta_{\mathbf{X}}$ = (4/3) $\pi(\Delta k)$ . (See, for example, E.D. Becker, "High Resolution NMR", 2nd Ed., Academic Press, N.Y. (1980), pp. 42–46.) One can estimate the difference in the volume BMS, $\Deltam{\kappa}$ (in ppm), from the magnetic moment,  $\mu_{eff}$ , and concentration, [ ] (in mM), of Ln(III) using a form of the Langevin-Debye equation:  $\Delta K \cong K_{Ln} = (2.84)^{-2} \mu_{eff}^2 [Ln] T^{-1} (L.N. Mulay, "Magnetic Susceptibility",$ Interscience, N.Y. (1963), pp. 1772). For 10 mM Gd(III) (  $M_{eff}$  is 7.94 bohr magnetons (BM) (Mulay, p. 1776)) at 291<sup>0</sup> K, one estimates  $\Delta_x$  to be 1.1 ppm, downfield. Brown, et al report the value for the shift induced by 10 mM GdEDTA to be 1.07 ppm, downfield (MRM paper). Those reported for the other two complexes are 1.42 ppm, 1.47 ppm, downfield, respectively. The small differences from the calculated  $igta_{\mathbf{x}}$ value could easily be due to the difficulty in measuring the positions of the broad lines or a (diamagnetic) complex formation (CF) shift.

The authors quote Malloy, et al (ref. 2; ref. 6, of <u>MRM</u> paper) as having reported a shift induced by GdEDTA<sup>-</sup>. However, we have already suggested in the literature (ref. 28, of <u>MRM</u> paper) that this was due to BMS effects. The authors also quote Bryden, et al (ref. 3; ref. 7, of <u>MRM</u> paper) as having reported dipolar (pseudocontact) shifts induced by Gd(III) complexes. However Bryden and coworkers did not actually state this. Brown, et al have possibly misread the legends of Figs. 5-8 of the Bryden paper

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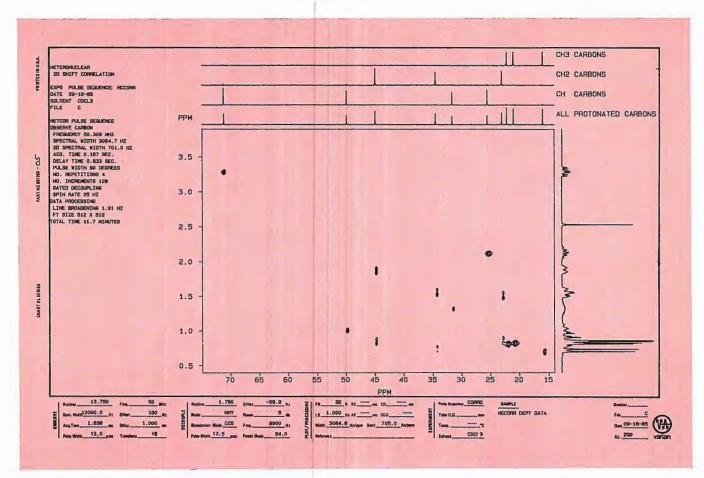


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With 1D spectral information in hand, MAGICAL next determined the minimum spectral width for the heteronuclear correlation experiment for both protons and carbons (using protonated carbons only, as determined from the DEPTGL experiment). The rest of 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.

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('measured' does not modify 'dipolar'). The small shifts (average, 0.25 ppm) reported by Bryden, et al could arise from a small contact contribution or incompletely compensated BMS and/or CF effects.

The lack of consideration of the BMS shift has also led the authors astray in the interpretation of the shifts induced by the Dy(III) analogs of the above complexes in their system. They observe a 1.99 ppm downfield shift induced by 10 mM DyEDTA (MRM paper). The value of  $\Delta_{\chi}$ , calculated as above ( $\mu_{eff}$  for Dy(III) is 10.6 BM), is 2.0 ppm downfield. The shift they reported induced by 10 mM DyDTPA<sup>2-</sup> (1.34 ppm), however, is smaller than  $\Delta_{\mathbf{X}}$  because the hyperfine (contact + dipolar) plus CF shifts are actually upfield for DyDTPA<sup>2-</sup> (Figure) and partially cancel the downfield BMS shift. We cannot very accurately estimate the values of the observed hyperfine and CF shifts in the solutions of Brown, et al from our data which were obtained at a different ionic strength and temperature (such shifts depend on these). However, the results are in qualitative agreement. The TPHA<sup>7-</sup> ligand was kindly supplied to us by Professor Peter Letkeman of Brandon University.

We are preparing a manuscript describing detailed determinations of BMS effects in solutions containing shift reagents (SR) of this type.

Sincerely yours,

Charlie

Charles S. Springer, Jr. Simon C. Chu Professor of Chemistry Research Assistant Research Assistant

William D. Roonev

Janis Szklawk

Janio Szklaruk Research Assistant

Chemical Shift Produced by Polycarboxylic Amines [Na+] =148 m

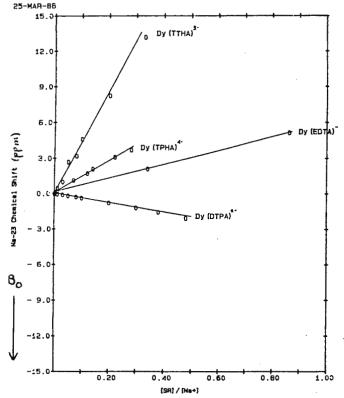


FIGURE LEGEND:

The observed sum of the isotropic hyperfine and CF shift induced in the <sup>23</sup>Na NMR signal by various aminepolycarboxylate complexes of Dy(III) as a function of the stoichiometric molar ratio of SR to Na. The [Na<sup>+</sup>] is held constant at 148 mM. The lines are intended merely to guide the eye. The temperature was ca. 294<sup>°</sup> K. Downfield shifts age reported as positive. Field-frequency locking on the <sup>2</sup>H resonance of 20% (v/v) D<sub>0</sub>O eliminates contributions from BMS to the extent that this signal suffers no hyperfine or CF shift.

LIGAND ABBREVIATIONS:

PPP<sup>5-</sup>, tripolyphosphate;

EDTA<sup>4-</sup>, ethylenediaminetetraacetate;

DTPA<sup>5-</sup>' diethylenetriaminepentaacetate;

TTHA<sup>0-</sup>, triethylenetetraminehexaacetate;

TPHA<sup>7-</sup>, tetraethylenepentamineheptaacetate.



#### University of Strathclyde

#### Department of Pure and Applied Chemistry

Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL Tel: 041-552 4400

9th June, 1986

Professor Barry Shapiro, Department of Chemistry, Texas A and M University, College Station, Texas, 77843-3255 U.S.A.

#### Dear Barry,

#### Bis-(N-benzylacetimidic acid ethyl ester)-dichloro-palladium

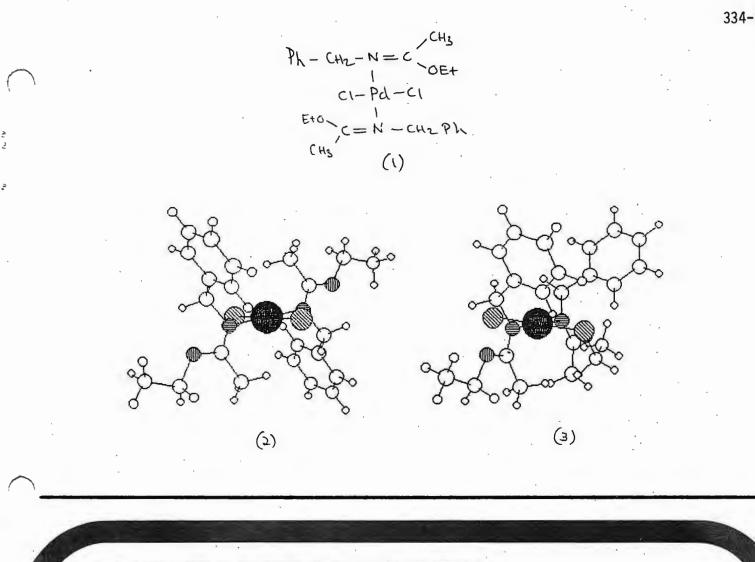
In work in collaboration with Professor Pauson and Dr. Tomasz Janecki, I had occasion to examine the variable temperature proton n.m.r. of the title compound(1). The X-ray crystal structure of this compound (obtained by Kevin McCullough of Heriot-Watt University) is the centrosymmetric one shown in (2).

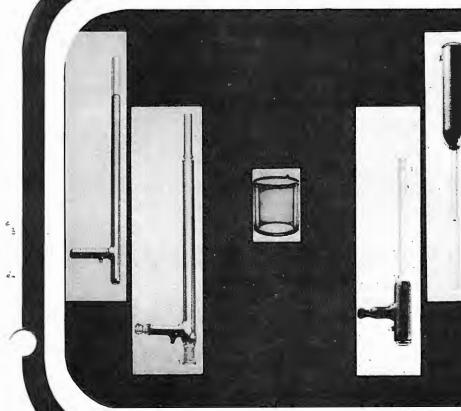
The n.m.r. spectra show evidence for the presence of a second conformer, since the peaks for the methyl groups, the benzylic methylenes and the aromatic ring protons are all duplicated at low temperature. At around room temperature the peaks of the methyl groups are broadened, and collapse occurs at 325 K; similar effects are noticed with the other duplicated resonances. It is believed that this second conformer (3) results from rotation of one of the organic ligands about the Pd-N bond. In addition to this effect it is noticed that while the resonances of the methyl and methylenes of the ethoxyl groups are not doubled, there is a marked shift of the methyleneoxy signals from  $\delta$  2.25 at 213 K to  $\delta$  = 3.25 at 373 K. A smaller shift of the resonance of the attached methyls from  $\delta$  = 0.45 to  $\delta$  = 0.60 was noted. This effect is attributed to a general flexibility of the ligands resulting in the positioning of the methyleneoxy protons in the deshielding regions of the aromatic rings, with these (presumably higher energy) structures being present to increasing amounts at the higher temperatures.

Kind regards and best wishes,

Yours sincerely,

Peter Bladon.





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DEPARTMENT OF HUMAN BIOLOGICAL CHEMISTRY & GENETICS Division of Biochemistry

Area Code 409 761-2811

June 17, 1986

Professor B.L. Shapiro TAMU NMR Newsletter Department of Chemistry Texas A and M University College Station, TX

#### LOW FIELD ALCOHOL PROTON SIGNALS

Dear Barry:

Installation of our JEOL GX270WB spectrometer was completed in February 1986 and we have been learning how to operate it since that time. Our "hands on" experience with a Fourier-transform spectrometer is necessarily limited, but we wish to report a spectral feature of peroxyalcohols not heretofore noted.

Survey spectra to  $\delta$  10 previously reported [1] for a series of secosterol peroxyalcohols with structures  $6\xi$ -alkoxy-5, $6\xi$ -epidioxy-5 $\xi$ -5,6-secochole-stane-3 $\beta$ ,5-diol (and their 3 $\beta$ -acetates) did not reveal a low field sharp one-proton singlet that we have since discovered in spectra recorded over a wider frequency range. The recently observed signals occur in spectra of these peroxyalcohols in the range  $\delta$  10.0-10.3 (in CDCl<sub>3</sub>), are not shifted on dilution, and are lost upon exchange with D<sub>2</sub>0.

As the structures of the peroxyalcohols are secure from their chemistry [2], these low field signals must represent the  $5\xi$ -hydroxyl intramolecularly hydrogen bonded to nearby peroxide oxygen, thus at particularly low field relative to previously recorded intramolecularly hydrogen-bonded hydroxyl proton signals. Indeed, these low field signals might be taken for hydroperoxide proton signals in the absence of other information. Alternative formulation of structure for the analytes as geminal hydroperoxy cyclic ethers, though excluded by relevant chemistry, could have been concluded from the chemical shifts, especially in light of report of hydroperoxyl proton signals at  $\delta$  9.22-10.64 for  $\alpha$ -hydroperoxy- $\alpha$ '-methoxy-cyclic ethers [3].

Infrared absorption spectra in CCl4 of the secosterol lower alkoxyl derivatives reveal sharp 3540 cm<sup>-1</sup> and broad 3450 cm<sup>-1</sup> (disappearing on dilution) bands associated with the  $3\beta$ -hydroxyl and hydrogen-bonded  $3\beta$ -hydroxyl features

respectively. Additionally, spectra of these sterols and their  $3\beta$ -acetates included sharp bands at 3280-3340 cm^l not disappearing on dilution associated with the 5g-hydroxyl hydrogen bonded intramolecularly to peroxide oxygen. The 3280-3340 cm<sup>-1</sup> absorption thus corresponds with the deshielded  $\delta$  10 proton signals from the same structural feature.

Yours

Leland L. Smith, Ph.D. Professor of Biochemistry

LLS/tw

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#### School of Chemical Sciences

at Urbana-Champaign

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505 South Mathews Avenue Urbana, IL 61801

June 13, 1986

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

#### Re: MASS Rotor Explosions

Dear Barry,

In recent months, we have had several Delrin "Andrew-Beams" type MASS rotors disintegrate "in flight," fortunately without serious damage to either operators or equipment.

The list of substances that we tried to investigate with MASS NMR is as follows, together with possible causes for the "explosions":

- 1) Silicotungstic acid,  $H_4[Si(W_3O_{10})_4] \cdot nH_2O$  (three rotors). Acid weakening?
- Tungsten hexabromide, WBr<sub>6</sub> (one rotor). Acid weakening? HBr buildup?
- 3) Freshly de-aluminated Na-Y zeolite, not washed or exposed to air (three rotors). Acid weakening? HCl buildup?
- 4) Tungsten carbide, WC, (one rotor). Too dense? 15.6g/cc
- 5) Boron phosphide, BP (three rotors). No explanation.

We report this here as a cautionary tale, and would welcome hearing from anyone who has experienced similar calamities with other, apparently inoffensive, solids. Further work on these systems is <u>not</u> underway!

Yours sincer ely,

Christopher T. G. Knight

Gary L. Turner

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#### School of Chemical Sciences 142B RAL, Box 34-1 1209 W. California Urbana, IL 61801

#### May 30, 1986

Professor B. L. Shapiro Editor, <u>TAMU NMR Newsletter</u> Texas A & M University College Station, Texas 77843-3255

> Title: Resolution and S/N Standards for Solid State <sup>29</sup>Si, <sup>13</sup>C and Solution <sup>11</sup>B NMR

Dear Professor Shapiro:

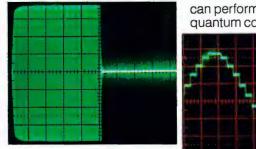
We are using our General Electric GN300 spectrometer for both solution and solid state NMR work and would like to discuss reference materials. As has been discussed in this newsletter,  $[Si_80_{12}](OSiMe_3)_8$ , otherwise known as  $Q_8M_8$ , is an excellent material for setting the Hartmann-Hahn match in <sup>29</sup>Si CPMAS experiments.<sup>1</sup> It also has the added attraction of a four-line pattern in the <sup>29</sup>Si solid state NMR spectrum which is very sensitive to the magic angle setting (see Figure 1). Its greatest drawback has been availability. We would like to inform your readers that this material is now available from Strem Chemicals (7 Mulliken Way, Dexter Industrial Park, P. O. Box 108, Newburyport, Massachusetts 01950). The material is completely inert and 1/4 to 1/2 gm is a sufficient amount for use as a standard. We would also like to recommend  $Si(SiMe_3)_4(TMSS)$  as a secondary reference for both <sup>13</sup>C and <sup>29</sup>Si FT/CPMAS experiments. It gives a narrow line (we have obtained a resolution of 2.5 Hz in the <sup>29</sup>Si CPMAS experiment and are resolution limited by the acquisition time), is inert, and non-volatile (at 25°C). Strem Chemicals is considering marketing this material.

I would also like to suggest 0.01 M NaBPh<sub>4</sub> in d<sub>6</sub>-acetone as a resolution and S/N standard for <sup>11</sup>B{<sup>1</sup>H} solution NMR. This solution is stable if sealed under nitrogen and gives a linewidth at half-height of 0.18 Hz in our hands, with S/N of >200:1 in one

(continued on page 33)

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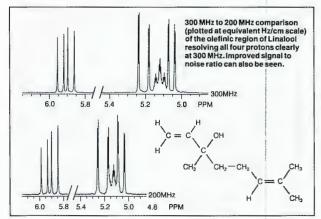
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scan (see Figure 2). It does not suffer from deuterium exchange with solvent as does  $NaBH_4/D_2O$ , which eventually broadens the <sup>11</sup>B lines.

Sincerely yours,

Vera U. Maing

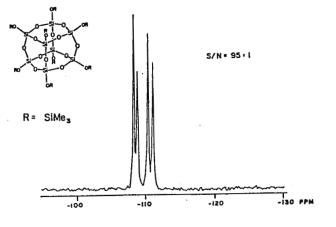
Vera V. Mainz, Director Molecular Spectroscopy Laboratory

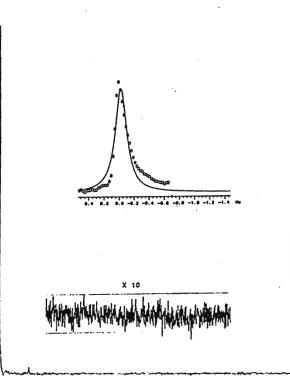
VVM:mo enclosures:

 E. Lippmaa, M. Magi, A. Samosan, G. Englehardt, A.-R. Grimmer, J. Am. Chem. Soc. 1980, 102, 4889.

Figure 1: <sup>29</sup>Si(<sup>1</sup>H) CPMAS NNR spectrum of [Si<sub>8</sub>O<sub>12</sub>](OSIMe<sub>3</sub>)<sub>8</sub> obtained at 59.6 MHz (8 scans, 15 sec repetitions, 25°C, 12 msec contact time).

Figure 2: <sup>11</sup>B(<sup>1</sup>H) NMR spectrum of 0.01 M NaBPh<sub>H</sub> in d<sub>6</sub>-acetone at 96.28 MHz (1 scan, 10 mm tube, 25°C); -5.38 ppm from BF<sub>3</sub>·OEt<sub>2</sub>(neat) (negative shifts are upfield of the standard).







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

9th May 1986.

Dear Professor Shapiro,

Microprogram for Selective <sup>13</sup>C {<sup>1</sup>H} NOE: Data Recycling and Frequency Switching for Broad Band Decoupling

Selective  ${}^{13}$ C { $^{1}$ H} NOE measurement is a useful technique for structure determination (1,2). The NOE difference technique requires that a control spectrum with the decoupler frequency moved off-resonance should be acquired during the same experiment while selective irradiation of a particular proton is performed. In order to get the best results it is necessary to recycle the data acquisition to average out changes in spectrometer conditions. If broad band decoupling is used, the broad band decoupler frequency should be set to the same value for both irradiation and the control. The MICROPROGRAM for a Bruker spectrometer incorporates both these features and can be used for any number of selective irradiations (Table 1).

The FQLIST.OON for the 'nth' irradiation contains two frequencies: (a) selective irradiation frequency; (b) broad band decoupling frequency, which is identical for each irradiation.

Figure 1A shows the control spectrum with NOE suppressed for 10% v/v 2,5-dichlorotoluene in CDCl<sub>3</sub> at 62.89 MHz. Figure 1B shows the NOE difference spectrum after selective irradiation of the CH<sub>3</sub> singlet at 2.3&. The experiment was recycled 8 times for a total of <sup>3</sup>64 scans. The delay D1 was set to 20 secs. to generate the NOE and a 0.4 sec. acquisition time was used. The difference spectra obtained after 256 scans are shown in Figures 2B, 2C and 2D respectively. The control spectrum is shown in Figure 2A. Good selectivity is obtained even for irradiation of H3 and H6 which are separated by 0.04 ppm. All the carbon resonances can be assigned by this method.

We hope this is useful to other Bruker users. Please credit this to the Pfizer, Sandwich account (David Bowen).

Yours sincerely,

M. Kinns

M. Kinns.

Directors: W.J.Wilson (Chairman and Managung) D.L.Crouch M.P. A.A.Dunning N.J.Hunter A.F.Impey J.Lisseman J.A.Mars M.F.Shorten E.A.Stevens T.I.Wrigley I.R.Young Registered in England: No. 526209 Registered Offica: Remsgate Road, Sandwich, Kent CT 13 9NJ.

### TABLE 1

### ED NOEHET

; ACQUIRES SERIES OF HETERO NOE SPECTRA

1	ZE	
2	WR # 1	; WRITE ZERO FILES TO DISK
3	IF # 1	;
4	LO TO 2 TIMES C	; C = NUMBER OF IRRADIATIONS + 1
5	RF # 1.001	; RESET DATA FILE EXTENSION TO .001
6	RF FQLIST.001	; RESET FREQUENCY LIST EXTENSION TO .001
7	FL FQLIST	; READ FREQUENCY LIST
8	RE # 1	; READ DATA FILE
9	D1 S1 O2 CW	; S1 = 50L FOR SELECTIVE IRRADIATION
10	D2 S2 O2	; S2 = 15H FOR BROAD BAND DECOUPLING;
		D2 = 50 MS FOR SWITCHING
11	GO = 9 BB	; ACQUIRE DATA
12	DO	; SWITCH OFF DECOUPLER
13		
	WR # 1	; STORE DATA
14	WR # 1 IF # 1	; STORE DATA ; INCREMENT FILE EXTENSION DATA FILE
14 15		,
	IF # 1	; INCREMENT FILE EXTENSION DATA FILE
15	IF <b># 1</b> IF FQLIST	; INCREMENT FILE EXTENSION DATA FILE ; INCREMENT FILE EXTENSION FREQUENCY LIST
15 16	IF # 1 IF FOLIST LO TO 7 TIMES C	; INCREMENT FILE EXTENSION DATA FILE ; INCREMENT FILE EXTENSION FREQUENCY LIST ;

### References:

- (1) M.F. Aldersley, F.M. Dean and B.E. Mann, J. Chem. Soc. Chem. Commun. 107 (1983)
- (2) K. Kakinuma, N. Imamura, N. Ikekawa, H. Tanaka, S. Minami and S. Omura, J.A.C.S. <u>102</u> 7493 (1980).

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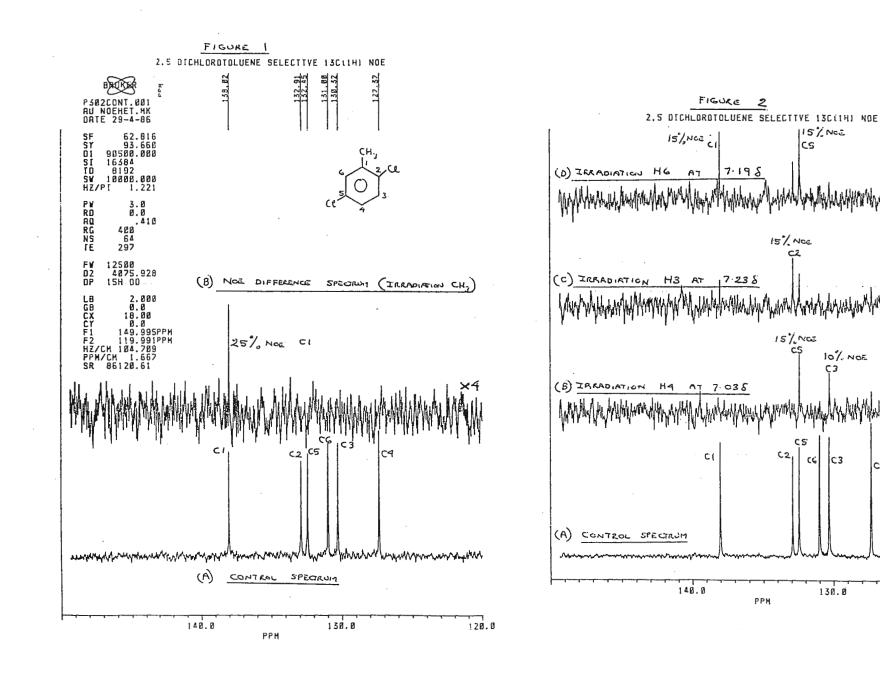
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Bernard L. Shapiro Editor/Publisher Russel R. Kirk Administrative Assistant

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Dr. Barry L. Snapiro Department of Chemistry Texas A & M University College Station, TX 77843 6-19-86

Phase Sensitive COSY Experiment
with Double Quantum Filtering
on a Varian XL-300.

Dear Barry:

The utility of the four-bond w-coupling rule for protons in establishing the geometry of organic molecules is sufficiently well established that it needs no farther explication here. Unfortuneately, this long range coupling is often lost in the line broadening of complex proton systems and is not readily evident even with the aid of highfield, high resolution proton instruments. One answer, of course, is to look to the  $\hat{z}-\hat{D}$ COSY experiment. The conventional COSY pulse sequence can be doctored to make such long range couplings show up ( see Bax and Freeman, J. Man. Reson., 44, 542(1982) and Uschkinat and Freeman, ibid., <u>60</u>, 164(1984). We have, however, been using the phase sensitive COSY experiment(States, Haberkorn and Ruben, ibid., 48, 286(1982) with double quantum filtering on our Varian XL-300 for this purpose.

To establish correct experimental parameters and judge how well the technique works, we have looked at some bicyclic molecules with well established structures. One of these is the phenylazide derivative of norbornene first examined by Huisgen, et al., (Ber., 98, 3992:(1965) with the aid of a Varian A-60 proton spectrum. They made the assignments for 3a and 7a based on chemical shift comparisons with the corresponding benzylazide derivative. Assuming these to be correct, the assignments published for H-7 and H-4 are reversed here on the basis of the The H-5,6 endo protons are seen to be coupled to COSY results. the bridge methylenes as are 7a and 3a. Unfortuneately, the chemical shifts for the methylene protons (reported as a singlet at 60 MHz) are still too similar to allow unambiguous assignments. Notice also the strong correlation between the two bridgehead protons.

(continued on page 43)

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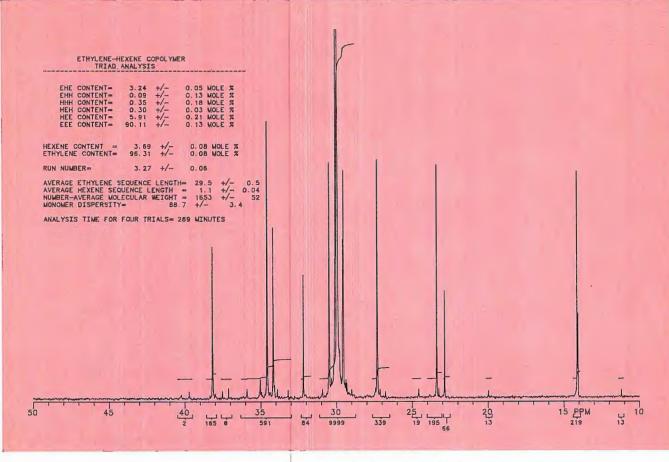
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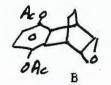
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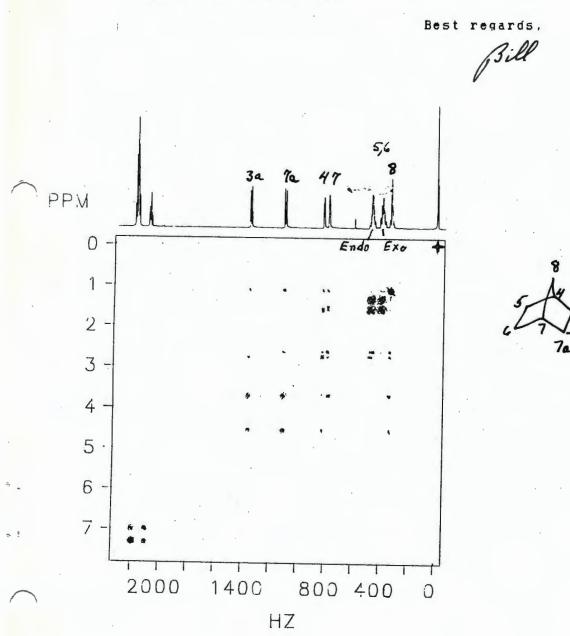
(continued from page 40)

To confirm the matter, we have looked also at the two known epoxides below. While the spectra are not shown here, the long range W-correlation is very clear in <u>A</u> and totally absent in <u>B</u>. We have now carried this useful technique on

OAc



to a number of bridged benzobicyclooctanes and various rearrangement products.





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DEPARTMENT OF RADIATION BIOLOGY AND BIOPHYSICS

May 1, 1986

#### Carbon-13 Spectral Line Broadening in Paramagnetic Solids

#### Dear Barry:

Solid state  $^{13}$ C NMR of paramagnetic systems has been an area of research activity in our laboratory. Paramagnetic compounds, with several notable exceptions, have resisted characterization using line narrowing methods. A common assumption about the failure of the experiments is that an efficient nuclear electron dipolar relaxation mechanism, modulated by the rapid electron relaxation times,  $T_{1e}$  and  $T_{2e}$ , can render the relaxation times of the observed carbon nucleus,  $T_{1C}$  and  $T_{2C}$ , sufficiently short that an unusually broad  $^{13}$ C spectrum results. Our experiments, based on carbon spin relaxation time measurements, on several compounds demonstrate that this assumption is incorrect, at least among the paramagnetic lanthanide systems studied.

The line broadening mechanism operative in the present case can be traced to the paramagnetic anisotropy of the samples. The bulk effects are demonstrated in Figure 1 which shows the spectra of adamantane and adamantane in samples where the paramagnetic praseodymium and dysprosium acetates are the host. These samples were prepared simply by grinding adamantane with these compounds with a mortar and pestle yielding a mixture of small crystals of each compound at random orientations. The magnetic anisotropy is largest for dysprosium and is about eight times smaller for the praseodymium compounds. Significant broadening of the adamantane spectrum is observed in both cases, with the effect being greatest for the dysprosium sample (Figure 1B and C), which has the greatest anisotropy. The inhomogeneous broadening of 4 kHz observed in the adamantane spectrum caused by the dysprosium host (Figure 1E) is averaged by magic angle sample spinning. However, the averaging is incomplete (M. Alla and E. Lippmaa, Chem. Phys. Lett. 87, 30, 1982), and the residual linewidth in the spinning spectra (213 Hz in Figure 1C) scale with the bulk magnetic anisotropy of the paramagnetic particles of the host. Nevertheless, the spin echo spectrum in the spinning experiment (Figure 1E) demonstrates that the relaxation times of adamantane are unaffected by this procedure, as expected.

(continued on page 47)

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(continued from page 44)

Our experiments therefore demonstrate that a serious source of line broadening in paramagnetic solids arises from the anisotropy of the magnetic susceptibility in the compounds, and not necessarily from a depression of the carbon relaxation times. Thus, one may expect to observe narrow rare spin spectra in compounds where the bulk magnetic anisotropy is small.

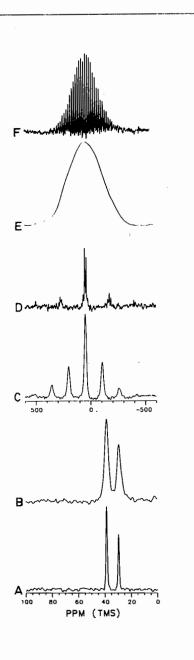
Yours sincerely,

Robert G. Bryant

S. Sanapathy

S. Ganapathy

/jh



### Figure 1

### Adamantane 13C spectra:

- A. CP-MASS
- B. CP-MASS with praseodymium acetate
- C. CP-MASS with dysprosium acetate
- D. Spin echo spectrum of the spinning sample C
- E. Static adamantane spectrum in powder of dysprosium acetate
- F. Spin echo static adamantane spectrum from sample E above

### UNIVERSITY OF GRONINGEN DEPARTMENT OF ORGANIC CHEMISTRY

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PHONE: 050-634235 TELEX: 53935 CHRUG NL Professor B.L.Shapiro Department of Chemistry Texas A and M University College Station , Texas 77843 USA

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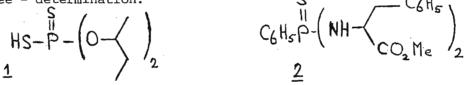
3 -

" <sup>31</sup> P NMR of Chiral Thiophosphates and Thiophosphonates "

Dear Professor Shapiro,

Recently we published a new method for enantiomeric excess (ee) determination of chiral alcohols based on  ${}^{31}$ P NMR analysis of derived phosphonates.<sup>1</sup>

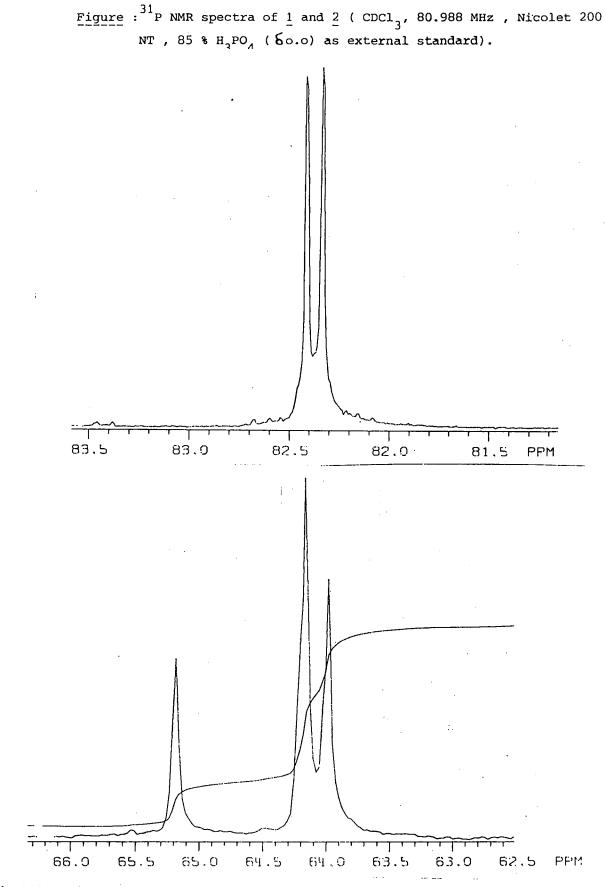
We have now investigated thiophosphates 1 and phenylthiophosphonicdiamides 2, prepared from racemic sec-butanol and racemic phenylalanine methyl ester respectively, as potential phosphorous derivatives for ee - determination.



Compound <u>1</u> exist as a mixture of a meso- isomer and a d,l pair and <u>2as a mixture of two meso- isomers and a d,l pair. The decoupled</u> <sup>31</sup> P NMR spectra (figure) clearly show the absorptions for each diastereoisomer in both cases. For <u>1</u> and <u>2</u> derived from enantiomerically pure sec - butanol and phenylalanine methyl ester single absorptions at 82.40 and 64.15 ppm respectively , are observed. Based on these results we are now developing a new <sup>31</sup> P NMR method for ee determination of chiral amines.

Please credit this contribution to the subscription of Dr WD Weringa. Sincerely yours,

Dr B.L.Feringa



1. B.L.Feringa, A.Smaardijk, H.Wynberg, J.Am.Chem.Soc., 1985, 107, 4798.

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University of New Mexico

DEPARTMENT OF CHEMISTRY Clark Hall 103 Albuquerque, NM 87131 Telephone 505: 277-6655

May 29, 1986

### Proton NOEs for Horse Met-cytochrome c

1. 5

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

Dear Barry:

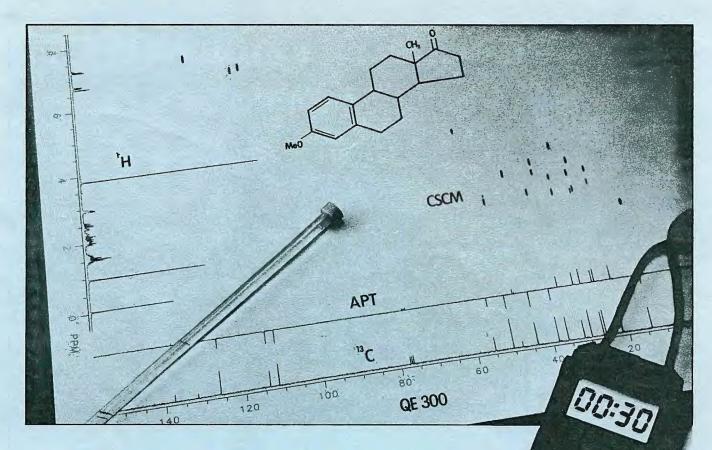
Our continuing attempts to study interprotein electron transport has brought us to examine physiologically relevant molecular redox complexes between yeast cytochrome <u>c</u> peroxidase and various cytochromes <u>c</u> The proton NMR spectra of ferric cytochromes <u>c</u> differs somewhat from species to species and we have encountered the need to make unambiguous assignments of hyperfine shifted resonances. The homonuclear proton nuclear overhauser effect has been shown to be valuable in this regard by several other workers and we have successfully followed in their paths. The results we have obtained on our GE 360 spectrometer, operating at 361MHz for proteins, is shown in the accompanying one dimensional difference spectra. In particular, our results have yielded assignments for several previously unassigned heme group protons which are proving valuable to our efforts at characterizing to molecular complexes.

With best wishes,

Jamés D. Satterlee Associate Professor

HEME CH, HIS 18 8 3 F зо 15 -S PPM 35 25 20 10 Ε n a k R A -95 25 20 ร่า 10 -s PPM

Caption. One dimensional homonuclear proton NDE's for horse met-cytochrome c with irradiation on the resonance indicated by arrow. A), B} heme methyl irradiation. The connectivities of the 3 resonances in C)-() indicate a spin system consistant with the C $\alpha$ -H, C $\beta$ -H<sub>2</sub> of the proximal histidine. F) Full cytochrome c Spectrum with assignments.



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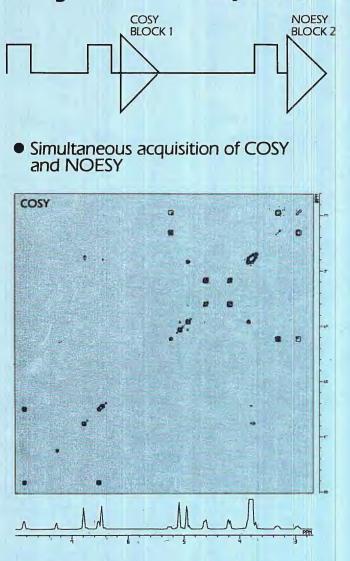
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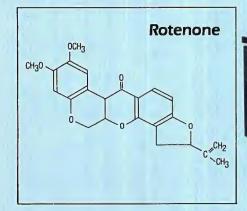
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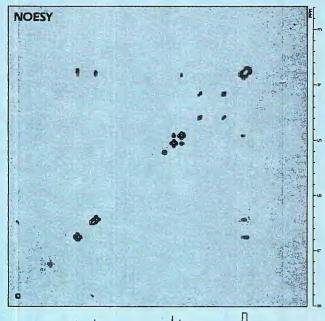
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