

No. 285

June, 1982

Podo, F., Carpinelli, G., Araco, A., Siracusano, A. and Vicari, G. ³¹ P NMR of Group A Meningococcal Polysaccharide	. 1
Earl, W. L. and Wageman, W. E. A Four-Phase Quadrature Generator for Pulse NMR.	. 3
Brück, W. and Dürr, H. ¹ H-NMR-Spectra of Sterically Hindered Cyclopropanes	. 5
Hill, H. D. W. Position Available	.10
Markley, J. L. and Chan, TM. Application of 2D Heteronuclear (¹³ C, ¹ H) Chemical Shift Correlation Spectroscopy to Ferredoxin	.11
Emsley, J. W. Quadrupolar Splittings in the Isotropic Phase of Liquid Crystals	.13
Kingsbury, C. A. Equipment Wanted	.14
Reinhold, M. Bruker Instruments, Inc Position Available	.15
Knight, S. A. Sunbury Newsletter; Polyethylene Carbon-13 Chemical Shifts	.18
Sternhell, S. Kinetic ¹³ C NMR Thermometer	.21
Wemmer, D., Mai, M., Ribeiro, A. and Jardetzky, O. Case Report: Patient "XL-100-15"	.24
Wagner, G. and Wüthrich, K. Exchange Rates of Individual Amide Protons in Proteins by 2D Correlated Spectroscopy (COSV)	25
(6031)	.25

Wade, C. G. Service Engineer Positions, NMR and Other Fields	.27
Gutowsky, H. S. (1) 0 ₂ Evolution and the Interactions of Ions with Thylakoid Membranes (2) Postdoc Opening.	.30
Kendrick, R. D., Macho, V. and Yannoni, C. S. CPMAS at Cryogenic Temperatures	.31
Fraenkel, G. Elements of Relaxation Operators; ⁶ Li NMR .	.33
Storm, C. B. Postdoctoral Position	.34
Bernardo Jr., M. L. and Lauterbur, P. C. The Loupe-Coil, or Half a Helmholtz is Better Than One	.35
Wasylishen, R. ¹³ C/ ¹² C Isotope-Induced ¹⁵ N Chemical Shifts.	.37
Smith, W. B. The C-13 NMR of Some Benzobicyclooctadienes and Epoxides	. 39
Gray, G. A. Applications Chemist Position Available	.41

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DEADLINE DATES: No. 286 5 July 1982 No. 287 2 August 1982

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

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 285

	Md1, M
	Markley, J. L11
5	Podo, F 1
	Reinhold, M15
	Ribeiro, A24
5	Siracusano, A1
1	Smith, W. B
	Sternhell, S21
	Storm, C. B
	Vicari, G 1
	Wade, C. G
	Wageman, W. E
	Wagner, G25
	Wasylishen, R
	Wemmer, D
	Wüthrich, K
-	Yannoni, C. S

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Rome, March 3rd, 1982 THEFGRAMMI: ISTISAN - ROMA TELEX RM071 ISTISAN

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

³¹ P NMR of Group A Meningococcal Polysaccharide.

Dear Professor Shapiro:

Capsular polysaccharides isolated from many serogroups of <u>Neisseria</u> <u>meningitidis</u> are immunogenic in humans and are effective as prophylaxis against disease caused by these bacteria, the immunological protection being antibody-mediated and group-specific.

It is well known that the immunogenic activity of meningococcal polysaccharides is closely related to their structural properties, in terms of both chemical composition and molecular size of the chains'aggregates. However the aggregation mechanisms are not well known, nor the role has been clarified so far of the backbone conformation(s) on the structural properties and immunogenic expression of these polysaccharides in solution.

Since the chemical shift of a phosphate group resonance is very sensitive both to its bonding pattern in a molecule (covalent linkages and local conformation), as well as to environmental parameters like pH, ion binding, etc., ³¹P NMR seems to offer a valid approach to the study of the structural properties of phosphorus-containing meningococcal polysaccharides.

We have undertaken a study on serogroup A polysaccharides (homopolymers of D-mannosamine phosphate, partially N- and O-acetylated) and on its thermally degraded forms, analysed by the parallel use of ³¹ P NMR and gel filtration.

The ³¹ P NMR spectra at 4°C of an undegraded sample showed the presence of several resonances: i) a main symmetric peak a at ~ 2.75 ppm upfield from external H_PO, 85%, assigned to the predominant form of phosphate groups in the backbone; ii) a low-field shoulder of the main peak, around 2.6 ppm (resonance b); iii) a band (c) of minor resonances around 3.3 ppm(Figure 1A). Since it is known that the molecular structure of these polysaccharides is highly thermolabile, and that in the absence of an appropriate stabilizer a decrease of molecular weight occurs in course of time unless the polysaccharide is freeze-dried and stored at -20°C or lower, the sample of Fig.1A was kept in solution at 37°C for 25 hours, in order to study the spectral effects of degradation. The thermal treatment not only induced a significant reduction of the average molecular size of the polysaccharide (as detected by gel filtration), but also induced conspicuous modifications at the level of the P NMR spectrum, in terms of spread of chemical shifts of the mentioned resonances, together with changes in their relative intensities(Fig.1B). The spin-lattice relaxation times of all the resonances (at 4°C) felt in the range 0.70+0.05 s, both before and after the treatment at 37°C.

The results suggest that the phosphate groups along the polysaccharide backbone are able to take different structural states, whose relative populations vary with degradation, and that backbone conformations and chains' aggregation are closely related properties of a group A meningococcal polysaccharide.





FIGURE 1

40.5 MHz 31 P NMR spectra at 4°C of a group A meningococcal polysaccharide (15 mg/ml in ammonium acetate 0.1 M) before (A) and after thermal treatment at 37°C for 25 hours (B). The relative intensity of each band was evaluated from weighted peak areas and expressed as percent of the total spectral profile: A) a = 70%; b = 21%; c= 9%; B) a= 50%; b = 30%; c = 20%.

285-2



Los Alamos National Laboratory Los Alamos, New Mexico 87545 Group CNC-4, Mail Stop C346

April 23, 1982

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

Dear Prof. Shapiro:

We are in the process of building a relatively low field (1.4 T) spectrometer which will primarily be used for carbon-13 cross polarization experiments in solids. One of the necessary components of such a spectrometer is a four phase generator and gates for the decoupler at 60 MHz (in fact, only three phases are needed if one only wants to cross polarize and decouple using spin temperature inversions). We have chosen to follow Ellett, et al's recommendation for generation of the four phases. Since the phase requirements for cross polarization are not as stringent as for multiple quantum or multipulse experiments we have used a Merrimac model QPS-3-65 quadripole network which has a phase tolerance of +2 degrees but only costs \$245 (for a higher price, Merrimac will provide a quadripole network with varactor phase trimming).

Double Balanced Mixers (DBM) can be used as gates for rf signals³ and will normally give an on/off ratio of better than 30 dB for a single DBM. Since it is possible to buy very good DBMs³ in a dual in line package for about \$10 we have built our gates using a pair of DBMs in series for each phase. Besides low price, DBMs have the advantage that the current used to turn them on and off may be programmed to provide output pulse shaping. This may be useful for ADRF experiments. The overall block diagram of our 60 MHz gates is shown in the figure below.

Basically, all four phases are treated identically. The resistor, R1, is a 10 ohm variable resistor used to match all four phases to the same amplitude. The 6 dB attenuator is inserted in the circuit because the QPS-3-65 likes to look into a 50 ohm load and when the gates are turned off the input impedance of the DBMs is essentially infinite. The attenuator thus helps stabilize the output phases of the QPS-3-65. The two double balanced mixers are in series with the RF port as the input, the LO port as the output and the IF port used for the on-off logic signal. The resistors, R2, are current limiting resistors chosen to give about 25 mA from the 5 v signal from our pulse programmer at the logic input. The four way power combiner is not necessary if only one phase is turned on at a time but it is a simple and inexpensive way to improve the isolation between phases.

Since all of the components except the resistors are in PC plug in packages in radio frequency isolation cans, our first attempt was to assemble it on 0.2" breadboard and simply wire the pins together. This proved to be a mistake because we were only able to obtain an on/off ratio of about 34 dB which is insufficient. We have turned to microstripline technology by etching the circuit on one side of double sided printed circuit board, the other side remains unetched and serves as a ground plane. The dimensions of the board and circuit elements are chosen to give a good impedance match at 50 ohms. We used 1/16 inch fiberglass board with one ounce copper cladding. (A copy of our circuit board complete with an error, can be obtained by contacting either of us.)

The final application uses a frequency synthesizer as an rf input. Since the gates have a total loss from input to output of 27 dB, they must be followed by quite a bit of amplification before the probe. With an input of 6.5 v(pp) we obtain an on/off ratio of 61 dB. If the input voltage is dropped to 0.65 v(pp) the on/off ratio drops to 46 dB which is not good enough for most NMR applications. So in use, all gain changes should be made following the gates described here.

 E. O. Stejskal and J. Schaefer, J. Magn. Reson. <u>18</u>, 560 (1975).
 J. D. Ellett, Jr., M. G. Gibby, U. Haeberlen, L. M. Huber, M. Mehring A. Pines and J. S. Waugh, <u>Advances in Magnetic Resonance</u> Vol. 5, p. 137 (1971).
 E. Fukushima and S. B. W. Roeder, <u>Experimental Pulse</u> <u>NMR</u>, Addison-Wesley Publishing Company, Reading, Mass. (1981) p. 417.
 H. P. Shuch, Ham Radio, p. 41 ff. September 1977.



Bill

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Fachbereich 14 - Orgamische Chemie Professor Dr. H. 'Dürr

Herrn

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

Dear Professor Shapiro,

¹H-NMR-Spectra of sterically hindered Cyclopropanes

In our studies on the reactivity of carbenes we prepared cyclopropanes <u>1a-e</u> and <u>2a-e</u> by carbene addition to substituted styrenes. These addition products show an ABX-pattern in the ¹H-NMR due to the cyclopropane protons. We have analyzed these ABX-pattern with the aid of LAOCOON III developped by Castellano and Bothner-By ¹⁾.



The correct assignments of the data obtained was checked by the program itself ($\Delta v \langle 0.01 \text{ ppm}; \Delta J \langle 0.2 \text{ Hz} \rangle$ and by a visual comparison of the experimental and the calculated spectrum (see figure 1).



Figure 1: Experimental and calculated spectrum of 1d

	protons	of <u>1a-e</u>	and <u>2a-e</u>				
	R	6 1	6 2	бз	J 12	^J 13	J ₂₃
			ppm			Hz	
1a	н	1.86	1.94	2.72	-6.30	8.50	10.70
b	р-СН _З	1.83	1.92	2.71	-6.24	8.15	10.12
с	p-OCH ₃	1.79	1.91	2.66	-6.90	8.30	10.91
d	p-Cl	1.86	1.95	2.68	-7.00	8.30	11.10
е	m-Br syn	1.75	1.96	2.70	-6.3	8.30	10.40
	anti	1.82	2.01	2.85	-6.70	8.31	10.52
2a	н	1.86	1.98	3.04	-6.06	8.09	9.95
b	p-CH3	1.90	2.04	3.11	-6.90	7.98	10.03
с	p-OCH ₃	1.87	1.98	3.07	-6.59	8.20	10.88
d	p-Cl	1.83	1.99	3.03	-7.10	8.40	9.60
е	m-Br	1.84	1.98	3.01	-6.11	7.71	9.81

Table 1: Chemical shifts and coupling constants of cyclopropane protons of 1a-e and 2a-e

In all cases the syn-isomer was obtained with a exception of $\underline{1e}$ were both the syn- and anti-isomer could be obtained.

The coupling constants of <u>1</u> and <u>2</u> were relatively independant from the substituent R. However, the chlorocompounds <u>1d</u> and <u>2d</u> show a slight increase of the geminal coupling constants ²J.

Substitution of oxygen by sulfur leads to a downfieldshift of the whole ABX-pattern in 2. It is interesting that the shift for H₃ is considerably larger than for H₁ and H₂. Since the hetero atom has the same distance to H₂ and H₃ inductive effects should produce the same downfield shift. Models show, however, that a syn-position of two phenyl groups produces sterical hindrance which effects the bond-angle on C₃. This steric effect should, however, be larger than the inductive effect of the substituent R, since a correlation of chemical shift versus the Hammet-sigma-constants ²⁾ shows no linear dependance.

Literature:

- 1) S. Castellano, A.A. Bothner-By, J. Chem. Phys. 3863 (1964).
- L.P. Hammet, Physical Organic Chemistry, McGraw Hill, New York 1970

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285-7

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June 4, 1982

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

Dear Barry:

We are expanding our NMR research group and are looking for a suitable candidate to fill a vacant position. The group is involved in the initial design and evaluation of new spectrometer systems and probes and in the development of NMR techniques. Our interests cover high resolution NMR in both liquid and solid state and there are opportunities for independent research.

The applicant should have a PhD. in physics or chemistry and have experience in the design and construction of NMR spectrometers and probes.

Interested applicants should send their resumes to my attention.

Yours sincerely,

Howard.

Howard D.W. Hill NMR Research & Technology Palo Alto Instrument Division

HDWH:jr

PURDUE UNIVERSITY DEPARTMENT OF CHEMISTRY

May 5, 1982

Dr. Barry L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77483

Dear Barry,

We would like to report the application of 2D heteronuclear (¹³C. , ¹H) chemical shift correlation spectroscopy to ferredoxin (a 2Fe·2S* protein involved in photosynthesis, Mr 11000).

Separate 2D spectra were taken for the aliphatic and aromatic regions in order to obtain better digital resolution in the proton frequency domain. They are taken with a Nicolet NT-200 wide bore spectrometer. The sample consisted of a 2.5 ml solution containing 150 mg of [ul 20% 13 C] ferredoxin dissolved in 2 H₂O in a spherical cell inside a 20 mm OD NMR tube. The ¹³C enriched ferredoxin was isolated from a cyanobacterium, Anabaena variabilis grown on [20% $^{13}C]CO_{2}$ as the sole carbon source.

The figure below shows the 2D spectrum (in contour plot) of the aromatic region along with two ¹³C spectra and the ¹H spectrum at 470 MHz. The ¹³C spectrum on the left side is the normal one-pulse spectrum, the one on the right side is a subspectrum that contains only resonances from the protonated carbons in the region. There are twenty resolved contour peaks, 12 of which can be assigned to specific C-H bonded pairs in the protein based on the known proton assignments.

This technique will be useful for assignment of resonances in ¹³C spectra of proteins, since it is usually easier to obtain assignments in the ¹H spectra.

ours sincerely, John L. Marklev

13 ylhan

Professor

T.-M. Chan

1. Freeman, R., and Morris, G.A. Bull. Mag. Res 1,5 (1979).



Chemistry Building West Lafayette, Indiana 47907

Dr. Barry L. Shapiro 5 May 1982

2. Chan, T.M., Westler, W.M., Santini, R.E. and Markley, J.L. (submitted to J.A.C.S.)

JLM:jr

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JWE/HN

6th May, 1982.

Professor B.L. Shapiro, Department of Chemistry, TEXAS A & M UNIVERSITY, College Station, Texas - 77843, UNITED STATES OF AMERICA.

Dear Barry,

Quadrupolar splittings in the isotropic phase of liquid crystals

MacLean and Lohman described small, field induced quadrupolar splittings of deuteron peaks in the spectra of solutions of such compounds as anthracene and other condensed aromatic compounds. The field has to be around 9T before such splittings are large enough to be resolved and are typically one or two hertz. They are dependent on the anisotropy in the molecular magnetic susceptibility and were used by MacLean and Lohman to measure this quantity. We are using this phenomenon to monitor the increase in orientational ordering which occurs as the nematic-isotropic transition is approached from the isotropic phase. The induced splittings increase drmatically, as shown in the figure and achieve magnitudes of about 30 Hz for the CD2 group nearest the biphenyl ring in 4-n-pentyl-4'cyanobiphenyl-d₄ . Such a pretransitional effect has been observed by other means, such as optical birefringence, but N.M.R. has the considerable advantage of producing data relating to several sites in the molecule. We are collecting more data on this interesting phenomenon using the Bruker WH 400 at the University of Warwick and we hope soon to try experiments at 11.7 T, where the splittings which are proportional to B^2 should be more pronounced.

Best wishes,

Jim

J. W. EMSLEY.



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The University of Nebraska-Lincoln

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May 17, 1982

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May 13, 1982

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

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$C_{50}H_{73}N_{15}O_{11}by$ 2-D NMR

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(1) Ad Bax and Ray Freeman, JMR 44, p. 542-561 (1981)

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SUNBURY NEWSLETTER; POLYETHYLENE CARBON-13 CHEMICAL SHIFTS

Since our last Newsletter contribution our NMR laboratory has undergone a complete transformation. In April 1980 we replaced our HFX 90 with a JEOL FX 200. Choosing a new instrument is quite a complex task, one selects not so much the good from the less good. but rather the instrument that suits ones particular needs the best. As a result of past experience we placed a particularly heavy premium on reliability in which we found the JEOL to excell. Installation of the FX 200 was completed in about a week and in two years of very intensive use we have not experienced any electronic faults and have been delighted with the performance and ease of operation of the instrument. Last November we took delivery of a multinuclear FX 270 to augment our NMR capability and although commissioning took longer than with the FX 200 due to magnet homogeniety problems the instrument is functioning well. Subsequently, the FX 200 was converted to the study of solids and we now have the capability for examining them by carbon-13 and silicon-29 NMR. To complete our new line-up we are in the process of installing a JEOL GX 400 equipped for hydrogen and carbon-13 studies.

About 70 per cent of our work is done using carbon-13 and most of the remainder with hydrogen NMR. The relatively small amount of heteronuclear work is done with ³¹P, ²⁹Si and ¹⁵N using 10 and 15 mm probes. While we have an array of pulse sequences such as 'INEPT' on tap, we find, as Dr Booth of Nottingham University remarked in a recent Newsletter, that simple chemical shift/band intensity data is adequate for most of our very heavy work-load. A possible explanation for this is that at higher field strengths the spectra do not have the assignment ambiguities that one encounters at lower fields.

Polymers, particularly chain branching in polyethylenes, are studied routinely. Contrary to opinions expressed in the literature we do find the increased field strength (over our old HFX 90) useful in making and confirming band assignments. For example the terminal methyl group bands for C_4 and C_6 chains can be distinguished (Figure 1).

Particularly well resolved are the methyl groups of the various types of ethyl side chains that occur in many low density polyethylenes (Figure 2). The 'isolated ethyl' CH_3 and the '1,3-diethyl' CH_3 are well resolved along with an as yet unassigned CH3 (X). Two 'quaternary-ethyl' types of CH3 are very clearly defined at 7.68 and 7.91 ppm. One problem encountered originally with band assignments was the variation in literature sources of the chemical shift for a given carbon type. As we find the reproducibility of a given chemical shift to be quite good v0.03 ppm we have tended to collect our own shift data. We have used the 'long chain' methylene (CH2)n as an internal reference for polymer 'solutions' in hexachlorobutadiene at 135°C and find it to be at 29.62 ppm from TMS and almost invariant over the temperature range 55-140°C. The hydrogen chains of 'paraffinic' petroleum fractions (MW 300-500) also give a band at 29.62 ppm in hexachlorobutadiene. Thus the polymer chains appear to have a high degree of mobility in this solvent. 'Saturated' solutions of polymer were used at 55°C but obviously these were quite dilute and required ~30,000 accumulations.

Most bands in the spectra of polyethylene type polymers show little variation with temperature (typically ~ 0.05 ppm), the noted exception being the terminal methyl group of chain branches where the variation is found to be 0.25 ppm to high field over the temperature range given above. Given in the Table are some chemical shifts found for some typical groups in polyethylenes and referenced to TMS - [(CH₂)n at 29.62 ppm].

S.A. Knight





FIGURE 1

FIGURE 2

CARBON-13 CHEMICAL SHIFTS FOR SOME SUBSTITUTED POLYETHYLENES

Туре	ppm	Туре	ppm	Туре	ppm	Туре	. ppm
(Q-Et)-CH ₃	7.68	LC-C(2)	22.51	CH ₃ -β	27.10	LC- α	34.39
(Q-Et)-CH ₃	7.91	Bu-C(2)	23.01	LC-Y	30.11	CH ₃ - α	37.26
1,3 DE-CH ₃	10.79	Et-C(2)	26.59	LC-C(3)	31.86	1,3 DE-CH	37.29
Et-CH ₃	10.96	1,3 DE-C(2)	26.63	Pt-C(3)	32.38	LC-CH	37.96
LC-CH ₃	13.75*	1,3 DE-β	26.63	CH ₃ - <u>C</u> H	32.97	1,3 DE-2CH ₂	39.11
Bu-CH ₃	13.77	LC-β	27.02	Bu-C(4)	33.99	Et-CH	39.52
CH- <u>C</u> H ₃	19.80	Et-β	27.04	Et-α	33.91	(CH ₂) _η	29.62

*14.0 at 55°C. Et = Ethyl; Bu = Butyl; Pt = Pentyl; 1,3 DE = 1,3 Diethyl LC = Long Chain = $(CH_2)_{\eta} \eta > 5$; $C(\eta) = \eta^{\frac{th}{t}}$ carbon of chain substituent. (Q-Et) = ethyl group attached to a quaternary chain carbon atom. Shift variations have been found to be small and seldom more than 0.05 ppm.



The Aniversity of Sydney

Department of Organic Chemistry

IN REPLY PLEASE QUOTE:

TELEPHONE: 692 1122.

DX 1154

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

May 12, 1982

0

Dear Barry,

KINETIC 13C NMR THERMOMETER

For a system containing an exchanging carbon site, the temperature corresponding to the coalescence of relevant ¹³C signals can be calculated in an obvious manner from the slow exchange separation of the signals (Δv_s) and the kinetic parameters obtained by some independent means, such as ¹H NMR spectroscopy.

If a system contained a number of exchanging sites corresponding to one exchange process and if Δv_s for each coalescence was much larger than the line width, it could serve as a "Kinetic Thermometer".

In connection with another investigation in these laboratories, Mr Ian Newsom prepared the imide undergoing the internal motion shown below:



285-21

¹³C NMR spectra of this compound at 15 MHz (JEOL FX60Q) showed doubling up for a number of signals and the temperature control dial settings corresponding to coalescence of each pair were determined by Mr Wayne Veigel and compared (table and figure) with those calculated from the Eyring relationship using the above kinetic parameters.

The plots show the expected linear relationship between the dial settings and the calculated values of T_c . Unfortunately, it can be also seen that the calibration curve is extremely sensitive to error in entropy. In other plots, we show that the plots are also sensitive to errors in enthalpy. Thus while in principle the "Kinetic ¹³C thermometer" represents a means of determining the temperature inside an NMR probe, the method is too sensitive to errors in kinetic parameters to be of practical significance.

Yours sincerely

Nes Henber

S. Sternhell Professor of Chemistry (Organic)

	Chemical Shifts at Ambient Temperature	Δν _s at T _c	Coalescence Temperature (Dial Setting)	Calculated T_c $\Delta s^* = -3.76$	Calculated T_c $\Delta S^* = -8.13$	Calculated T_c $\Delta s^* = -12.5$
_	(Hz)	(Hz)	т _с (°С)	(°C)	(°C)	(° C)
	2142.58 2132.33	10.25	138	133	141	149
	2105.46 2098.17	6.29	122	126	133	141
	2085.88 2083.98	1.90	91	109	116	124
	1971.68 1969.48	2.20	93	111	118	126
	1940.75 1935.55	5.20	118	123	. 131	138
	1883.79 1879.64	4.15	105	120	127	135
	679.69 672.54	7.15	123	127	135	143
	257.81 237.85	19.10	155	143	· 151	159

2



285-23

STANFORD UNIVERSITY STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

(415) 497-4062 (415) 497-6153

May 24, 1982

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

Dear Barry,

Case Report: Patient "XL-100-15"

We, as most old XL-100 owners probably do, have noticed signs of age in our system. Even after a "coil lift" to replace a very leaky pair and a "heart transplant" when the circulatory system failed completely, we still observed unstable "blood pressure" and occasional "fever spikes" in the left coil. Fortunatley, with measurement of "blood pressure" and "temperature" in the right places we were able to diagnose the disease! Perhaps this knowledge will help some other ailing system.

The pressure and part of the temperature problems were caused by having the passive throttling valve in the distilled water loop stick in the nearly closed position. The pressure in the closed loop rose and fell with the active "modulating" valve position. Since virtually no water was going through the heat exchanger, the magnet temperature fluctuated with ambiant temperature.

The difference in temperature between the coils was traced to severe "arteriosclerosis" in the left "coronary arteries and veins." This was remedied by "catheterization": vigorous application of a buret brush and extensive flushing and back flushing. A large amount of "plaque" was removed.

After surgical treatment, the patient has recovered and has been doing very well. Prophylactic chemotherapy was deemed unnecessary and hopefully the patient will continue an active life for many years to come.

BLS

Wenner

Sincerely, Michael Hai Anthony Ribeiro M. Mai A Pitrain

D. Wemmer

* A "no-credit" contribution.

Institut für Molekularbiologie und Biophysik Prof. Dr. K. Wüthrich

HPM-Gebäude Durchwahl-Nr.: 01/3772473 Telefonzentrale: 01/3774411

Postadresse: Institut für Molekularbiologie und Biophysik ETH -Hönggerberg CH-8093 Zürich Prof. B.L. Shapiro Dept. of Chemistry Texas A & M University College of Science

College Station, Texas 77843

USA

Zurich, May 7, 1982

Exchange Rates of Individual Amide Protons in Proteins by 2D Correlated Spectroscopy (COSY).

Dear Barry,

We have recently used COSY for studies of amide proton exchange rates in the basic pancreatic trypsin inhibitor (BPTI). Since each COSY recording takes several hours, a quench technique was applied. E.g. solutions of BPTI in D_2O were kept at higher temperatures for variable periods of time and then cooled to $24^{\circ}C$ where the COSY spectrum was recorded (Fig. 1). The principal advantage compared to corresponding measurements with one-dimensional NMR is the improved spectral resolution. Combined with the previously obtained individual resonance assignments for the ¹H NMR spectrum of BPTI¹, 52 of the total of 53 backbone amide protons could from the COSY data be classified according to the individual exchange rates.

Sincerely yours,

hand Wagher

Dr.G.Wagner

Prof.K.Wüthrich

1. G. Wagner and K. Wüthrich, J. Mol. Biol. <u>155</u>, 347-366 (1982).

Sequential Resonance Assignments in Protein ¹H Nuclear Magnetic Resonance Spectra. Basic Pancreatic Trypsin Inhibitor. 1085



Fig. 1 Spectral region of the NH-C^{α}H cross peaks in absolute value 500 MHz ¹H COSY spectra of 0.02M solutions of BPTI in ²H₂O recorded at different times after the protein was dissolved. The solutions were freshly prepared at 24^oC and then kept at 36^oC to allow exchange of protein amide protons with ²H of the solvent. At the times indicated in the figure, a particular solution was cooled to 24^oC and a spectrum was recorded in 12 hrs.. Resonances which disappeared during the experiment are identified in the last spectrum where they are represented by a strong peak by the one-letter code for amino acid residues and the location in the sequence.

40 West Brokaw Road San Jose, California 95110

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

May 7, 1982

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

Re: Service Engineer Positions, NMR and other fields

Dear Barry:

We have several openings for Service Engineers in Nuclear Magnetic Resonance instrumentation. A variety of positions exist within our organization. Some of these require extensive knowledge of NMR instrumentation or data systems; others merely require an electronics background. Our present instrument line includes several superconducting magnet NMR spectrometers, an 80 MHz electromagnet NMR spectrometer, and a 20 MHz pulsed NMR process analyzer. At the Experimental NMR Conference, we announced a laboratory computer which also has NMR applications. A Service Engineer typically handles several of these instruments including the data systems.

At present our major Customer Support Centers are in Danbury, CT and San Jose, CA. We have a demonstration center near Chicago and plans for other demonstration and service locations across the U.S. Service Engineers might be located at any of these sites.

It is the policy of IBM to take positive actions to ensure equal opportunity in the conduct of all its business activities without regard to race, color, religion, national origin, age or sex.

Would you please post this announcement or pass it along to anyone who might be interested? Candidates should contact me in confidence at the address or the toll free numbers listed above. Although I am not directly involved in our other instrument lines (EPR, FT-IR, liquid chromatography, electrochemistry), I'll be happy to serve as a contact point and forward applications for Service Engineers for those instruments to the pertinent persons at IBM. Thank you.

Yours truly,

Chas. G. Wade NMR Manager, West Coast

THE

DATA SYSTEM

MHD

FLP

LIGHT PEN/ KEYBOARD

JEC-32 2 BIT WORD NMR DATA PROCESSOR

12" CRT WITH GRAPHICS DISPLAY

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PLEXUS: An interwoven network of parts There is no better way to describe the data or elements in a system. processing philosophy incorporated into the GX-400/500 FT-NMR spectrometers. To accommodate the increased demands placed on an FT-NMR data system, the PLEXUS data system deviates from the USUAl single Computer approach. A multi-computer network using distributed processing software work using distributed processing sortware is employed to achieve trend setting levels of performance for speed, efficiency, and

The center of the PLEXUS data system ine center of the PLEAUS data system is the Digital LSI "system control processor." All interaction between the operator and the flexibility An interaction between the operator and the spectrometer pass through this hub. Job spectrometer pass intrough this nub. JOD assignments are determined by this processor and distributed to the appropriate hardware and distributed to the appropriate naroware for execution, for example; printing, plotting, disc storage or spectrometer operation. If uise storage of spectrometer operation. If actual data is to be acquired or manipulated actual value is to be acquired of manipulated (Fourier transformation, phasing, etc.) these (rouner transformation, phasing, etc.) these jobs are assigned to a second, highly specialivus are assigned to a second, nignly special-ized "NMR data processor," the JEC-32. The JEC-32 is a 32-bit computer, capable of accommodating 256K words of accommodating of accommodating 256K words of memory. or accommonance and specialized design, Because of its unique and specialized design, because on its unique and specialized design, fast Fourier transformations of 8K words of data (32 bit words) are done in less than are uone in less man 3 seconds! The real value of this amazingly fast FFT time can be appreciated more fully

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when considering large data sets, especially when considening large data sets, especially 2-dimensional FFT, where transform times are decreased dramatically, making 2-D NMR a much more practical and efficient

The spectrometer system is made complete by total computer control over all piere by total computer control over all spectrometer functions by the PLEXUS data experiment. spectrometer functions by the FLEAUS data system. Through the "system control processystem. Intrough the system control processor, sor" and "spectrometer control processor, PLEXUS totally controls all spectrometer variables, including lock offset, lock phase, locklevel, receiver gain and all irradiation and observation phases allowing any NMR param-

eter to be changed, stacked or iterated under unattended computer operation. The acquired experimental data is sent from the S-Con, experimental data is sent nom the 5-001, over distortion-free fiber optics cables, to the JEC-32 where data treatment is carried out. A further benefit of the PLEXUS concept is the SIC diagnostics (Status Integrity Check) which monitors all of the spectrometer hardware through status registers located on each ware intough status registers located on each board. Valuable service information concerning NMR hardware and computer components ing NNIT natiowate and computer components can then be extracted directly from the GX spectrometer or remotely.

For further information, call ... 235 Birchwood Ave., Cranford, NJ 07016 201-272-8820



University of Illinois at Urbana-Champaign²⁸⁵⁻³⁰

School of Chemical Sciences 505 South Mathews Avenue Urbana, Illinois 61801

May 11, 1982

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

O₂ Evolution and the Interactions of Ions with Thylakoid Membranes
 Postdoc opening

Dear Barry:

This time I'm responding to your green sheet, but I don't want it to establish a precedent. A year ago we reported some preliminary CL-35 NMR studies of binding of Cl⁻ to chloroplasts isolated from certain salt-tolerant plant species. This work on the oxygen evolving mechanism of photosynthesis has been continued by I. C. Baianu, C. Critchley, Govindjee and myself, with some interesting results which appear to be converging.

In particular, two lines of evidence are consistent with the hypothesis that the transfer of positive charge during an oxygen evolving cycle is facilitated by the transient binding of anions to the oxygen evolving system. First, we have found that the effects of anions on the Hill reaction rate of halophyte and spinach thylakoid membranes are correlated with their ionic radii or ionic field strength. Small anions such as F⁻ or OH⁻, which are surrounded by relatively strong ionic fields, inhibit oxygen evolution, possibly by trapping the positive charge in the oxygen evolving system. Large anions such as PO4³⁻ and SO4²⁻ are without discernible effect. The Cl⁻ and Br⁻ anions, of intermediate size, give optimal oxygen evolution.

Second, information about interactions between the ions and thylakoid membranes is being obtained from high-field NMR line shapes. Line shapes for the spin I=3/2 nuclei Cl-35, Br-79, Na-23 and K-39 in the aqueous monovalent ions are subject to quadrupolar broadening by asymmetric electrostatic interactions. The line shape for K⁺ is not affected by thylakoids (dark-adapted), while that for Na⁺ consists of superimposed broad and narrow components from bound and unbound ions respectively. The line shapes for both Cl⁻ and Br⁻ are broadened by ion/thylakoid interactions but the exchange rate is fast enough ($\geq 10^3 \sec^{-1}$) to give a single broadened line. This rate is in the same ball park as the optimal recycle time for oxygen evolution. For Cl⁻, a binding constant of $1.1M^{-1}$ was obtained from the dependence upon [Cl⁻] of its line width. This value, combined with the temperature dependence of the line width, gives a binding energy of ~9 kcal/mole, characteristic of weak ionic interactions.

The research is being supported by NSF grant PCM 79-11148. There probably will be an opening during the next few months for a postdoctoral with NMR background and interests, for work in this and/or other areas.

Sincerely yours,

S. Gutowsky S. Director

I. C. Baianu C. Critchley Govindjee

xc:



RESEARCH LABORATORY K34/281

International Business Machines Corporation

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

May 10, 1982

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

Dear Barry:

Even running an ENC does not escape your relentless sequence of more ominously colored warnings!

Volker Macho, a visitor in my laboratory from the Physics Department at the Free University of Berlin, has succeeded in obtaining well-resolved

 13 C spectra using CPMAS techniques at very low temperatures. We have previously reported CPMAS spectra of polypropylene at temperatures down

to 100K, showing disappearance of the methyl resonance.¹ Using a cyrogenic MAS apparatus, we have obtained spectra of polypropylene down to 17K, as shown in the accompanying figure. The methyl resonance reappears around 77K, and the spectrum then remains unchanged down to 17K. We believe the signal broadens due to the generation of spectral density at zero frequency when molecular motion (in this case, methyl group rotation) has a strong Fourier component at the proton decoupling

frequency (110 kHz).²

We are in the process of writing a report on the apparatus used to obtain these and other CPMAS results obtained at cryogenic temperatures.

Best regards,

R. D. Kendrick

C. S. Yannoni

1. W. W. Fleming, C. A. Fyfe, R. D. Kendrick, J. R. Lyerla, H. Vanni and C. S. Yannoni, ACS Symposium Series <u>142</u>, 193 (1979).

2. W. P. Rothwell and J. S. Waugh, J. Chem Phys. <u>74</u>, 2721 (1981).

(Short Title: CPMAS at Cryogenic Temperatures)

:

The Ohio State University

Department of Chemistry

140 West 18th Avenue Columbus, Ohio 43210 Phone 614 422-2251

May 14, 1982

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

< 6H3 >

Elements of Relaxation Operators; ⁶Li NMR

Dear Barry,

To take account of specific relaxation mechanisms in calculations of NMR line-shapes one includes in the density matrix equations the appropriate relaxation operator which has the form

 $-R\tilde{\rho} = \sum_{s,\alpha} j(\alpha\omega) [I_s, \alpha [I_s^{-\alpha} \tilde{\rho} - \rho_0]].$ (1) The expansion of (1) for quadrupole relaxation contains 47 terms each of which is a product of five operators. Some time ago I pointed out in this Newsletter that in the spin product representation non-zero matrix elements of the relaxation operator can be efficiently generated from closed formulas. Albert Chow, in my group, has written a program which generates these matrix elements from his formulas and has compiled relaxation Li 44-16 MHz matrices for a variety of commonly encountered systems. Relaxation mechanisms handled are for electric quadrupole, intramolecular dipolar, chemical shift anisotrophy and random field, interactions respectively. One set of coefficients apply at the extreme narrowing approximation while the other is listed as coefficients of the individual $j(\alpha\omega)$ specral densities. The tables are also useful for double resonance line-shapes where dipole-dipole relaxation transmits the NOE enhancements. Finally, Alan Marshall has discussed the dynamic shift one expects between the 1/2, -1/2and the coincident 3/2, -1/2 and -1/2, -3/2transitions, respectively of a spin 3/2 nucleus subject to quadrupole induced relaxation short of the extreme narrowing limit.

May 14, 1982

Dr. B. L. Shapiro

Using our tables this shift is rapidly found to be in ppm

 $10^{5} \frac{(e^{2}q0)}{\pi}^{2} \frac{\tau_{c}}{1 + \omega^{2}\tau c^{2}}$,

with quadrupole coupling constant and ω in radians/sec.

We are continuing our studies of organolithium structure using 6 Li NMR. The accompanying figure shows the spectrum of 2M 2-butyllithium in cyclopentane at -50°. The ⁷Li spectrum is a broad blob about 100Hz wide, due to quadrupole relaxation.

Regards.

Yours sincerely,

Gideon Fraenkel Professor of Chemistry

HOWARD UNIVERSITY

WASHINGTON, D. C. 20059



May 28, 1982

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

Dear Barry:

Re: Postdoctoral position

I will have available in July a postdoctoral position for research on modified hemoglobin and myoglobin. The work is in collaboration with Professor Winston Anderson, Department of Zoology, Howard University, and involves both NMR and physiological studies of modified materials.

I may be reached by phone at 202-636-6908. I appreciate your bringing this to the attention of your readers.

Sincerely yours,

Carlyle B. Storm Graduate Professor of Chemistry



StonyBrook

Department of Chemistry State University of New York at Stony Brook Long Island, NY 11794 telephone: (516) 246-5050

17 May 1982

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

"The loupe-coil, or half a Helmholtz is better than one"

Dear Barry:

Sometimes there may be good reasons not to wrap coils all around the head or body in a 'whole-body'' NMR zeugmatographic imaging machine. If only a part of the body is of interest in a particular diagnostic situation, coils of appropriate shape and size can be wound to maximize the filling factor for the region of interest and to minimize the problems that can arise when the length of conductor is not very small compared to the wavelength, or when the rf penetration into the body is limited. The simplest example of such a local coil is the flat loop "surface" coil. The two Figures shown below show slices from reconstructed three-dimensional images of an array of six water-filled ping-pong balls, and of a human back, normalized to the signal intensities in a reference object. These are largely mobile hydrogen density images. As all readers of this Newsletter know, it is no mean feat to get good T_1 and T_2 values in bad B_1 fields, and those used in this work are about as bad as you can get. There will obviously be more work, and more responses like this one to colored notices before all such problems are solved.

Yours truly,

M. Burardo. J.

Marcelino L.

'Paul C. Lauterbur

285-36



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61,2 0

31





285-37



THE UNIVERSITY OF WINNIPEG WINNIPEG, CANADA R3B 2E9

19 May 1982

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

Dear Barry:

13C/12C Isotope-induced 15N Chemical Shifts

We have recently observed ${}^{13}C/{}^{12}C$ isotope-induced ${}^{15}N$ shifts of 0.06 to 0.10 ppm for the cyanide ion and several transition metal cyanides. In each case, the ${}^{15}N$ resonance of the ${}^{13}C$ labelled isotopomers is to high field of that in the corresponding carbon-12 species. These isotope shifts are more than twice the ${}^{15}N/{}^{14}N$ isotope effect on ${}^{13}C$ chemical shifts (0.02-0.04 ppm) observed in these same complexes (1). These observations are readily understood using a theoretical model developed by Jameson (2). For a diatomic, such as the cyanide ion, she has shown that the isotope shift, $\Delta\sigma$, is given by equation [1].

$$\Delta \sigma \simeq - (\mu^{1} - \mu) f_{anh}(T) \left(\frac{\partial \sigma}{\partial r}\right)$$
[1]

where the μ 's are the reduced masses of the isotopomers, and $f_{anh}(T)$ is the anharmonic vibration constant which depends on the spectroscopic constants B_e , ω and α . The greater sensitivity to isotopic substitution of ¹⁵N compared with ¹³C chemical shifts results mainly from the relative values of the last factor in equation [1]. For Ŀ

example in the two molecules N_2 and CO which are isoelectronic with CN^- , $(\partial\sigma/\partial r)_e$ has been measured to be -776 ppm/Å (¹⁵N) and -226 ppm/Å (¹³C). Using the observed isotope shifts and known spectroscopic constants for the cyanide ion, equation [1] predicts:

 $(\partial \sigma (^{15}N) / \partial r)_{a} = -872 \pm 160 \text{ ppm/Å}$

and $(\partial \sigma (^{13}C) / \partial r)_e = -473 \pm 90 \text{ ppm/Å}$.

Yours sincerely,

Id and

Rod Wasylishen Department of Chemistry

RD/we

1. R. E. Wasylishen, D. H. Muldrew and K. J. Friesen, J. Magn. Reson, 41, 341 (1980).

2. C. J. Jameson, J. Chem. Phys. 66, 4983 (1977).

- 3. C. J. Jameson, A. K. Jameson, S. Wille and P. M. Burrell, J. Chem. Phys. 74, 853 (1981).
- P.S. As of August 1, 1982 my address will be Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4H6, Canada.

It is the annual subscription renewal time. Letters and invoices will be mailed out on July 6, 1982. If you have not received your subscription renewal notice and invoice in a reasonable length of time, please inform our office so a duplicate copy can be sent. Our office telephone number is (713)845-7716.

B. L. Shapiro

Department of Chemistry



5/24/82

Dear Barry:

The attached table is from an ms in preparation and consists of the carbon-13 chemical shifts for a series of benzobicyclooctadienes and the <u>anti</u> and <u>syn</u> epoxides derived therefrom. The numbers correspond to the following structures:



For the most part, these data resemble the related study on a series of substituted bicyclooctane epoxides recently reported by Cristol, et al., OMR, <u>17</u>, 110(1981). The <u>syn</u> and <u>anti</u> <u>C</u>-effects of the epoxide oxygen on the ethano carbons are small and shielding in both cases.

In our system, however, there is a fairly large and regular \underline{syn} - \underline{v} -effect of the epoxide on the aromatic carbons 4a, 8a. The perturbation does not spread beyond these carbons. One might dare to postulate an interaction of the oxygen lone pairs with these carbons perhaps producing a change in the excitation term of the Ramsey shielding mechanism. A similar shift is seen in the Cristol data for a couple of cases where there is a corresponding double bond in the molecule. Thus, the observation may prove useful to some as a configuration assignment aid.

Lest we go too complacent in assuming we know when to anticipate such a $syn-\underline{J}$ -effect, I offer the case of the two alcohols shown below. While there appears to be a $syn \underline{V}$ -effect here, it is certainly reduced in magnitude.



Best regards,

William B. Smith

Table 3. Carbon Chemical Shifts for the 5,8-DiX-1,4-ethanonaphthalenes and Epoxides

..

jh.

 θ_{χ}

		Chemical Shift(ppm)							
C	ompound	1,4	2,3	9,10	4a,8a	5,8	6,7	${ m CH}_3$, ${ m CO}_2$	
(5)	5,8-Dimethoxy	33.1	135.2	25.1	134.0	148.1	108.0	56.3	
(la)	5,8-Dimethoxy- <u>anti</u> -2,3 epoxide	30.8	58,0	22.8	133,5	149.8	109.2	56.3	
(1b)	5,8-Dimethoxy- <u>syn</u> -2,3-epoxide	29.6	48.8	21.8	127.7	148.8	109.0	56.1	
(6) ^a	6-Nitro-5,8 dimethoxy-	33.4 34.4	134.8	25.0 24.5	140.0 140.3	142.5 149.2	140.7 104.5	63.1, 56.1	
(2a) ^a	6-Nitro-5,8-dimethoxy- <u>anti</u> -2,3-epoxide	31.1 32.2	57.1	22.3 22.7	139.2 140.2	143.9 151.0	141.5 105.4	63.5, 57.1	
(2b) ^a	6-Nitro-5,8-dimethoxy syn-2,3-epoxide	29.8 30.4	48 .2	21.3 21.6	134.0 134.9	143.3 150.3	141.6 105.4	63.2, 56.0	
(7)	5,8-Diacetoxy	34,5	134.7	24.6	137.7	142,3	118.8	20.7, 169.2	
(3a)	5,8-Diacetoxy- <u>anti</u> -2,3-epoxide	32,6	57.1	22.2	136.9	144.1	120.2	20.7, 169.3	
(3b)	5,8-Diacetoxy- <u>syn</u> -2,3-epoxide	31.3	48.4	21.3	131.5	143.4	120.2	20.8, 169.2	

a. The second entry goes the carbon with the higher number.

285-40

Varian / 611 Hansen Way / Palo Alto / California 94303 / U.S.A.

Tel. (415) 493-4000 Telex 34-8476



June 3, 1982

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

APPLICATIONS CHEMIST POSITION AVAILABLE

Dear Barry:

We have an opening for an Applications Chemist in our Palo Alto Laboratory which we would like to fill as soon as possible. We are looking for a Ph.D. chemist with some post Ph.D. experience with a solid background in fundamentals as well as a good deal of experience as a practicing spectroscopist. This person should be conversant with new techniques in NMR and have a record of research NMR experience. Experience in areas such as 2D NMR, new pulse sequences, "other nuclei," solids, etc. will be valued significantly.

Typical responsibilities will include demonstrations, evaluations of new hardware and software, definitions of new hardware and software, collaborative and independent research and publication of such research. Varian has a long history of supporting and encouraging its chemists to be contributing scientists as well as Varian's interface to the scientific community.

Those interested should write me directly at the address given above including all pertinent details regarding education, research, experience and interests.

Sincerely yours,

Sense

George A. Gray NMR Applications Laboratory Varian Instrument Division

GAG/bry

Nicolet Supercon FT-NMR Spectrometers

Uncompromising performance, limitless adaptability.

Our spectrometer systems have been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, they represent a completely modular approach to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding Nicolet features include these:

• A full range of superconducting magnets from 4.7T to 11.7T (200MHz to 500MHz proton frequency range), in both widebore and narrow-bore configurations.

• Multinuclear observation with a wide variety of fixed-tune and broadband probes.

• Simultaneous acquisition, processing, and plotting for greater sample throughput.

• Simplified control of spectrometer operations and parameters by using easy keyboard commands.



• Extended dynamic range performance with 40-bit acquisition and floating-point processing.

• An expandable pulsesequence library, including T₁, T₂, Redfield, INEPT, homoand hetero- 2D-FT, etc.

• Convenient computer control of field shimming, observe and decoupling frequencies, sample temperature, and probe-tuning. • Precise digital plotting with full annotation of spectral parameters and flexibility of hardcopy format.

The versatile Nicolet spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

Some of these are: • High resolution studies of solids with Waugh-Pines crosspolarization and magicangle spinning.

• High sensitivity wide-bore ¹³C studies of high molecular weight polymers. • Automated T₁ and T₂ measurements.

• Chemical dynamics studies.

• Temperatureprogrammed experiments.

• ³¹P experiments on living organs.



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