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NO. 297

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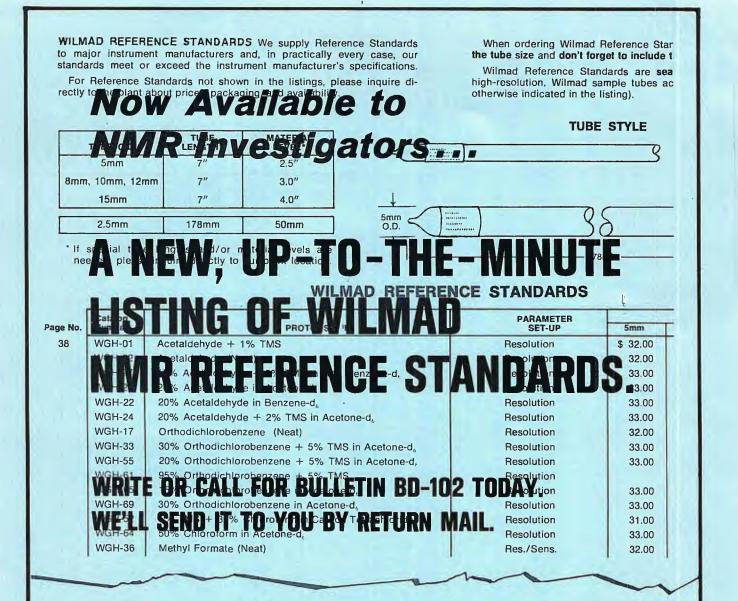
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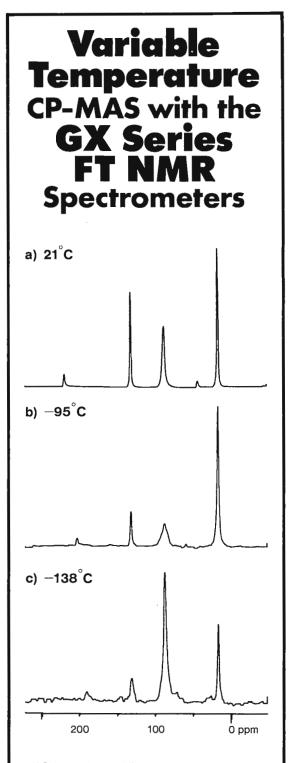
<u>DEADLINE DATES</u> No. 298 4 July 1983 No. 299 1 August 1983

All Newsletter Correspondence, Etc., Should Be Addressed To:

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

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 $^{\rm 13}{\rm C}$ (50.1 MHz) VT/MAS spectra of hexamethylbenzene. a) and c) $^1{\rm H}\text{-}^{\rm 13}{\rm C}$ cross polarization. b) Bloch decay. The peak at \sim 90ppm is due to the Delrin rotor.



297-1



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Ottawa, Canada K1A 0R6

March 29, 1983.

Prof. B.L. Shapiro Department of Chemistry Texas A and M University College Station, TX 77843 U.S.A.

Dear Barry,

UPDATING AN XL-100

We are still getting our spectra with a Varian XL100 interfaced to a Nicolet 1180 computer via a Nicolet 293B unit with a Nicolet 1010A pulse amplifier. As supplied such a system cannot pulse both the observe transmitter and the decoupling transmitter with computer control of both phase and duration of pulses at the two frequencies. It was also not possible to switch between C.W. and noise decoupling under computer control. Since modern software exists for doing these operations for experiments such as INEPT or $^{1}H^{-13}C$ chemical shift correlation, we decided to adapt the hardware of our spectrometer to carry out these functions.

It soon became apparent that the Varian Gyrocode Decoupler was not sufficiently stable to give good control of relative phases. Instead a frequency from the synthesizer normally used for heteronuclear studies was used to replace the offset VCO module. An extra power amplifier and modulator "brick" was put in the Varian console. A few circuits were slightly modified and the spectrometer now behaves as before or with the added capabilities. A circuit diagram showing all changes and using the manufacturer's numbering is included. The only significant cost was an extra 100 MHz "brick", which we happened to have in any case.

Yours truly,

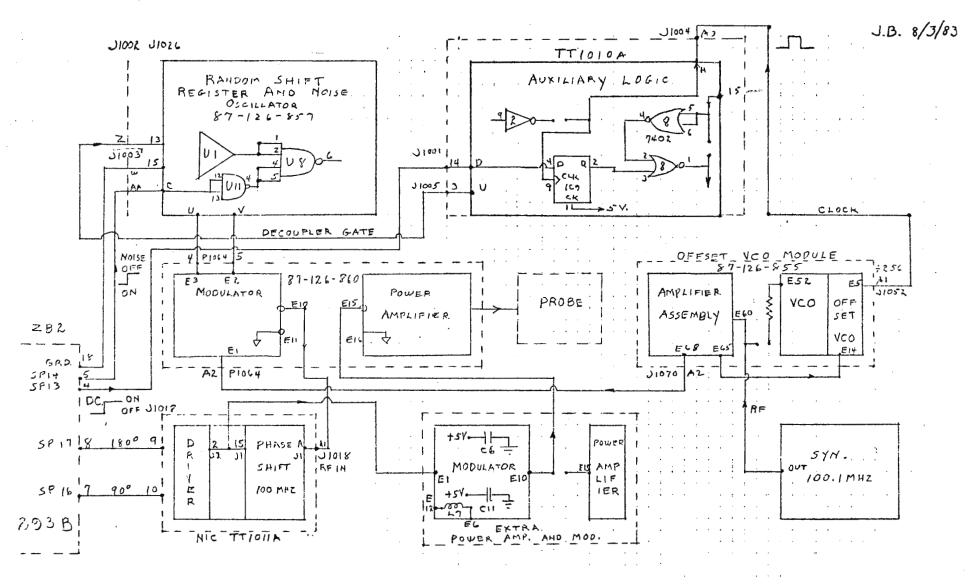
Dornaus Parques.

J. BORNAIS

S. BROWNSTEIN

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INSTITUTE OF CHEMICAL PHYSICS AND BIOPHYSICS ACADEMY OF SCIENCES OF THE ESTONIAN SSR

Lenini puiestee 10, Tallinn 200001, USSR Tel. 44-13-04, 60-57-59, 44-14-32

April 26, 1983 Ref.No. 33

ННСТИТУТ ХИМИЧЕСКОЙ И БИОЛОГИЧЕСКОЙ ФИЗИКИ АКАДЕМИЯ НАУК ЭСТОНСКОЙ ССР

200001 Таллии, бульвар Ленина, 10 Тел. 44-13-04, 60-57-59, 44-14-32

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

High Speed Ceramic MAS

Dear Professor Shapiro:

We have been using cylindrical air bearing supported MAS rotors since 1975 because they provide extremely stable and reliable orientation of rotation axes.* In early years and low magnetic fields the spinning speeds of few kHz were found quite acceptable for high resolution studies of proton decoupled ¹³C spectra of solids that allowed to use traditional precise glass tubes for rotor cylinders. Later, with increasing magnetic field (4.7 and 8.5 T wide bore supercons are currently in use in our laboratory) we had to look for stronger carbon-free materials to achieve remarkably higher speeds. Several oxide ceramic materials are probably most promising. We tried Al₂O₂ and exploded a ϕ 9 × 0.7 mm piece at 7 kHz, the frequency quite close to that one may expect. Ohters seem to be quite safe at speeds up to ~5 kHz. Unfortunately, precise machining of this material is possible only with diamond tools that is unacceptable for most NMR labs.

During several years we have successfully used machinable glass ceramic Macor (Corning) for both rotor and stator parts of the spinning system. Of course, to reach the same speeds one needs smaller diameter cylinders. The maximum speed of a 9 mm O.D. Macor spinner is about 5 kHz, and to obtain long time safe operation at this frequency we reduced the diameter down to 7 mm but increased accordingly the length of the rotor to accommodate the same amount of the sample (0.4 cm^3) . An NMR coil is machined from a copper tube for higher mechanical stability and it has now 11 turns very close to the sample (the radial clearance between the coil and the rotor is only 0.2-0.3 mm). The attached figure gives the dimension of the rotor together with a typical dependence on driving pressure.

We also managed to avoid any mechanical touch of any stator part with the spinning rotor, i.e. it is completely fixed by the air bearing system.

*For details see U.S. Patent No. 4254373 or Canadian Patent No. 1098170.

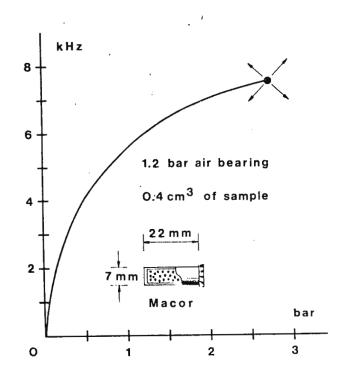
Sincerely yours,

Ξ

hau M.Alla E.Lipphaa

A.Salumäe

T.Tuherm



Instruments Inc.

40 West Brokaw Road San Jose, California 95110

Telephone: 800-538-7792 800-662-6203 (In California)

May 20, 1983

Dear Colleague:

Subject: Positions at Magnetic Resonance at IBM Instruments

We anticipate a number of postdoctoral and permanent job positions in the next six months for NMR and ESR scientists at our facilities in San Jose, California and in Danbury, Connecticut.

The positions involve applications, research, development, and marketing support. It is anticipated that most of the appointments will be at the Ph.D. level, although applications from highly motivated individuals at any degree level will be considered. A strong interest in instrumentation is a fundamental prerequisite for most of the positions; the specific area of scientific training (e.g. chemistry, physics, electronics, biochemistry, etc.) is of lesser importance.

Postdoctoral research positions are available beginning this summer. These positions allow the successful candidate to pursue some of his or her own research interests; very little contact with customers is anticipated. These are typically one year appointments with a strong possibility for renewal for a second year. An NMR postdoctoral position is available in my group at San Jose; the emphasis will be on applications of NMR to biological systems, including intact cells. An ESR postdoctoral position is available in Dr. Paul Kasai's group in Danbury. Both positions include an opportunity to interact with other scientists and to use the extensive facilities available at IBM. Our present instrument lines include NMR to 270 MHz, ESR, FT-IR, liquid chromatography, electrochemistry, process control apparatus, and the CS9000 laboratory computer. The salaries of the postdoctoral positions are competitive with beginning industrial salaries. Applicants should arrange to have a resume and three letters of reference mailed to me at the above address or to Paul Kasai, IBM Instruments, Inc., P. O. Box 332, Orchard Park, Danbury, CT 06810.

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Would you please pass this announcement to anyone who might be interested. Thank you.

Yours truly Chas. G. Wade

Manager Magnetics West Coast

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RESEARCH LABORATORY K34/281

International Business Machines Corporation

5600 Cottle Road San Jose, California 95193 (408) 256-5590

April 19, 1983

Prof. Bernard L. Shapiro Texas A&M University Department of Chemistry College Station, Texas 77843 Orientation of the Magic Axis for Small Samples Using the Centerband ⁷⁹Br Resonance in KBr

Dear Barry:

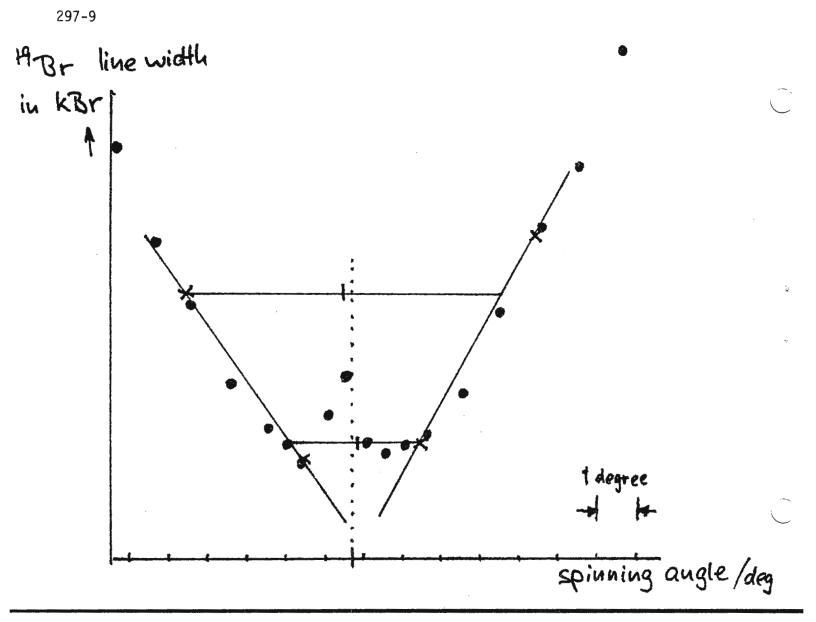
A simple method has been devised for orienting the magic axis in $^{13}\mathrm{C}$ MAS experiments using the ratio of centerband to sideband intensity in the ⁷⁹Br resonance of KBr. 1 Often, we use a small sample container (~70 $\mu l)$ in our low temperature MAS work, and it is not practical to use the large amounts of KBr necessary to obtain adequate sideband intensity in a reasonable time. Frye and Maciel have also pointed out the sensitivity of the width of the centerband to the orientation of the spinning axis. We have made some careful measurements of the variation of the centerband linewidth in the vicinity of the magic angle. Our results shown in the accompanying figure are similar to those shown in Fig. 4 of reference 1. The result which is important to us is that this kind of linewidth sensitivity as a function of angle can be obtained with a small amount of material (12 mg = 4.4 μ l of KBr) in a short time - (each point takes 40 seconds). We estimate that only four experiments are needed to get the angle to within 0.5°. Two lines are drawn through two points on each side of the curve, and the horizontal half way distance of these lies provides the angle setting used. The total measuring time for the four points was 160 The $^{79}\mathrm{Br}~\mathrm{T_1}$ relaxation time seems fairly constant from ambient seconds. temperatures to -170°C, where the data shown here were taken. Thus the technique may be quite fast, even at cryogenic temperatures.²

Best regards,

-M. Vieth

C. S. Yannoni

- J.S. Frye and G.E. Maciel, J. Magn. Reson. 48, 125 (1982). 1.
- 2. V. Macho, R.D. Kendrick and C.S. Yannoni, J. Magn. Reson. 50, 0000 (1983).



Another Application of Coexistence (cont. from p.10)

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- 2. C. L. Khetrapal and A. C. Kunwar, Chem. Phys. Lett. 82, 170 (1981).
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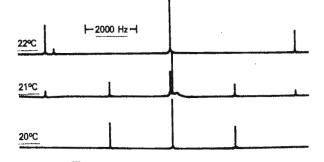


Fig. 1. Proton NMR spectra of acetonitrile oriented in the nematic phase of a mixture of EBBA and ZLI-1167 at 270 MHz. Solute concentration: 3.3 wt% in 77.57% ZLI-1167 and 22.43% EBBA.

DEPARTMENT OF HEALTH & HUMAN SERVICES



Building 2, Room 109

Public Health Service

National Institutes of Health Bethesda, Maryland 20205

May 12, 1983

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

Dear Professor Shapiro:

Title: Another Application of Coexistence!

I am currently in coexistence with the National Institutes of Health and the Raman Research Institute and this contribution may be credited to my Indian account. The results, described herein though arise from such a coexistence, are based upon a different type, namely the observation of two types of spectra at a critical concentration and temperature in mixed liquid crystals of opposite diamagnetic anisotropies.^{1,2} At the critical point where the two spectra coexist, the dipolar couplings are related by a factor of -2 (Figure 1, central trace). Though the applications of such spectra have been well exploited for the (1) determination of chemical shift anisotropy without a reference compound or without changing experimental conditions,^{2,3} (2) determination of diamagnetic anisotropy of liquid crystals⁴ and (3) determination of indirect and direct dipolar couplings between heteronuclei, ^{5,6} the present contribution describes another application towards the determination of spectral parameters which otherwise cannot be obtained.

It is well known that the NMR spectrum of an oriented AB system (which shows 4 lines) does not provide all the three parameters namely the indirect spinspin coupling (J), the direct dipolar coupling (D) and the chemical shift (δ) between the two nuclei, from the line positions which have only two independent spacings. The observation of the spectrum at the critical concentration and temperature which provides two spectra due to the coexistence of two types of orientations corresponding to the alignment of the liquid crystal optic axis along and perpendicular to the direction of the magnetic field, provides such information. In the two spectra, the D values are related by a factor of -2 and hence 4 independent parameters--namely one J, one D and 2δ 's have to be determined from the 4 spacings and this is always possible.

Yours sincerely,

C.L. Khet Sapal

C. L. Khetrapal Laboratory of Chemical Physics National Institute of Arthritis, Diabetes, and Digestive and Kidney Diseases

(Cont. p. 9)



UNIVERSITY OF UMEA Department of Organic Chemistry

Professor Bernard L. Shapiro April 28, 1983 Texas A&M University College Station, TX 77843

Dear Barry:

Artificial Intelligence in Carbon-13 NMR: Prediction of C-13 NMR Chemical Shifts of Aromatics Using Partial Least Squares Data Analysis.

We have recently examined C-13 NMR SCS of a variety of substituted aromatic species. The eigenvector projections in the M-dimensional variable spaces showed a similar clustering behaviour of C-13 SCS as the grouping noticed for monosubstituted benzenes¹. However, the relative positions of the subclasses, i.e. donors, acceptors, alkyls and halogens and/or the extensions of these subclasses vary compared with the situation in the benzene SCS variable space. The "similarity" or the common components of the two data blocks could be quantified by a suitable rotation of the two variable spaces. A "soft" modeling metod called partial least squares (PLS) data analysis can achieve this "rotation",

Initially, the C-13 SCS data were divided into two blocks X and Y, as shown in Figure. Each of these blocks was then modelled by a product of two smaller matrices , a loading matrix (B and C, respectively) and a score matrix (T and U, respectively) i.e. X= TB + El and Y= UC + E2, where El and E2 are residuals. The matrices B and C were calculated so that both ||X-TB|| and ||Y-UC| were small and so that U and T were correlated with each other columnwise.

As an example of this approach, the PLS data analysis was applied on a benzene shift matrix (X) and a 2-substituted naphthalene shift matrix (Y). The C-13 NMR SCS of "unknown" naphthalenes can then be predicted provided that the corresponding benzene data exist. The $\Delta\delta$ (exp-calc) values were in all cases better than 0.6 ppm i.e. close to the interlaboratory accuracy.

Thus for the prediction or assignment of C-13 NMR SCS of monosubstituted aromatics, the following conditions must be fulfilled for the use of PLS analysis:

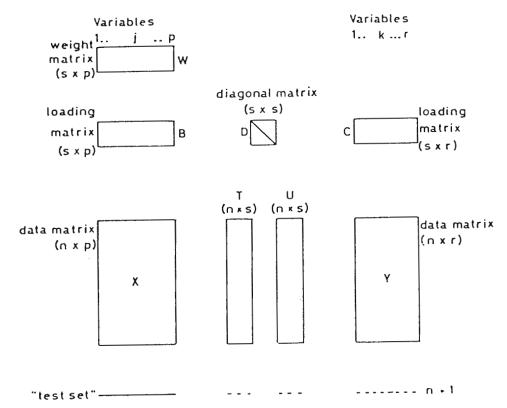
a. Correctly assigned C-13 NMR data for at least 6-8 representative substituted compounds should exist for the series of interest (Y-matrix). Since most of the shift variance is explained by the interclass behaviour, at least one substituent from each of the alkyl, donor, acceptor and halogen class is needed.

ي_

2

b. Correctly assigned benzene data (X-matrix) for the same substituents as in the Y-matrix.

Shift predictions can then be made for unassigned compounds (test set) for which the corresponding benzenes have been measured. Steric effects which are absent in the benzene model can of course not be predicted in the Y-set.



1.D. Johnels, S. Clementi, W. J. Dunn III, U. Edlund, H. Grahn, S. Hellberg, M. Sjöström and S. Wold, J. Chem. Soc. Pekin 2, in press.

Best regards Tuf Ulf Edlund

297-13



ST. LOUIS, MISSOURI 63130

DEPARTMENT OF CHEMISTRY

May 2, 1983

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

Dear Dr. Shapiro:

S/N in MAS Spectra of Solids

The relation between S/N, H_0 and sample size has been discussed^{1,2} but the effect of spinning sidebands on sensitivity has not been addressed. A new analysis is not difficult if dielectric losses are ignored and S/N for a fixed number of acquisitions, as opposed to a fixed time, is desired. These two simplifications result in overstatement of the benefits of high field.

Since a discrete Fourier transform is just a sum we have

$$\frac{S}{N} = \frac{\text{Induced Voltage • FID Duration}}{\text{Noise Voltage • (Noise Duration)}^{1/2}}$$
(1)

the square root since noise adds incoherently.

The induced voltage is proporational to $d\Phi/dt$ or to $H_0^2 D^2$. H_0 affects both dt and, though the Boltzman factor, Φ . Φ varies as sample volume or D^3 (diameter) if only sample size varies or as D^{-1} if only the coil size varies, so D^2 is appropriate if both change to maintain a constant shape and filling factor.

Noise voltage is (AC resistance) $^{1/2}$ which goes as $H_0^{1/4}$. Increases in conductor length and width cancel so size has no influence on noise.

If there are no spinning sidebands the FID duration is 1/line width. Noise duration is usually set to FID duration by apodizing the data.

Chemical shift anisotropy (CSA) large enough to cause sidebands reduces FID duration, not at its end, but throughout, in patches spaced a spinner period apart. If CSA is measured in units of spinning speed and rounded up to the next integer, then FID duration varies roughly as CSA^{-1} . Substituting in eq. 1 gives

 $\frac{S}{N} = H_0^{7/4} D^2 (line width)^{-1/2} CSA^{-1}$ (2)

This assumes neither PASS^{3,4} nor TOSS is used to manipulate spinning sidebands. Combining independent PASS spectra or FID's simply multiplies FID duration and noise duration by the number of FID's used. The number required is about CSA so with PASS we have

$$\frac{S}{N} = H_0^{7/4} D^2 \text{ (line width)}^{-1/2} CSA^{-1/2}$$
(3)

Dr. Bernard L. Shapiro May 2, 1983 Page 2

Cutting up an ordinary spectrum with scissors and consolidating spinning bands gives the same result as PASS.

At high field, line width is proportional to $H_0.5$ We find no improved resolution of 15 N lines in cell components on changing from 90 to a 200 MHz spectrometer. Changing from 60 to 200 MHz does improve 13 C resolution in polymers however. Perhaps most line widths increase with field at above 100 MHz proton frequency.

Both Mach number and centrifugal stresses limit the surface velocity of spinners to a constant. This makes $CSA = H_0D^{-1}$. Substituting into eqs. 2 and 3 we get

 $\frac{S}{N} = H_0^{1/4} D$ without PASS and (4)

$$\frac{S}{N} = H_0^{3/4} D^{3/2}$$
 with PASS (5)

If one holds the sidebands at a constant, tolerable height, either without PASS or with a fixed number of PASS spectra then CSA is a constant and D = $1/H_0$ so

$$\frac{S}{N} = H_0^{-3/4} \text{ or } \frac{S}{N} = D^{3/4}$$
 (6)

Very high fields improve sensitivity dramatically in liquids but in common solids over half and perhaps all of this benefit is irretrievably lost to broader lines and spinning sidebands.

Please count this letter toward the Monsanto subscription.

Sincerely,

Ion Dieon

W. Thomas Dixon

- 1. A. Abragam, Principles of Nuclear Magnetism, 83 (1961).
- 2. D.I. Hoult and R.E. Richards, J. Mag. Resn. 24, 71 (1976).
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297-14

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Professor B.L. Shapiro Dept. of Chemistry Texas A & M University College Station, TX 77842 U S A



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Isotope Effects of Benzylic Deuterons on ortho 13 C Chemical Shifts Correlate with $C^{1}-C^{2}$ π -Bond Order

Dear Dr. Shapiro:

Benzylic deuterons (e.g. in $CD_3-C_6H_5$) cause surprisingly small isotope shifts of the ortho carbons. Wesener and Günther¹ have explained this by the counteraction of "normal" (i.e. shielding) and hyperconjugative (i.e. deshielding) effects of the deuterons. One should be able to verify this interpretation by studying a series of compounds containing a $CD_3-C^{1---}C^2$ fragment in which the $C^1-C^2 \pi$ bond order is systematically varied between 0 and 1. If the π bond order is small, the "normal" effect should dominate, whereas large π bond orders should allow better (hyper)conjugation and hence cause deshielding of the ortho carbons. Our data in the Table show that this is indeed the case. The π bond order, P_{π} , and the isotope shift over three bonds, ${}^{3}\Delta = \delta_{RD} - \delta_{RH}$, show a nice linear correlation (Figure)

$$^{3}\Delta$$
 [ppb] = 88.4 P_m - 54.9 (r = 0.993)

which proves the conjugative component of this isotope shift. This correlation, however, holds only strictly if the geometries of the compounds compared are very similar. Steric factors, e.g. the interference of ortho substituents as in 1-(trideuteromethyl)naphthalene, cause such a strong disturbance of the isotope shift that the above equation is no longer applicable.

A communication relating to the contents of this letter is in press (JACS).

Sincerely yours, LudgesEmst

1. J.R. Wesener, H. Günther, Tetrahedron Lett. 23, 2845 (1982).

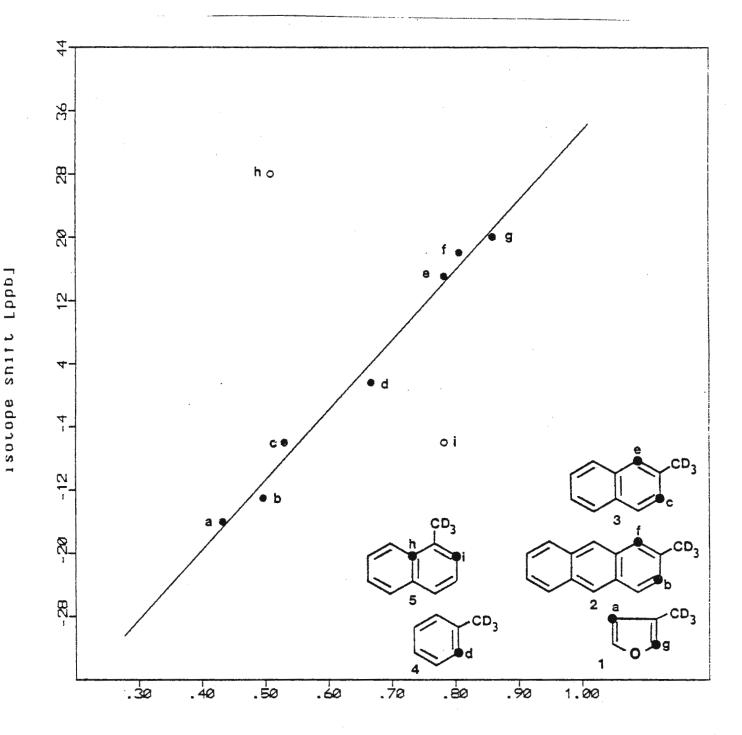
Encl. (Figure and Table)

Table. Deuterium Isotope Effects^{a,b} on ${}^{13}C$ Chemical Shifts of ortho Carbons and C_{ipso}-C_{ortho} π Bond Orders^C in Compounds 1 - 5

Compound	carbon	isotope shift	bond	π bond order
1	C-4	-16	C-3/C-4	0.432
2	C-3	-13	C-2/C-3	0.496
3	C-3	- 6	C-2/C-3	0.530
4	C-2	+ 1.6 ^d	C-1/C-2	0.667
3	C-1	+15	C-1/C-2	0.782
2	C-1	+18	C-1/C-2	0.806
1	C-2	+20	C-2/C-3	0.859
5	C-2	-6	C-1/C-2	0.782
5~~~	C-8a	+28	C - 1/C-8a	0.509

- ^a Values given in ppb (0.001 ppm); positive sign denotes deshielding in the deuterated compound.
- ^b Measured at 100.6 MHz of mixtures of the protium and deuterium analogues; digital resolution better than 0.5 ppb; error estimate ± 2 ppb.
- C From INDO molecular orbital calculations (QCPE program No. 141) of benzene, naphthalene, anthracene and furan; experimental geometries used as input.

^d From reference 1.



pi bond order

Figure. Correlation between the deuterium isotope effects on vicinal carbon chemical shifts and the $C_{ipso}-C_{ortho}$ π bond order in compounds 1 to 5. Only points a to g (filled circles) were considered in the calculation of the least squares line.

BOSTON COLLEGE CHESTNUT HILL, MASSACHUSETTS 02167

(617) 969-0100

DEPARTMENT OF CHEMISTRY

May 25, 1983

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

Dear Barry:

POSITION AVAILABLE

We have an opening for an electronic and instrumentation engineer which we would like to bring to the attention of your readers. The position requires thorough knowledge of solid state electronics including experience in the repair and operation of NMR (including Fourier transform) spectrometers, a facility with computer hardware and software as well as expertise in the design and construction of computer-instrument interfaces and the maintenance of various computer accessories such as terminals and tape-disc drives.

The individual, who will report to the Chairman of the Chemistry Department, will be responsible for the repair and maintenance of instrumentation in the Chemistry and Geology Departments. Working from schematics, he will troubleshoot state-of-the-art instrumentation including a mass spectrometer, IR, UV, AA, GC, HPLC, ESR, scintillation counters, multichannel analyzers and centrifuges, many of which are under microprocessor or computer control; will establish a workshop and procure necessary equipment.

BENEFITS: Boston College offers an attractive benefit program including tuition remission and a full range of insurance programs. Founded in 1863, Boston College is one of twenty-eight Jesuit colleges and universities in the United States, with a full-time and part-time enrollment of over 14,000 men and women. The University consists of ten schools and Colleges. Administration and faculty number approximately 2,300. Located only a few miles from Boston, the University has the advantage of proximity to a large metropolitan center while at the same time enjoying a 200-acre site in Chestnut Hill and a second attractive 40-acre campus in Newton just a mile away.

Cover letter, resume and salary history should be sent to Mary McMillan, Personnel Office, Boston College, Chestnut Hill, MA 02167.

Sincerely,

D.J. Sardella Professor of Chemistry

DJS/rr

The University ____of ____

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THE COLLEGE OF LIBERAL ARTS AND SCIENCES Department of Chemistry

10 May 1983

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

NMR Bilayer Signature --- A Rubber Stamp?

Dear Prof. Shapiro:

Handwriting analysts continually try to ferret out forgeries in the humanities. However, for a number of years, the practice of inferring molecular structural features from subtle changes in the quadrupolar splittings of deuterium labeled phospholipids in bilayers and membranes perturbed by the addition of drugs, cholesterol, proteins, etc., has continued unchallenged.

Figure 1 shows the DMR spectrum of myristic acid-d27 solubilized in a thermotropic nematic solvent. The quadrupolar splitting pattern is indistinguishable from that reported for aliphatic fatty acids in many lyotropic bilayer phases. The emblematic NMR Bilayer Signature -- emphasized in the plot of the C-D order parameter versus methylene segment number in Figure 2 -- is exhibited despite the absence of a water-lipid interface! Moreover, it is not a fortuitous consequence of 'anchoring' one end of the chain via dimerization of the acid in the uniaxial organic solvent; the methyl ester of myristic acid-d27, apart from differences at the α -methylene, exhibits a similar order parameter profile.

Attempts to solubilize a deuterium labeled <u>ionic</u> phospholipid (DPPC-d₆₂) in several nematic solvents have not been successful. Phase separation occurs when the solution is cooled below the istropic-nematic transition. However, on the basis of other DMR studies of n-alkanes and substituted alkanes in liquid crystal solvents, it seems probable that the quadrupolar splitting pattern of a labeled phospholipid in a nematic melt would be a carbon copy of that reported for bilayers and membranes.

Very truly yours,

(cont. p. 22)

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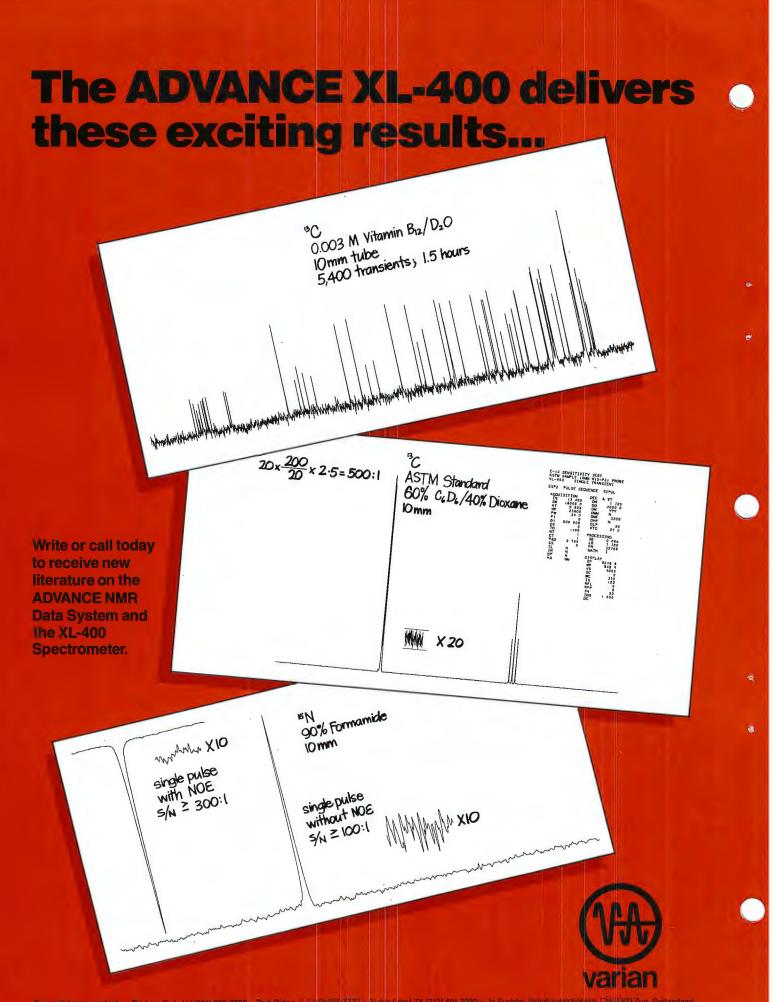
Flexible and easily expandable. This system lets you add commercially available peripherals to meet specific application requirements. This capability and our expandable Pascal-based software keeps your instrument "state-of-the-art" in the rapidly evolving field of NMR research.

Send for literature now. For details concerning Varian's new ADVANCE XL-400 Spectrometer, call the Varian sales office nearest you. Or write: ADVANCE XL-400, Varian Associates, D-070, 611 Hansen Way, Palo Alto, CA 94303.



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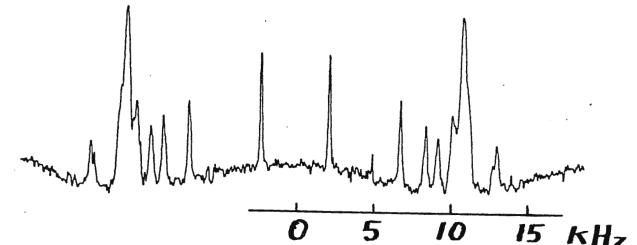
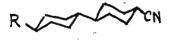


Figure 1. The DMR spectrum of $CD_3(CD_2)_{12}COOH$ solubilized (1% wt.) in the nematic solvent ZLI-1167, a eutectic melt of



where R = n-propyl, n-pentyl and n-heptyl (1:1:1 mixture). The spectrum is an average of 1000 FID's at 335 K ($T_{red} = 0.95$); 13.8 MHz.

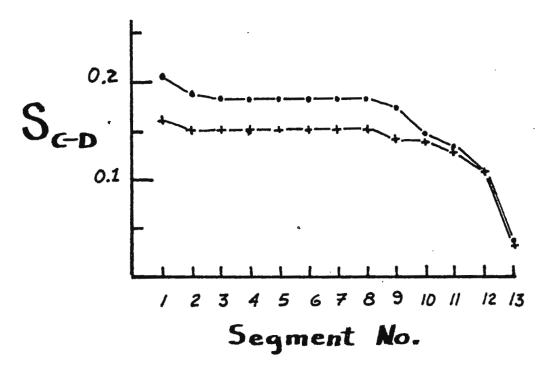


Figure 2. Order parameters versus methylene segment number (increasing with distance from the acid group) derived from the quadrupolar splittings:

$$\Delta V_{i} = \frac{3}{2} (168 \text{ kHz}) S_{C-D}^{i} P_{2} (\cos \beta).$$

 $\beta = 90^{\circ}$ as the diamagnetic anisotropy of ZLI-1167 is negative;

• - $CD_3 (CD_2)_{12}COOH$ + - $CD_3 (CD_2)_{12}COOCH_3$. 297-22

THE EIGHTH MEETING OF THE INTERNATIONAL SOCIETY OF MAGNETIC RESONANCE NMR . NQR . EPR Applications in Physics . Chemistry . Biology . Medicine

August 22-26, 1983

Chicago, Illinois

The aims of the International Society of Magnetic Resonance are to advance and diffuse knowledge of magnetic resonance and its applications in physics, chemistry, biology, and medicine, and to encourage and develop international contacts between scientists.

The Society sponsors international meetings and schools in magnetic resonance and its applications. Past meetings have been held in Japan, Australia, Brasil, Israel, India, Canada, and The Netherlands. In addition it publishes as its house and quarterly review journal, <u>The Bulletin of Magnetic Resonance</u>.

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The Eighth Triennial Meeting Of The International Society Of Magnetic Resonance will cover the broad field of magnetic resonance, including the theory and practice of nuclear magnetic resonance, electron paramagnetic resonance and nuclear quadrupole resonance spectroscopy. Included will be applications in biology, chemistry, medicine and physics. The meeting will strive to foster interaction among scientists in different fields of magnetic resonance and to encourage interdisciplinary exploration.

The program will feature approximately 45 invited speakers. In addition, researchers whose abstracts have been selected will present them as short talks, in four concurrent sessions, or as posters on Monday or Tuesday evening. All presented abstracts will be published in an abstract booklet to be available at the meeting.

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PLENARY AND KEYNOTE SPEAKERS

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	R. L. Armstrong:	Dimer Creation and Annihilation Dynamics in Hydrogen Noble Gas Mixtures
	P. W. Atkins:	Magnetic Reactions
	R. Blinc:	Magnetic Resonance in Incomensurate and Chaotic Systems
	F. Buonanno:	NMR Imaging of the Central Nervous System
	V. F. Bystrov:	NMR Study of Protein Solution Structures Dynamics and Conformational Transitions
	G. Chidicimo:	Molecular Dynamics and Structure of Liquid Crystal System by NMR Line Shape Analysis
	L. E. Crooks:	Instrumentation and Reconstruction Techniques in Imaging
	R. Damadian:	NMR Scanning in Modern Medicine
	T. P. Das:	¹⁹ F* Asa Probe for NQR Investigation of Flourine Compounds
	H. Dehmelt:	Geonium Spectra and the Finer Structure of the Electron
	G. Eaton:	Metal-Nitroxyl Interactions
`	D. Fiat:	Biophysical Applications of ¹⁷ O NMR
	J. Freed:	ESR and Molecular Dynamics
	J. T. Gerig:	Flourine NMR Spectroscopy of Protein
	R. M. Golding:	Recent Developments in the Theory of NMR Shifts in Paramagnetic Systems
	M. Goldman:	Rotating Helical Nuclear Magnetic Ordering
	D. Gorenstein:	³¹ P NMR of Nucleic Acid
	E. Hahn:	Spin Echo Phenomena
	K. H. Hausser:	Microwave Induced Optical Nuclear Polarization
	T. L. James:	The Dynamic Structure of Nucleic Acids
	V. J. Kowalewski:	Latest Results of Indor Spectroscopy
	P. Lauterbur:	Zeugmatography in Science and Medicine
	E. Lippmaa:	High Resolution Nuclear Magnetic Resonance Spectroscopy of Quadru- polar Nuclei in Solids
	J. L. Markley:	Homonuclear and Heteronuclear Two Dimensional Fourier Transform NMR Spectroscopy of Protein
	A. R. Margulis:	NMR Imaging in Medicine

297-25

PLENARY AND KEYNOTE SPEAKERS (continued)

H. M. McConnell:	Magnetic Resonance Spectra of Membranes						
W.B. Mims:	Accessibility of the Active Site in Metalloproteins as Studied by Electron pin Echo Envelope Ratio Analysis						
M. Nechtschein:	Magnetic Resonance Studies of Spin Dynamics in One-Dimensional Systems						
J. Norris:	Nanosecond Time Resolved Magnetic Resonance of the Primary State of Bacterial Photosynthesis						
E. Oldfield:	High Resolution NMR of Inorganic Solids						
M. M. Pintar:	NMR and Tunnelling						
M. Punkkinen:	NMR and Liberational Tunnelling in Some Ammonium Compounds						
L L. Pykett:	Applications of NMR Imaging to Biology and Medicine						
H. Ruterjans:	¹⁵ N-NMR Spectroscopy in Biochemistry						
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J. Smidt:	Coal Research by Means of Magnetic Resonance						
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E Zaitlart	NMP Imaging of Thoracic Structures						

E. Zeitler: NMR Imaging of Thoracic Structures

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Santa Cruz, California 95064 May 2, 1983

MODIFICATION OF ANALOG-TO-DIGITAL CONVERTER FOR THE JEOL FX-60 NMR SPECTROMETER

Dear Dr. Shapiro:

It has been determined that after an Analog-To-Digital Converter(ADC) malfunction or failure on the FX-60 NMR Spectrometer, a direct replacement ADC cannot be purchased, insofar as DATEL-Model ADC-N12B3C is no longer manufactured or supported by DATEL and JEOL respectively.

Recently I devised a permanent modification of the standard FX-60 NMR spectrometer's ADC Board (JEOL, AD-00611A) replacing the ADC-N12B3C and its associated external components and connections with DATEL Model ADC-L12B2C4.

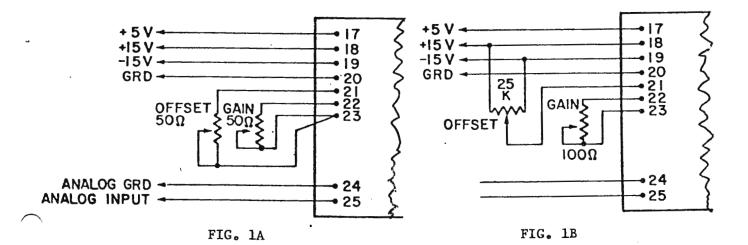
With this modification, not only is the obsolete ADC circumvented, the ADC-L12B2C4 is directly interchangable with the ADC for the JEOL FX-100 NMR Spectrometer. (1)

CONSTRUCTION

A schematic diagram (Fig. 1A & B) shows the Gain and Offset external adjustment connections for ADC-N series and ADC-L series for 2's Complement (BiPolar) output format.

ADC-L Series

ADC-N Series



ADC-N Series

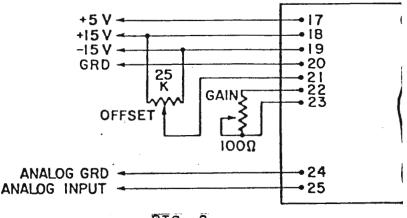
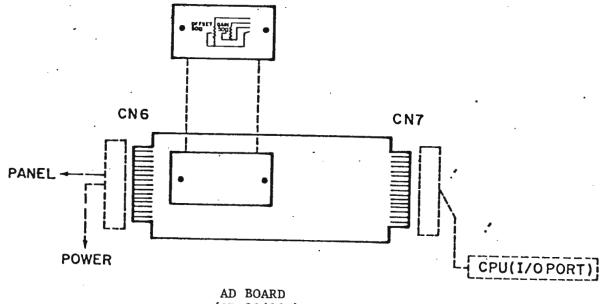


FIG. 2

The ADC-N12B3C Gain and Offset external connections (Fig. 2) are disabled by either removing the Offset and Gain Potentiometers from the AD Board (JEOL AD-00611A) or by electrically opening the circuit connections between the two potentiometers and the ADC socket connector (Pins 21, 22, & 23).

The ADC-L12B2C4 Gain and Offset potentiometers are both 50 ohm multiple turn. They are electrically and physically constructed on a $2\frac{1}{2}$ IN x 1 IN Vector Board, and conveniently mounted with two standard 3/8 IN standoffs on existing hole mounts (Fig. 3). Electrical connections are made to the ADC socket, pins 21, 22, & 23 with hook-up wires (Fig. 1A).



(AD-00611A)

FIG. 3

The analog input to the ADC must be inverted. The ADC-N12B3C Binary Coding is 0's with +5.00 VDC full scale (2) whereas the ADC-L12B2C4 registers all 1's with the same input signal (3). The input signal can be reversed by interchanging the leads at pins 1 and 2 at the AD INPUT connector, CN2 or reversing the two leads at the AD RANGE sensitivity switch, SW2b, pins 1 and 2 which is actually easier and more conveniently accessable (4).

RESULTS

Calibration of the ADC Gain and Offset is not necessary, because the primary purpose of the computer is time averaging. The ultimate results are therfore relative.

I have already incorporated this modification in our FX-60. It takes around one to two hours to do and there are absolutely no observable difference in resultant data.

If there is interest in the calibration of the ADC Gain and Offset potentiometers, I will be glad to forward a calibration sheet to any person wanting one.

Yours sincerely, 00 James L. Loo

REFERENCES

- 1. Circuit Diagram, FT-NMR System (IC-E055), Schematic No. 8, AD Board, JEOL LTD, Tokyo, Japan
- Data Sheet, ADC, Model ADC-N Series, DATEL INTERSIL, Mansfield, MA (1976)
- 3. Data Sheet, ADC, Model ADC-L Series, DATEL INTERSIL, Mansfield, MA (1979)
- 4. Circuit Diagram, FT-NMR System (IC-E055), Schematic No. 6, AD-DA Unit Connection, JEOL LTD. Tokyo, Japan

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Prof. Dr. O. Lutz

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Texas 77843

U.S.A.

Ihr Zeichen

Unser Zeichen

Ihre Nachricht vom

Lu/Kr

Some more on Wine NMR Spectroscopy: 23 Na and 39 K

Dear Barry,

when I saw the contribution by Martin, Martin and Mabon in the April issue I remembered on some earlier NMR investigations in this laboratory on natural products. Once we investigated the ²³Na and ³⁹K NMR signal in a small part of a bottle of Ruländer^{*} (1976). As one can derive from the spectra, the content of sodium is relatively small compared with that of potassium, if one takes into account the large difference between the receptivities for the two nuclei. We hope that the vine has accumulated the potassium!

Sincerely yours WW (Otto Lutz)

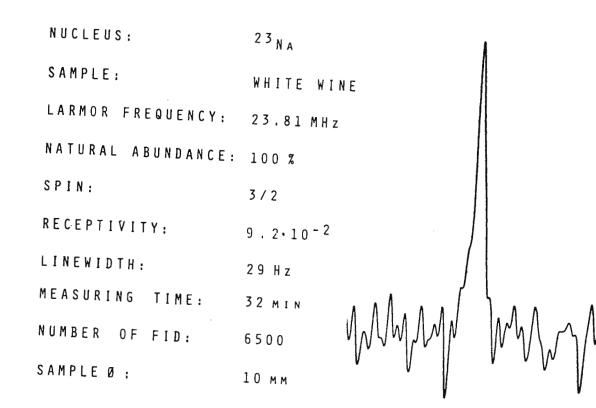
a. thousand

(Günther Kössler)

a famous sort of wine

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39_K NUCLEUS: SAMPLE: WHITE WINE LARMOR FREQUENCY: 4.20 MHz NATURAL ABUNDANCE: 93.1% SPIN: 3/2 RECEPTIVITY: 4.7.10-4 LINEWIDTH: 15 Hz MEASURING TIME: 30 MIN NUMBER OF FID: 8849 SAMPLE Ø : 10 MM

THE INSTITUTE FOR CANCER RESEARCH

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May 19, 1983

Professor B. L. Shapiro Department of Chemistry Texas A and M University College Station, Texas 77843 Photo-Induced CIDNP of Nucleoside Triphosphate Analogs

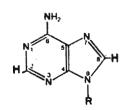
Dear Barry.

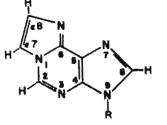
I have been busy setting up my new lab at the Institute for Cancer Research and have not done much experimental work. However, we have some results with photo-induced CIDNP of nucleoside triphosphate analogs which were obtained on a Bruker 360 MHz instrument at the University of Pennsylvania with the help of Dr. George McDonald. Etheno nucleotides (structures shown below) react with photo-excited flavin in a cyclic reaction resulting in nuclear spin polarization of the nucleotides and the flavin. Fig. 1 presents ¹H spectra of etheno ATP and etheno CTP obtained with a special Bruker CIDNP probe designed so that the light from the argon ion laser (Coherent, 2 watt) enters the sample at the center of the receiver coil at a right angle to the long axis of the sample tube. The strongest CIDNP enhancement is observed for the etheno-7 proton of the etheno-nucleotides; in addition the C2 and C8 protons of the adenine moiety of etheno ATP are enhanced more than those of ATP. The etheno analogs are good substrates for many ATP utilizing enzymes and CIDNP spectra may prove useful in studying protein-ligand complexes because of the enhancement and simplification of the CIDNP spectra.

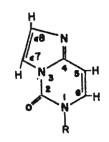
Sincerely yours,

mildred Cohn Julie C. Scheff Julie E. Scheffler

Mildred Cohn







Adenosine

I.N⁶-ethenoadenosine

3, N⁴-ethenocytidine

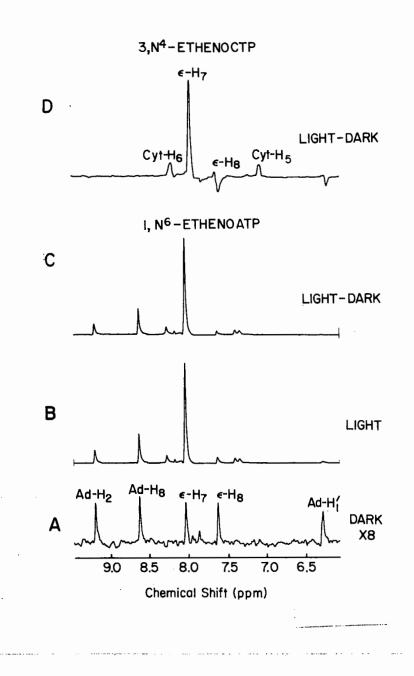


Fig. 1 - Spectra A, B, C: 1 mM etheno ATP, 0.2 mM N¹⁰ carboxyethyllumiflavin; pH 7.5, 32 scans, 0.6 sec irradiation, 10 ms delay after irradiation; spectrum D, same conditions except 1 sec irradiation and 1 ms delay.

CASE WESTERN RESERVE UNIVERSITY · CLEVELAND, OHIO 44106

SNU12

May 31, 1983



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

Heteronuclear 2D-NOE Spectroscopy

Dear Professor Shapiro:

The homonuclear 2D-NOE¹ and 2D-exchange² experiments are extremely useful for structure elucidation. We have developed the counterpart of these experiments which allows the correlation of the chemical shifts from heteronuclei when there is cross relaxation between these nuclei.

The pulse sequence for observing Heteronuclear 2D-NOE spectra is shown in Scheme I. The pulse and receiver phases are adjusted in a four cycle sequence as shown in order to eliminate the large unmodulated signal component and to achieve the equivalent of quadrature phase detection in the second dimension. FG is a field gradient pulse which eliminates multiple quantum coherence and residual transverse magnetization from imperfect 90° and 180° pulses.

Although there are more efficient ways of correlating 1 H and 13 C chemical shifts (via J-modulated experiments) the Heteronuclear 2D-NOE spectrum of 2-bromobutane (Figure 1) is useful example which clearly 13 illustrates the appearance of such spectra. The dipolar relaxation of 13 C is primarily determined by directly bound protons. The shifts of the carbons are correlated with the shifts of those protons which contribute to the 13 C NOE.

This experiment should be more useful for studying hydrogen bonding to carbonyls in proteins, for studying metal (M) ion binding sites in large molecules using $M{H} - 2DNOE$, and for studying exchange of amide protons using $N{H} - 2DNOE$.

Please credit this contribution to the account of Bill Ritchey.

Incere Peter L. Rinaldi

Assistant Professor of Chemistry

PLR:ar

- 1. J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, <u>J. Chem Phys.</u>, 71, 4576 (1979).
- 2. Y. Huang, S. Macura, and R. R. Ernst, J. Am. Chem. Soc., 103, 5327 (1981)

Department of Chemistry

(cont. p. 36)

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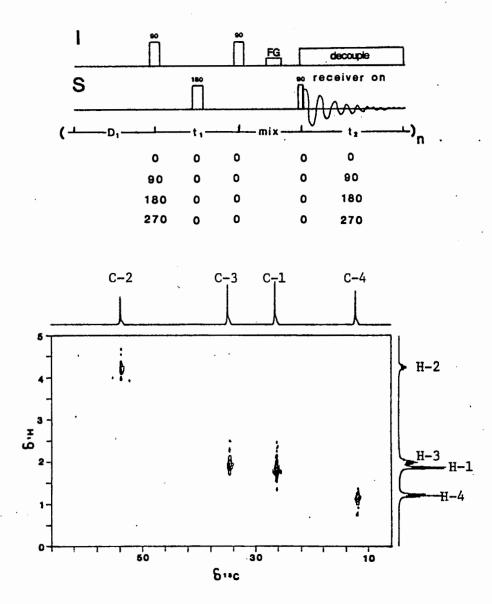


Figure 1. Contour plot of the ${}^{13}C({}^{1}H)$ heteronuclear 2D-NOE spectrum of 2-bromobutane. Spectral acquisition parameters were: 15 and 40 as 90° pulses for ${}^{13}C$ and ${}^{13}H$, respectively, 0.085s acquisition time, 3000 Hz sweep width in the ${}^{C}C$ frequency dimension, and a 2.0s mixing time; 128 spectra (8 transients each) were accumulated with t_1 incremented to provide the equivalent of a 1000Hz sweep width in the H frequency dimension. After Fourier transformation with respect to t_2 , the 128 points in the second time domain were zero filled to 512 before Fourier transformation with respect to t_1 . The 2D-NMR spectrum is displayed in the absolute value mode to avoid phasing problems. The normal one-dimensional ${}^{13}C$ and H NMR spectra are also shown along their respective chemical shift axes for comparison. The 4 Hz data point resolution in the H frequency dimension of the 2D-spectrum is insufficient to allow resolution of the proton multiplicities.

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GRUPPO MONTEDISON

MONTEOIPE

lay 30 1983

Professor Bernard Shapiro Dept. of Chemistry Texas A & M University College Station - TX 77843 - USA MONTEDIPE/PM/CER Stab. Petrolchimico Via della Chimica 30175 Porto Marghera (Venezia) ITALY

Dear Professor Shapiro,

13C NMR CHARACTERIZATION OF THE HPLC FRACTIONS OF POLYETHER POLYOLS.

Polyether polyols used as intermediates in the manufacture of polyurethane foams, namely flexible foams, are charact<u>e</u> rized by the distribution of their molecular weights, as well as by the distribution of the molecular species with different polarity. This is evidenced through HPLC.

The interpretation of ¹³C NMR spectra of the polyether poly ols was based on the work by Whipple and Green (1973), while the quantitative characterization was carried out on the ex perimental work previously conducted by the MONTEDISON Labo ratories. Random and block copolymers, either produced by us or by the competition, were quantitatively analyzed. In this paper one of our polyols and one of the competition have been taken into account. Though fairly similar for com position, they are appreciably different for applicative behaviour. The HPLC allowed to detect a wide difference in the distribution of the species of different polarity. The analy sis has then been further deepened by applying the preparat<u>i</u> ve HPLC.

The fractions were characterized through 13 C NMR spectroscopy. A progressive enrichment of the molar fractions of ethylene oxide X_E was observed on increasing the elution time. The in crease of the latter parameter involved also an increase in the content of primary hydroxyles, that is the percent of CH₂OH end groups. Within the experimental error of the method,

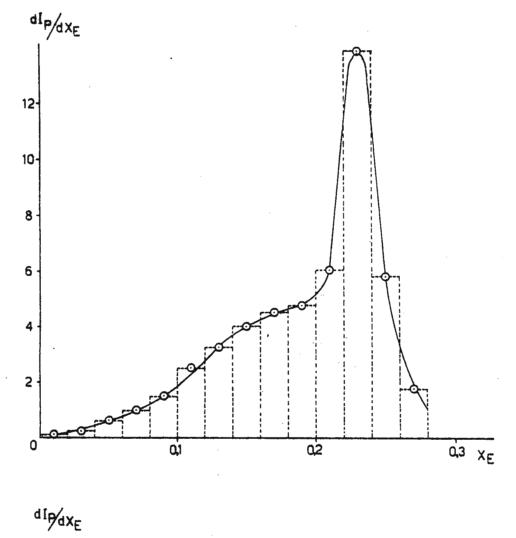
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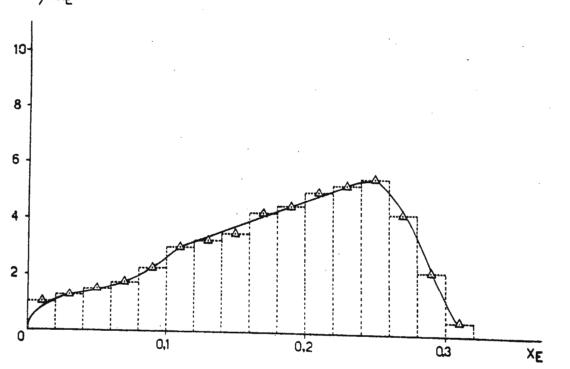
no substantial difference was found in both the equivalent weight and the molar fraction of the F_{EP} units. The correlation between the elution times and the molar fractions of ethylene oxide X_g did not appear highly satisfactory due to the dispersion of the resulting data and the correlations were different for the two products. This could be imputed to the effect of structural factors other than the total content of ethylene oxide on the polarity of the species. In spite of the fact that the competitive sample had a total ethylene oxide content possibly higher than our sample (X_g equal to 0.19 and 0.17, respectively), in the latter case, in all the fractions, the quantities F_{EE} (oxyethylenic units in sequence) were on the average higher than in the competitive polyol. The integral distribution curves X_F , X_p , F_{EF}

and F_{pp} were calculated. Taking into account the integral distribution curve versus X_E , a closer distribution of the <u>e</u> thylene oxide in proximity of the mean value was observed. In order to represent in a more evident way this finding, the differential distribution curves of both polyols were plotted calculating the derivative of the curve starting from the integral distribution curves.

As it can be observed, the ratic of the area of the plot included between the values 20% and 26% of the molar fraction of the ethylene oxide and the total area is appreciably higher (O) for the competitive polyol than the ratio obtained for our sam $ple(\Delta)$

> Sincerely yours Giorgio Gurato G. Gurato





Université de Lausanne - Faculté des Sciences

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

3, place du Château 1005 Lausanne (Suisse)

1st of June, 1983.

119Sn MAGNETISATION TRANSFER-A DREAM COME TRUE!

Dear Barry,

The recent acquisition of a CXP-200 spectrometer has allowed us to resume work on one of our favourite systems; that of the various ligand exchange reactions encountered in solutions of Tin(IV) tetrahalide with neutral Lewis bases in inert solvents¹.

In general the octahedral SnX4.2L adducts exist simultaneously in both the cis and trans configurations, and, in the presence of excess ligand, the system may be characterised by three rate constants:kiso for the cis-trans isomerisation; kcis for the cis-free ligand exchange; and k_{trans} for the trans-free ligand exchange. Using ¹H NMR we have been able to show² that k_{cis} is considerably greater than both ktrans and kiso; so much so, in fact, that on increasing the temperature, the signals of the cis isomer and the free ligand coalesce long before any exchange is apparent on the trans signal. And therein lies the rub! For it is now not possible to ascertain whether the eventual broadening of the trans signal is due to exchange with the free ligand or whether it is the result of an isomerisation between the two forms. The answer, so we thought, was obvious: record the 119 Sn NMR spectrum as a function of temperature; if the trans isomer is exchanging with the free ligand the spectrum will remain unaffected. If, however, cis-trans isomerisation is responsible the ¹¹⁹Sn signals will broaden, and may even coalesce. Unfortunatly, things are not that simple: any broadening that may appear as a result of cis-trans isomerisation is swamped by what we believe are the effects of tin-halogen scalar coupling.

Université de Lausanne - Faculté des Sciences

INSTITUT DE CHIMIE MINÉRALE ET ANALYTIQUE

3, place du Château 1005 Lausanne (Suisse)

Line shape analysis is, however, not the only way of squeezing quantitative data from exchanging systems, and we felt that a magnetisation transfer experiment might yield comparable results. The Figure illustrates the effects of selectively inverting the resonance of the cis isomer in a 0.2m solution of SnCl₄.2(Me₂S) in CD₂Cl₂ at 283 K using the so called 1:2:1 pulse sequence³. Two processes are apparent: a slow return to equilibrium due to T_1 relaxation, and a transfer of magnetisation on a considerably faster timescale due, we believe, to cis-trans isomerisation.

We feel that this represents a small step for mankind, but a giant leap for ¹¹⁹Sn NMR spectroscopists!

Yours faithfully,

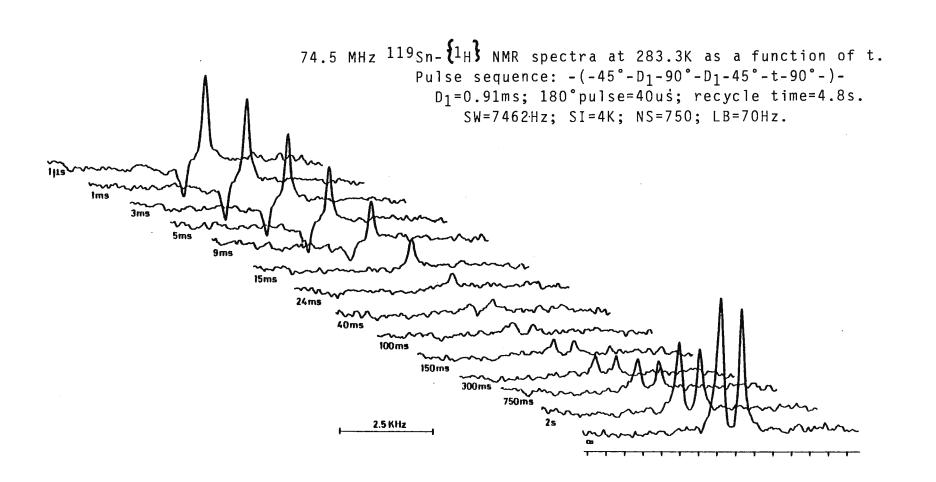
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The Ohio State University

Department of Chemistry

140 West 18th Avenue Columbus, Ohio 43210

Phone 614 422-2251

11 May, 1983

Postdoctoral Positions: DISPA; FT-ICR

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

Dear Barry,

Postdoctoral positions will be available in my laboratory, starting anytime after about 1 July, 1983. Salary will be approximately \$16,000 plus benefits. The Ohio State University is an affirmative action, equal opportunity employer. The successful candidate(s) will be expected to participate in one of the following projects:

(A) <u>Dispersion vs. Absorption (DISPA) Line Shape Analysis</u>. The DISPA technique offers a simple, sensitive, direct, reliable means for identifying and quantitating the line-broadening mechanism(s) for an inhomogeneously broadened NMR or ESR signal, based on graphical data reduction of a single digitized spectrum.¹ We are anxious to apply the technique toward analysis of carbon-13 NMR lineshapes in polymers, quadrupolar NMR lineshapes,^{2,3} and other types of NMR line-broadening, using our new NIC-300 and NIC-500 FT-NMR spectrometers, as well as ESR hyperfine couplings and other non-NMR lineshapes.

(B) <u>Stochastic Fourier Transform Ion Cyclotron Resonance Mass Spectrometry</u>. We plan to modify our new Nicolet FT/MS-1000 spectrometer for stochastic excitation/detection. Technically, the experiment has much in common with stochastic NMR.⁴ Proposed applications include MS/MS using a single mass spectrometer, and the first truly simultaneous multiple-ion monitoring. Additional theoretical activity will build on our earlier FT-ICR line shape analyses.⁵,6

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Interested candidates should submit a vita and graduate transcript, and have three letters of recommendation sent to:

Professor Alan G. Marshall Department of Chemistry The Ohio State University 140 W. 18th Avenue Columbus, OH 43210

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