Texas A M

H. Pyszora

No. 243

University

N - M - R

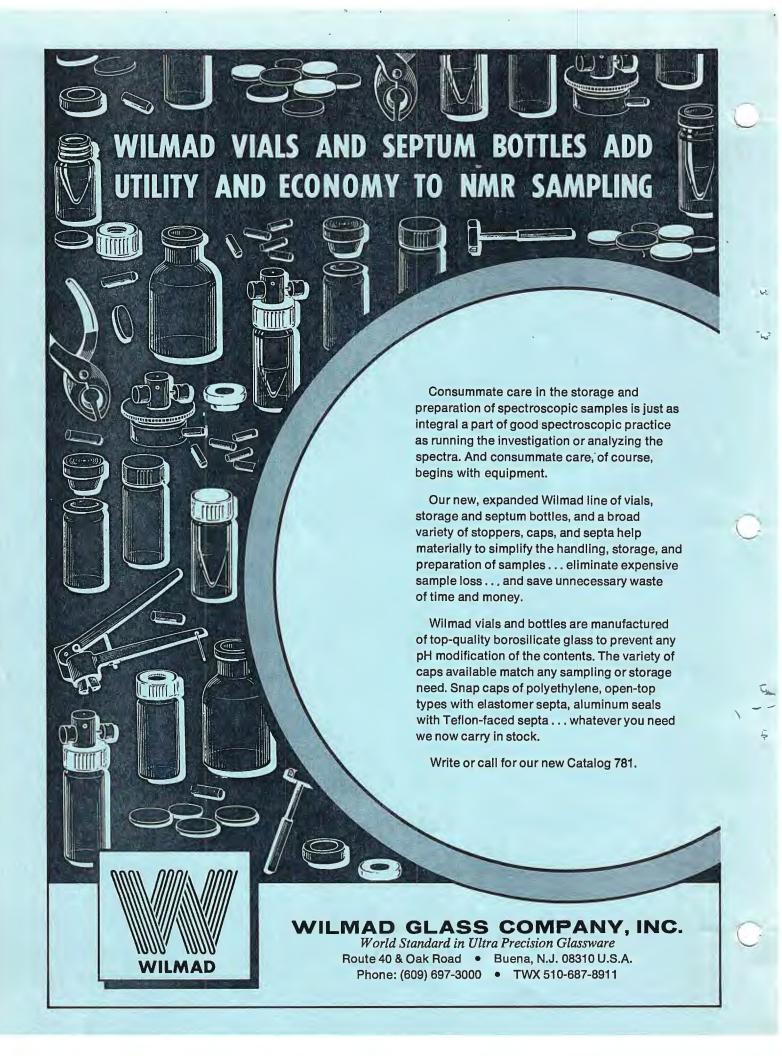
December, 1978

Newsletter

	The Formation of Polyformals and Hemiformals in Phenol-Formaldehyde Condensation Reactions - ¹³ C Study		Conformational Effects in Spectra of Ketone Peroxides
	Daniel Fiat Positions Available	J.	L. Dallas Selective T_1 Inversion Recovery
A Description	W. J. Freeman and F. FL. Ho Position Available - NMR Spectroscopist 5	Α.	S. Mildvan, G. Smith and R. K. Gupta Dipolar Correlation Times for Determination of Mn ²⁺ -Substrate Distances on Enzymes
	G. Hagele Proton and ³¹ P Spectra of Some Symmetrical Organo- phosphorus Compounds of the Type [RR'P(X)] ₂ Y 7	U.	Edlund TMEDA as a Complexation Agent; Steric Hindrance to Cation Solvation
	W. Bremser Estimating CNMR Spectra	R.	L. Vold, R. R. Vold and G. Bodenhausen Two-Dimensional Spin Echoes from Liquid Crystal- line Samples
	R. E. Carney CMR CuSO ₄ Titration of the Aminoglycoside Seldo- mycin Factor 5 - An Aid to Spectral Assignment 11	D.	A. Netzel 13C NMR Identification of Olefins in Shale Oil; 21st Annual Rocky Mountain Conference
4	K. Hamer, F. Balza, N. Cyr and A. S. Perlin On Completing a Karplus Curve for $^3J_{13}C_{-0}-C_{-1}H$: .13	S.	Berger $^{13}\mathrm{C}^{13}\mathrm{C}$ Spin Coupling Constants Additive or NOT? 39
	J. Kowalewski and A. Laaksonen Finite Perturbation - Configuration Interaction Calculations of Nuclear Spin-Spin Coupling		Stilbs Tetramethylurea Revisited 41
	J. Blackbourne and P. A. Hart	R.	L. Lichter Postdoctoral Position Available
	Software Frequency Control on a Bruker HX90E 17	Ε.	Martinelli and P. Gironi Ionization of 3- and 4-Substituted Rifamycins by
	A. Bax and A. F. Mehlkopf A SEFT-Like 2D Experiment		¹ H NMR Spectroscopy
1	J. Schaefer and E. O. Stejskal Characterization of Photorespiration Using	Ε.	D. Becker and R. Tschudin Modernize Your Supercon
KAT 3	G. Bodenhausen and P. Bolton Some Applications of Heteronuclear Two-Dimensional	E.	Santoro, F. Campadelli and F. Visani Quantitative FT ¹ H NMR Determination of End Groups in Polycarbonates from Bisphenol A (BPA)47
	NMR Spectroscopy on Cellular Phosphates 23	C.	B. Storm Spectrometer (Parts) For Sale 49
	S. Sternhell and L. D. Field Van der Waals Radii from Oriented NMR Spectra 25		

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

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.



TAMU NMR NEWSLETTER - ADVERTISERS

Bruker Instruments, Inc. - see p. 18

JEOL Analytical Instruments, Inc. - see p. (i) and outside back cover

Nicolet Instrument Corporation - see inside back cover

Varian Instrument Division - see p. 32

Wilmad Glass Co., Inc. - see inside front cover

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
Bruker Instruments, Inc.
Eastman Kodak Company
JEOL Analytical Instruments, Inc.
Dr. R. Kosfeld, Abt. Kernres., Inst. f. Phys. Chem.,
TH Aachen (Germany)
The Monsanto Company
Nicolet Technology Corp., Palo Alto, CA
(formerly Transform Technology, Inc.)
Shell Development Company
Unilever Research
Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

The British Petroleum Co., Ltd. (England)
E. I. DuPont Deflemours & Company
The Lilly Research Laboratories, Eli Lilly & Co.
The NMR Discussion Group of the U.K.
The Perkin-Elmer Company
Pfizer, Inc.
The Procter & Gamble Co., Hidmi Vailey Labs
Programmed Test Sources, Inc.
Union Carbide Corporation
Xerox Corp., Webster Research Center

DEADLINE DATES: No. 244: 8 January 1979 No. 245: 5 February 1979

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. 243

For those who expect more in FT NMR Spectrometers . . . it's JEOL



The FX60Q, FX90Q & FX100 Feature:

- (DQD) DIGITAL Quadrature Detection System
- Multi-Frequency TUNEABLE Probe observation
- Dual Frequency probes
- 4-channel DIGITAL phase shifters (DPS)
- Comprehensive auto-stacking system
- Foreground/Background system
- Computer based pulse programmer with Multiple Pulse Sequence Generator
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- T₁ρ/spin locking system
- Disc storage systems
- Multi-Mode HOMO/HETERO decoupling capabilities
- Programmable Variable Temperature
- Simplex Y/Curvature gradient controller



BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND:

THE FORMATION OF POLYFORMALS AND HEMIFORMALS IN PHENOL-FORMALDEHYDE CONDENSATION REACTIONS. 13C STUDY

The complexity of phenol-formaldehyde addition/condensation reactions has so far prevented the study of short-lived intermediates. As the reactions are carried out, in most cases in aqueous solutions proton NMR has been of limited use, although the equilibria in water for some model systems, eg formaldehyde-methanol, formaldehyde-benzyl alcohol and formaldehyde-phenol systems have been determined.(1)

We have used 13C NMR to study the redistribution reactions (in aqueous solution) of formaldehyde-methanol-para- and orthomethylolphenols, components which are present in the initial stages of phenol-formaldehyde addition reactions.

Fig 1 and 2 show the spectra of aqueous solutions of formaldehyde (37 % w/w formaldehyde containing 12 % w/w methanol) and ortho- and para- methylolphenols, respectively. The assignments (internal methanol taken as 49.30 ppm) are given in the table.

Although our prime interest was in the assignments of the resonances in the 45-95 ppm region and in the direct measurement of the concentration of monomeric formaldehyde hydrate (82.42 ppm) the use of ^{13}C NMR should allow the following equilibria present during the phenol-formaldehyde condensation reaction to be quantified :

n
$$HOCH_2OH \implies HO(CH_2O)_nH + nH_2O$$

$$CH_3OH + HOCH_2OH \implies CH_3OCH_2OH + H_2O \qquad)$$

$$CH_3OH + HO(CH_2O)_nH \implies CH_3O(CH_2O)_nH + H_2O \qquad)$$

$$O- \text{ and } P- HO.C_6H_4.CH_2OH + HOCH_2OH \implies HO.C_6H_4CH_2OCH_2OH + H_2O$$

o- and p-
$$HOCH_2 \cdot C_6H_4 \cdot CH_2OH + HOCH_2OH \longrightarrow HOCH_2C_6H_4 \cdot CH_2OH + H_2O$$

o- and p- $HOCH_2 \cdot C_6H_4 \cdot CH_2OH + HOCH_2C_6H_4 \cdot CH_2OH + H_2O$

o- and p- $HOCH_2 \cdot C_6H_4 \cdot CH_2OH \longrightarrow HOCH_2C_6H_4 \cdot CH_2OH + H_2O$

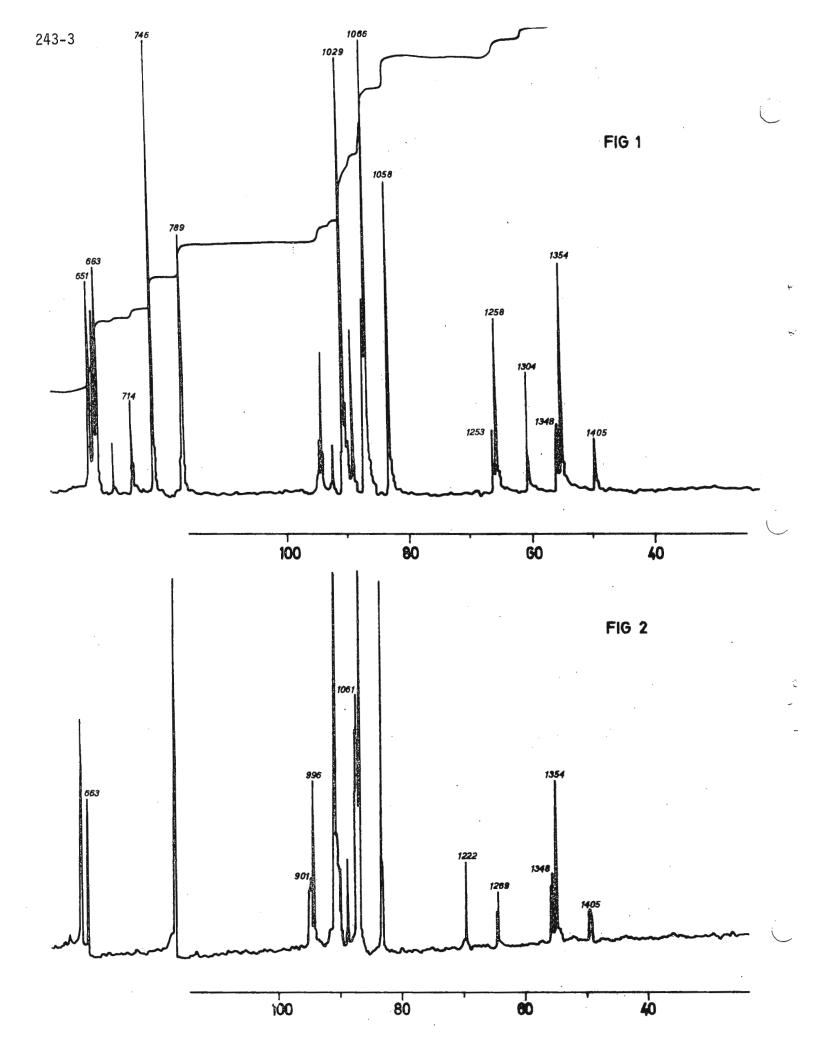
C

From our studies it appears that no hemiformals of the phenolic hydroxy are formed suggesting that the magnitude of the equilibrium constants for the addition of methylene glycol to phenol, methylolphenols, and methanol is in the order A > B > \sim .

Shift	Assignment	Shift	Assignment
49.30 54.80 55.45 60.19 63.97 65.16 65.69 69.04 82.42	CH ₃ OH CH ₃ OCH ₂ OH CH ₃ O(CH ₂ O) ₂ H O-ArCH ₂ OH P-ArCH ₂ OH O-ArCH ₂ OCH ₂ OH O-ArCH ₂ OCH ₂ OH O-ArCH ₂ OCH ₂ OH HOCH ₂ OH	85.87 86.06 87.81 88.25 89.00 89.97 91.48 93.31 93.86 93.96	HOCH2OCH2OH HOCH2OCH2OCH2OH p-ArCH2OCH2OH o-ArCH2OCH2OH HOCH2OCH2OH HOCH2OCH2OCH2OH C-ArCH2OCH2OCH2OH CH3OCH2OH CH3OCH2OH CH3OCH2OH CH3OCH2OH CH3OCH2OCH2OH

(1) P.W. Kopf and E.R. Wagner, J. Poly. Sci. Chem. Ed. <u>11</u>, 939, 1973.

H. Pyszora H. Pynna.



SCHOOL OF BASIC MEDICAL SCHOOL S.

UNIVERSITY OF ILLINOIS AT THE MEDICAL CENTER

P.O. BOX 6998, ROOM E - 207 - MSA BUILDING

901 SOUTH WOLCOTT STREET

CHICAGO, ILLINOIS 60680

PROFESSOR DANIEL FIAT

TELLPHONE: OF FICE (312) 996 - 7609

November 2, 1978

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

Dear Barry:

Research assciate (post doctoral) and research assistant (graduate student) positions are available for nuclear magnetic resonance studies in Biophysics (theoretical and applied) and for synthetic work that involves stable isotope labeling of molecules of physiological interest.

Our NMR laboratory is equipped with the most modern instrumentation (Bruker CXP-180 and WH-360 superconducting high power and high resolution NMR spectrometers and Varian DP-100 electromagnet spectrometers.) The research opportunities at our school are therefore excellent and we have all of the required additional research facilities.

Please send resume and three reference letters to Dr. Daniel Fiat or phone at (312) 996-7609 or 996-4672.

Sincerely yours,

Daniel Fiat



HERCULES INCORPORATED

RESEARCH CENTER - WILMINGTON, DELAWARE 19899 - TELEPHONE: 302-995-3000

October 18, 1978

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

Dear Dr. Shapiro:

POSITION AVAILABLE -- NMR SPECTROSCOPIST

With this contribution we would like to open a subscription to the Newsletter.

Hercules Incorporated is seeking immediately a PhD-level chemist to work and provide technical leadership in a group involved in the application of NMR spectroscopy to problems of corporate interest. These areas include NMR studies of polymer microstructure by solution techniques, development of analytical NMR methods for determination of components in mixtures and application of multinuclear NMR techniques to problems of concern to Hercules.

A strong background in organic or physical organic chemistry and a strong interest in applied NMR spectroscopy are necessary qualifications. A minimum of three years technical experience with both ^{13}C and ^{1}H NMR of polymeric and nonpolymeric systems and/or superconducting systems is essential.

Our current NMR-ESR equipment consists of a Varian EM-390 (1 H & 19 F), an A-60D, a Bruker HFX-90 (13 C, 31 P, 1 H, & 19F), a Varian Model V-4500 X-Band ESR and a soon to be delivered (February 1979) Nicolet NT-360 widebore spectrometer (1 H and multinuclear capabilities from 94 to 24 MHz with 12 mm probes and including 13 C with 20 mm and 2 mm probes).

We feel that this equipment and the current staffing of the laboratory which includes, in addition to the authors, several very capable technicians and a B.S. chemist makes this an attractive position. The physical surroundings are also quite nice. The Research Center is located in suburban Wilmington in a sylvan setting and is surrounded by the Hercules Country Club and golf course.

B. L. Shapiro

October 18, 1978

Qualified applicants should send their resumes including salary requirements in strict confidence to:

Dr. P. B. Welldon Research Center Hercules Incorporated Wilmington, DE 19899

The authors may be reached directly at 302-995-3249 or 302-995-3209.

Sincerely,

Walter J. Freeman

F. F.-L. Ho

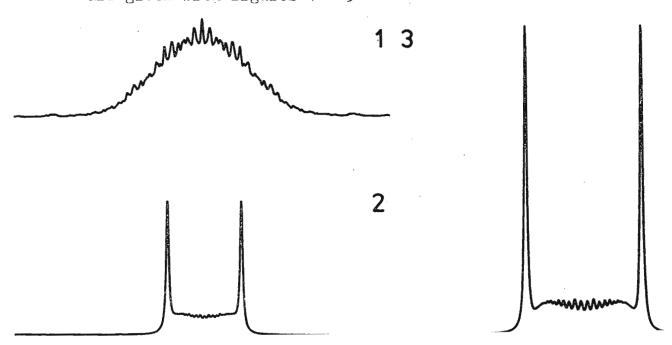
Gerhard Hägele Institut für Anorganische und Strukturchemie der Universität Düsseldorf 4000 Düsseldorf, 25.10.78 Universitätsstrasse 1 G. F. R.

to

Prof. Dr. B. Shapiro
Texas A & M University
College of Science
College Station
Texas 77843
U. S. A.

Dear Professor Shapiro!

I am sorry about delays with our contribution to TAMU NMR Newsletter giving rise to your blue and red reminders. Recently we looked into some symmetric organophosphorus compounds of type $[RR^{\bullet}P(X)]_2Y$ and analyzed corresponding 1H - and ^{31}P -NMR-spectra. Meso- $[CH_3(t-C_4H_9)P(S)]_2O$ was explained in terms of an $[AR_tX_n]_2$ -spinsystem. Explicit algebaic expressions for transition frequencies and relative intensities for this system were programmed in DOKI78 and DOKI77 to calculate the Phosphorus (A) and Proton $(R_t$, X_n) NMR spectra. Appropriate Lorentzian plots are given with figures 1 - 3



Parameters for	r meso [C	H ₃ (t-C ₄ H ₉)P(S	S)] ₂ 0 25%	solution	in	^C 6 ^D 6
----------------	-----------	--	------------------------	----------	----	-------------------------------

Phospl	norus	A - part	figure 1		
δ_{p}	ppm		110.517	•	
J _{PP} .	Hz		56 ± 1		
$\mathtt{HW}_{\mathtt{P}}^{+}$	$H\mathbf{z}$		1.7		
Scale	Hz/cm		18.444		
Proton	ns	R - part	figure 2 CF	X - part	figure 2 t-C4H9
8 _H	ppm		1.696		1.097
N	Ηz		11.7 ± 0.5		18.4 ± 0.5
Ļ	Hz		12.2 ± 0.5		18.4 ± 0.5
$J_{ m PH}$	Hz		11.95 ± 0.5		18.4 ± 0.5
$J_{\mathrm{PH}}^{\bullet}$	Hz		0.25 ± 0.5		0.0 ± 0.5
${\tt HW}^{ m N}$	Hz		0.50		0.50 0.5
HWx+	Hz		0.75		0.80
Scale	Hz/cm		6.000		6.000

^{*)} HW = Halfwidth of Lorentzian lines. Different halfwidths were used fitting N- and α -lines.

Lit.:

G.Hägele, R.K.Harris and Mrs.J.Nichols; J.Chem.Soc.Dalton Trans. 1973,79

- G.Hägele and R.K.Harris; Ber.d.Bunsen Ges. 76,910(1972)
- G.Hägele; Ber.d.Bunsen Ges.. 78,43(1974)
- G. Hägele and J. Lorberth; Org. Magn. Res. 9,325(1977)

Yours sincerely

attagell

(Prof.Dr.G.Hägelc)

Dr. W. Bremser c/o
BASF Aktiengesellschaft
Hauptlaboratorium



Telefon (0621) 601 (Vermittlung)
Telex 464811 basf d (Zentrale)
Telegramme: BASF Ludwigshafenrhein
Bankverbindung: Landeszentralbank
6700 Ludwigshafen, Girokonto 54507300
Luftpost

BASF · 6700 Ludwigshafen

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

Texas 77843

USA

Ihre Zeichen

Ihre Nachricht vom

Unsere Zeichen
WHE-WBr/Dg

Telefon-Durchwah! (0621) 60- **8401**

Telex 464Ludwigshafen 30.10.1978

Betreff

Dear Barry,

Estimating CNMR spectra

the correlation between coupling constants and chemical environment by means of substructure codes (HOSE /1/) was illustrated in our last contribution /2/. A similar procedure can be applied for chemical shifts in order to estimate the CNMR-spectra of various chemical compounds. The corresponding register contains for each individual HOSE-code the average chemical shift with standard deviation, the number of resonances found in the data collection /3/ as well as the highest and lowest chemical shift values observed. Additionally a modified average is calculated after eliminating every sixth chemical shift with the highest deviation from the mean. These entries in the register give typical ranges of chemical shifts expected for certain structural elements. Furthermore the hierarchical ordering often allows the estimation of chemical shifts from the neighbouring entries when the precise substructure is not contained in the register (see interpolation in example). Expected chemical shifts can also be derived for ranges of substructure codes with identical first, second or third sphere, and strong deviations point to specific interactions between the substituents or errors in the data collection which can be automatically detected this way.

As shown for the substructure search /4/ this procedure can also be computerized fully in order to estimate the complete CNMR spectrum of a postulated chemical structure. An interactive program allows building and visualizing the desired compound, generation of the topological matrix and calculation of the HOSE codes. Finally the desired entries are looked up in the above register, and the expected chemical shift ranges for the individual carbon atoms are tabulated, including standard deviation and number of entries, as shown in the enclosed example.

Best regards,

W. Branser

References:

- /1/ W. Bremser, L. Ernst and B. Franke, Carbon-13 NMR Spectral Data, Verlag Chemie, Weinheim (1978)
- /2/ TAMU-NMR 231, 47 (1977)
- /3/ BASF-GBF CNMR Data Collection with presently 16500 spectra of 12500 different compounds
- /4/ W. Bremser, Anal. Chim. Acta, in press (1978)

UND WEITER?

GESCHAETZTES CNMR SPEKTRUM :

```
42 BEISPIELE)
      114.3 PPM
                       0.3 PPM
 1
C 2
      138.0 PFM
                       1.1 PPM
                                  (INTERPOLIERT)
                  書
C 3
       32.0 PPM
                       2.0 PPM
                                  (INTERPOLIERT)
С
                       3.4 PPM
                                  (INTERPOLIERT)
 4
       37.5 PPM
                  ŧ
С
 5
       58.8 PPM
                  #
                       1.0 PPM
                                  (INTERPOLIERT)
C
                       0.9 PPM
                                  (INTERPOLIERT)
 6
        43.1 PPM
С
                       3.0 PPM
                                  (INTERPOLIERT)
 7
      201.7 PPM
C 8
        27.5 PPM
                       2.1 PPM
                                  (INTERPOLIERT)
```

Pharmaceutical Products Division

Abbott Laboratories North Chicago, Illinois 60064

November 1, 1978

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

Dear Professor Shapiro,

CMR CuSO $_4$ Titration of the Aminoglycoside Seldomycin Factor 5^* - An Aid to Spectral Assignment

A CMR CuSO₄ titration is run in a similar manner to a pH titration except that the peaks do not shift position but are broadened. The degree of broadening is related to the proximity of the particular carbon to the site of copper binding. The broadening can be used to make specific carbon assignments when there is a clear primary binding site.

Fig. A shows a spectrum of seldomycin factor 5 (1) before the addition of CuSO₄ solution. Early in the titration it was noticed that all the ring carbon resonances of the seldose sugar broadened and eventually could not be seen at all (Fig. B). Then the ring carbon resonances of the 4-deoxy-diaminoglucose sugar began to broaden and at the end of the titration there remained only the OCH₃ of the seldose sugar and the resonances for 2-deoxy-streptamine (Fig. C).

The CMR CuSO titration of seldomycin factor 5 indicates that Cu¹¹ binds first to the ⁴vicinal 2", 3" diamino system and somewhat less to the 2', 3' amino alcohol.

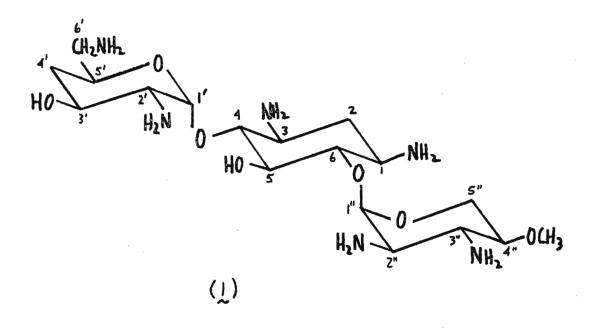
R. S. Stanaszek

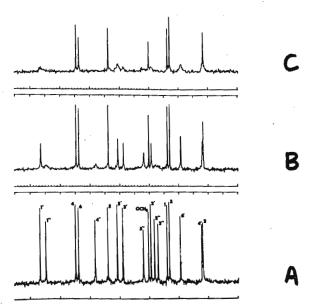
R. S. Egan

J. B. McAlpine

R. E. Carney

R. E. Carney and J. B. McAlpine: Use of Copper II Ion in Selective Acylation of Seldomycin Factor 5, Abstracts of the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 13-17, 1978, Paper Carb. 46.







Department of Chemistry Pulp and Paper Building

November 1, 1978.

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

On completing a Karplus curve for ${}^3J_{13}_{C-0-C-1}H$

Dear Barry:

Since our most recent mail strike is over, we no longer have an excuse for delaying our contribution to the Newsletter.

In studying conformations of disaccharides and larger carbohydrates in solution, we have been measuring $^3J_{C-H}$ involving nuclei across glycosidic bonds 1 , e.g., coupling between C-1 and H-4 (or C-4 and H-1) in the structure represented by $\underline{1}$. This requires a knowledge of the torsional angle dependence of $^3J_{C-H}$. A number of values are available from carbohydrate model compounds for $^{13}C\text{-O-C-}^{1}H$ arrays of nuclei 2 , the type of array found in $\underline{1}$, but it is difficult to find molecules that can furnish appropriate data for the 0°-60° region of a Karplus curve. One molecule that fits the bill is cyclohexaamylose, or α -cyclodextrin (formula $\underline{1}$ depicts three of its six glucose residues): according to crystallographic and theoretical studies, the glycosidic bonds are so constrained by its cyclic structure that the torsional angles (ϕ and ψ) are about $\pm 10^\circ$.

Although C-1 (or C-4) in $\underline{1}$ may couple with several protons other than H-4 (or H-1), and hence give rise to a complex signal $\underline{1}$, we have been able to improve things materially by introducing deuterium at positions 2,3 and 6, through a facile H-D catalytic exchange $\underline{3}$. Analysis of the C-1 signal (A) for deuterated $\underline{1}$, with the aid of computer simulation, has given a value of 4.8 Hz due to the inter-residue coupling between C-1 and H-4. Similarly, from the C-4 signal (B) (a broad multiplet prior to deuteration) a value of 5.2 Hz has been obtained for $\underline{3}_{C-4,H-1}$ ($\underline{2}_{C-4,H-5}$ is -3.5 Hz).

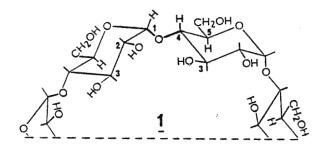
With these data, the Karplus curve has been extended to cover the overall range, as shown in the accompanying Figure. The use of this curve

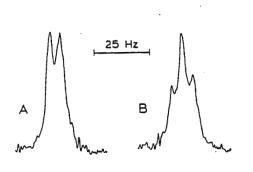
Postal address: 3420 University Street, Montreal, PQ, Canada H3A 2A7

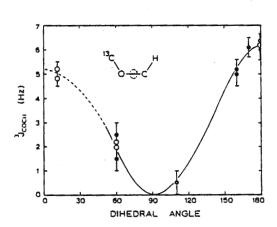
in examining the conformation of methyl β -cellobioside is described in an article to appear shortly⁴. Here again, the study has been facilitated through the preparation of the disaccharide deuterated at eight readily-exchangeable positions. Analogous studies on other extensively-deuterated carbohydrates are in progress.

G.K. Hamer F. Balza N. Cyr Sincerely yours,

- A.S. Perlin, N. Cyr, R.G.S. Ritchie and A. Parfondry, Carbohyd. Res., 37, C1(1974); A. Parfondry, N. Cyr and A.S. Perlin, Carbohyd. Res., 59, 299(1977).
- 2. A.S. Perlin and B. Casu, Tetrahedron Lett., 2921(1969); J.A. Schwarcz and A.S. Perlin, Can. J. Chem., 50, 3667(1972).
- 3. F. Balza, N. Cyr, G.K. Hamer and A.S. Perlin; H.J. Koch and R.S. Stuart, Carbohyd. Res., 59, C7(1977); H.J. Koch and R.S. Stuart, Carbohyd. Res., 59, C4(1977).
- 4. G.K. Hamer, F. Balza, N. Cyr and A.S. Perlin, Can. J. Chem., in press.









UNIVERSITY OF STOCKHOLM ARRHENIUS LABORATORY Physical Chemistry

1 November 1978

Dr. Bernard Shapiro Departement of Chemistry Texas A & M University College Station, Texas 77840

Title: Finite Perturbation - Configuration Interaction Calculations of Nuclear Spin-Spin Coupling Constants

Dear Dr Shapiro,

A vast majority of the quantum chemical calculations of nuclear spin-spin coupling constants published to date are based on the theoretical foundations due to Pople and coworkers more than ten years ago. First, the non-contact mechanisms are assumed negligible for the couplings involving protons 1 . Second, the calculations of the Fermi contact term are carried out using a coupled Hartree-Fock type treatment and the INDO approximation 2 . Recently, Guest and coworkers 3 published results of non-empirical coupled Hartree-Fock calculations of the coupling constants in the first row hydrides, including all the coupling mechanisms and using large basis sets. For the geminal proton-proton coupling constants in 2 0, 2 1 NH 3 2 and 3 3 and 3 4 they find that the coupled Hartree-Fock values of 3 1 H 3 1 in all three molecules are about 3 2 (compared to the experimental 3 2 in 3 3, 3 4 in ammonia and 3 4 in methane) and that the variation in the series is reproduced if the non-contact mechanisms are included (the calculated orbital contribution in water is about 8 Hz!).

At this laboratory, we have since many years been interested in the correlation effects on the coupling constants.⁴ As a continuation of this project we have recently started doing non-empirical finite perturbation CI calculations. We are at present concentrating on the Fermi contact contribution, which we believe to be the most sensitive to correlation effects. For the coupling constants in the first row hydrides, we find the following: (1) upon going from the Hartree-Fock to the CI level the contact contributions are reduced in magnitude by about 50% for the proton-proton couplings and by about 25% for the proton-first row atom couplings.(2) the differences in the proton-proton couplings within the series cannot probably be explained without including the non-contact mechanisms. (3) The finite perturbation approach works better than the

conventional second order perturbation theory. (4) the results are basis set sensitive. This last point is especially true for the one-bond couplings and we wish to illustrate it with the results for the hydrogen fluoride molecule (for which it is possible to go to large basis sets without getting bankrupt after paying your bills to the computer center) presented in the table below.

Basis set	٦FC					Jother		
			Hart Fock	ree-	Correl.		Total	Hartree- Fock
<4,2/3,1>			254		- 49		205	
<5,3,1/3,1>			457		-123		334	
<8,4,2/4,2>			473		-126		347	
<11,8,3/10,3> ^a			478				·	187
J ^{calc} = J ^{FC} Hartree-Fock	+	J ^{FC} correl	. +	J ^{other} Hartr	ee-Fock	=		
= 480	-	130	+	190		=	540	
J ^{exp} = 530								

afrom Guest et al³

The numbers adding up to the J_{calc} are crude guesses of what would correspond to the limit of infinite basis. Even though there is a certain amount of wishful thinking behind these numbers, we still hope that the table provides a good illustration of how well the quantum chemistry today can perform for the coupling constants when the accuracy is pushed as far as possible for the small molecules.

Yours sincerely

Jozef Kowalewski

Aatto Laaksonen

REFERENCES

^{1.} J.A. Pople and D.P. Santry, Mol. Phys. 8,1 (1964)

^{2.} J.A. Pople, J.W. McIver, Jr and N.S. Ostlund, J.Chem. Phys. 49, 2965 (1968)

M.F. Guest, V.R. Saunders and R.E. Overill, Mol. Phys. 35, 427 (1978)

^{4.} J. Kowalewski, Progr.NMR Spectr. 11,1 (1977)

University of Wisconsin



CENTER FOR HEALTH SCIENCES School of Pharmacy 425 North Charter Street Madison, Wisconsin 53706

Telephone: 608/262-1416

November 21, 1978

Professor Barry Shapiro Department of Chemistry Texas A and M University College Station, Texas 77843

Software Frequency Control On a Bruker HX90E

Dear Professor Shapiro:

Since we built our own quadrature detector, we've used NTCFT software. That software is designed to allow spectrometer frequency control, but not for Bruker instruments. The adaptation is as follows.

Address 4427 (be sure know where this statement is actually stored) of the NTCFT program module NTCCON was changed from 2111554 (MEMA BCDCD) to 3111557 (MEMA CDFREQ). The Bruker instrument does not require the binary coded decimal. Address 4431 was changed from 4731 to 4241 (DAC1) or 4234 (DAC2). There are two complete digital to analog converters on the DAC board of our Nicolet 293 pulse programmer.

The DAC was modified to reduce gain by removing and replacing with a jumper the precision lK resistor associated with op amps 301A number one and two. To bring the ero into range the precision 10K resistor that connects with the wiper of the ZERO potentiometer was changed to lK. The converter output (from DAC) was fed by way of a coaxial cable directly to the voltage to frequency converter board via a single pole double throw switch that allows either software or manual frequency control. If frequencies are entered at the teletype as negative numbers, the gain and zero can be set such that spectrometer frequency ranges from -4097 to -8192 adjustable to l Hz. The entered frequencies differ somewhat from the actual spectrometer frequencies, thus some calibration is necessary.

Sincerely yours

James Blackbourn

Phillip A. Hart



DATA SYSTEMS

ASPECT₂₀₀₀



The ASPECT 2000 is a complete data acquisition and processing system which can be used efficiently wherever the time dependence of physical observables must be stored and analyzed. It is a high performance minicomputer with dual-input A/D converters and numerous interfaces. Together with its comprehensive software, the ASPECT 2000 offers unmatched capabilities for data-collection, calculation, analysis and output.

- 24-bit word length
- Fast A/D converter: 250 KHz @ 12-bits
- 2 programmable real-time clocks
- 2 direct-memory-access channels
- 3 arithmetic registers
- 4 index registers for addressing
- 7 vectored interrupt levels
- Fast MOS solid-state memory capacity of up to 80 K
- Hardware multiply-divide
- ROM binary tape loader and disk bootstrap

The ASPECT 2000 is included as the superior data system in all Bruker high resolution NMR, pulsed NMR, EPR and FT/Infrared spectrometers.

Ideally suited as a general purpose laboratory data system, complete with a wide array of accessories and software.

Call or Write for Details or a Demonstration

BRUKER INSTRUMENTS, INC.



TECHNISCHE HOGESCHOOL DELFT

Laboratorium voor Technische Natuurkunde

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

Uw kenmerk

Uw brief van

Ons kenmerk

Lorentzweg 1, Delft 8, telefoon (015) 133222 November 1, 1978 toestel:

Onderwerp

A SEFT-like 2D experiment

Dear Professor Shapiro,

Various homonuclear and heteronuclear 2D techniques have been implemented on our home-built 7 Tesla HR-NMR spectrometer¹. One of these techniques is the homonuclear two-dimensional J-resolved method², which is illustrated in figure 1. Figure 1.a. shows a method in which the sampling along the t₁-axis is achieved by varying the time between the 90° and 180° pulse. In the method of figure 1.b. this sampling is achieved by changing the number of 180° pulses in the succeeding pulse trains. The purpose of the 180° pulses in figure 1.b. is to minimize the signal loss due to the diffusion in the sample, which gives the opportunity to get the natural line width. Both experiments are suggested by Aue, Karhan and Ernst², the experiment according to figure 1.a. has been carried out by them.

We performed the experiment shown in figure 1.b., but with the sampling of all the echoes between the 180° pulses. This can be done with our on-line time-averaging on the disc, by which the number of data-points can be over 10° double precision, and the sampling frequency can be up till 45 kHz¹, 3. With this method a complete 2D experiment can be done in a shorter time than in the case where only the last echo is sampled. The relative gain in time (G_t) can be calculated as:

$$\frac{1}{2} v_{m} a T_{2} < G_{t} < v_{m} a T_{2}$$
 (1)

where ν_m is the total maximum multiplet width and a T_2 is the longest t_2 value used. a has to be in the order of 3 to avoid line broadening in the ω_1 -direction. The sampling frequency and thus the time distance between the 180° pulses (τ) is set by the theorem of Shannon, which results in:

$$\tau < (v_m)^{-1} \tag{2}$$

There can be two reasons wich do not allow such a short pulse distance:

- 1. 180° pulses which are close to each other can introduce severe distortions in the 2D spectrum. This applies also to situation in which no signals are sampled between the echoes.
- 2. A short pulse distance allows only a short sampling time of the echoes, which gives a poor resolution along the ω_2 -axis after fourier transformation. This only applies if the echoes are sampled between the 180° pulses.

The solution of both these disadvantages is a pulse sequence which consists of N pulse trains of the form:

$$90^{\circ} - n \tau/2 - 180^{\circ} - (n \tau/2 + N \tau/2) - 180^{\circ} - N\tau - 180^{\circ} - N\tau - 180^{\circ} \dots$$

where $n = 1, 2, \ldots, N$ and τ still has to satisfie relation (2).

This pulse sequence gives still a 2D spectrum with line widths along the ω_1 -axis only determined by T_2 and a relative gain in time given by:

$$\frac{1}{2N} v_{\rm m} \ {\rm a} \ {\rm T}_2 < {\rm G}_{\rm t} < \frac{1}{N} v_{\rm m} \ {\rm a} \ {\rm T}_2$$
 (3)

Figure 2 shows the proton 2D spectrum of 1,1,2-trichloro-ethene which is obtained from the echoes of one single CPGM pulse train.

Yours sincerely,

A. Bax A.F Mehlkopf

1. A.F.Mehlkopf, thesis, Delft 1978

2. W.P. Aue, J. Karhan and R.R. Ernst, J. Chem. Phys. 64, 4226 (1976)

3. A. Bax and A.F. Mehlkopf, to be published

4. A. Allerhand, J. Chem. Phys. 44, 1 (1966)

Please credit this contribution to Prof. J. Smidt

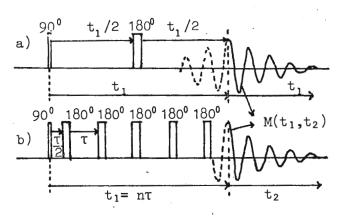


Fig. 1. Two basic schemes for 2D J-resolved spectroscopy. (a) Single echo experiment (b) Spin echo sequence. From ref.(2).

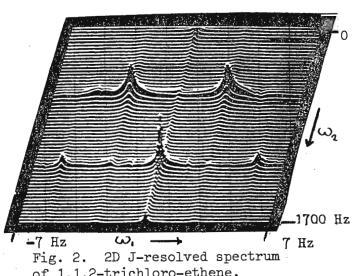


Fig. 2. 2D J-resolved spectrum of 1,1,2-trichloro-ethene. The total measuring time was about 10 sec. (G_{+} =100)

Monsanto

CORPORATE RESEARCH LABORATORIES

Monsanto Company 800 N. Lindbergh Boulevard St. Louis, Missouri 63166 Phone: (314) 694-1000

November 8, 1978

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

Dear Barry:

Characterization of Photorespiration Using 13CO2 Labeling

Photorespiration is a light-stimulated oxidation of the products of photosynthesis to CO_2 . Efforts to characterize photorespiration in the past have involved the simultaneous measurement of transient $^{12}\mathrm{CO}_2$ and $^{14}\mathrm{CO}_2$ labeling chamber concentrations in equilibrium with actively photosynthesizing leaves. This method has a serious limitation in that the specific activity of $^{14}\mathrm{CO}_2$ inside the leaf need not approach the external specific activity so that no reliable estimate of internally refixed CO_2 is possible. Efforts to measure $^{14}\mathrm{C}$ labeling in various early photosynthetic metabolites such as 3-PGA, glycine, and serine are complicated by the possible neterogeneity of these pools interferring with comparisons of absolute activity observed from one leaf labeling experiment to another. Nevertherless, qualitatively, these early experiments clearly demonstrated that $^{12}\mathrm{CO}_2$ generated by photorespiration of unlabeled substrate diluted entering $^{14}\mathrm{CO}_2$ and so prevented the isotopic saturation of the Calvin cycle and its immediate products for times on the order of 30 minutes.

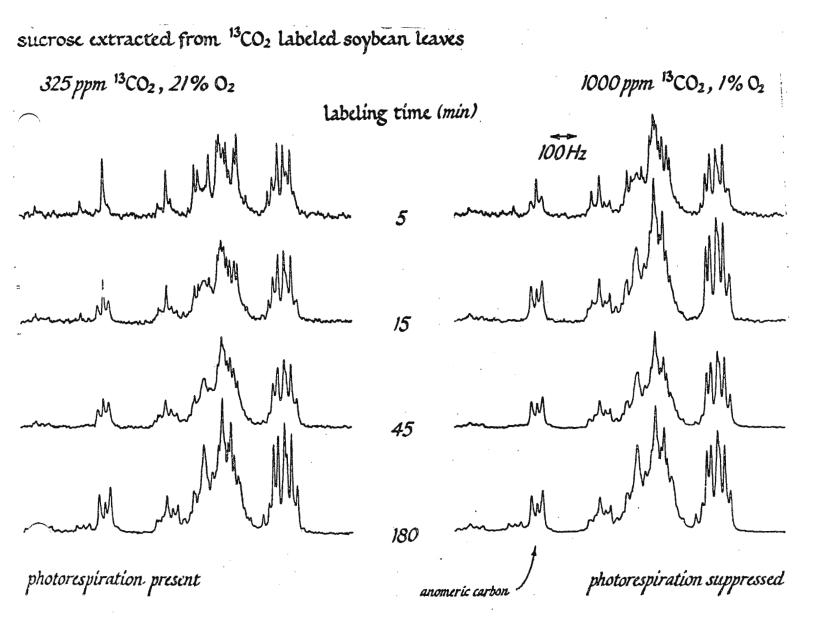
We have established that by labeling intact leaves as a function of time with 90% enriched $^{13}\mathrm{CO}_2$, the distribution of label among pairs of carbons ($^{12}\mathrm{C}-^{13}\mathrm{C}$, $^{13}\mathrm{C}-^{13}\mathrm{C}$) in triose products of the Calvin cycle can be determined from the $^{13}\mathrm{C}$ nmr spectra of sucrose extracted from the leaves. This is illustrated in the attached figure. The spin-spin multiplet pattern of the protonated anomeric carbon of sucrose is simple because of the presence of only one nearest-neighbor carbon. Thus, the ratio of singlet to doublet can be interpreted directly as the ratio of $^{12}\mathrm{C}-^{13}\mathrm{C}$ concentration to $^{13}\mathrm{C}-^{13}\mathrm{C}$ concentration in labeled triose fragments of sucrose. (We have converted sucrose to lactic acid and confirmed that the labeling pattern of this anomeric carbon is representative of the labeling patterns of all carbons of sucrose). As you can see, under conditions of high CO2 and low O2 concentrations, where photorespiration is likely to be suppressed, the isotopic saturation of the protonated anomeric carbon of sucrose extracted from labeled soybean leaves is reached in less than 15 minutes. That is, the ratio of doublet to singlet integrated intensities reaches the 0.9 value of the isotopic composition of the labeling $^{13}\mathrm{CO}_2$ in less than 15 minutes. Isotopic saturation requires more than 45 minutes with labeling under normal gas concentrations.

The time dependence of these labeling distributions can be interpreted in terms of photosynthetic and photorespratory processes using a relatively simple dynamic model we have developed. We estimate that the total photorespiration in soybeans (including internally refixed ${\rm CO}_2$) is about 50% of the apparent photosynthetic rate. Similar

experiments on corn have established that photorespiration in that species is much smaller. These determinations are free from ambiguities of comparisons of kinetic data derived from experiments on separate leaves because the 13CO2 labeling is internally standardized. That is, we derive information about carbon metabolism by analyzing ratios of nmr signal intensities. This avoids the difficulties of standardizing activities to variations from leaf to leaf in photosynthetic rates, homogeneity of pools, and distribution of label among products (sucrose, starch, etc.). Consequently, examining the distribution of label in a component of a final product such as sucrose is a practical matter. This technique, of course, does not depend on equilibration of gas concentrations internal and external to the leaf.

Sincerely,

Jacob Schaefer E. O. Stejskal



UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO



SANTA BARBARA . SANTA CRUZ

SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

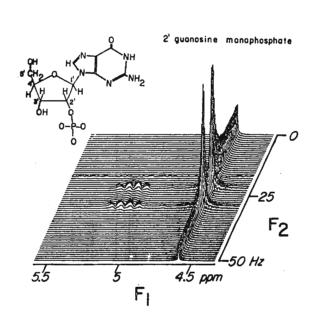
November 9, 1978

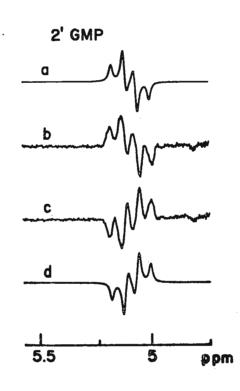
Professor B. L. Shapiro Department of Chemistry Texas A&M University College Station, Texas 77843

Dear Dr. Shapiro:

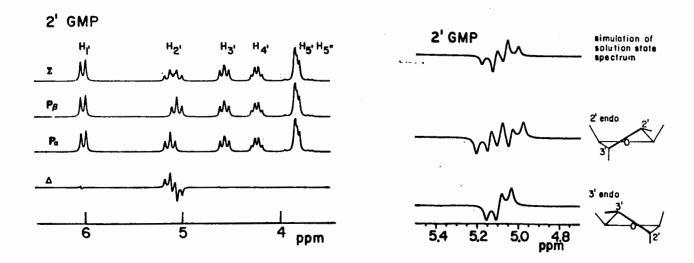
We have recently tried some applications of heteronuclear two-dimensional NMR spectroscopy on cellular phosphates. The experiments were performed in a manner analogous to those described by Ernst (1) and Freeman (2) with carbon-13/proton systems, observing phosphorus-31 instead of carbon-13. Phosphate groups act as convenient "spies" planted in strategic locations like the backbone of polynucleotides. Fortunately, these spies have a tendency to be short-sighted and only report on the protons in their immediate vicinity, as long range scalar couplings tend to be small. As a result, the two-dimensional method provides some intelligible information for systems whose actual proton spectrum is too crowded to be of any use. The perennial problem of the solvent peak is side-stepped entirely since there is no transfer of information in the absence of scalar coupling.

A JEOL spectrometer with a 40 MHz phosphorus probe could be convinced to provide the appropriate proton pulses through the 100 MHz decoupler coil. With the help of Nicolet's 1180 software the signals obtained from a sample of 2' guanosine monophosphate were swiftly transformed into the familiar absolute value mode display shown below on the left. Less pretty, but more informative, are the phase sensitive spectra shown below on the right. The traces (b) and (c) are parallel to the F_1 proton axis at the frequencies of the phosphorus doublet resonances.





The figure below on the left illustrates how the two-dimensional spectrum can be "synthesized" on theoretical grounds. The ordinary 100 MHz proton spectrum (top) can be split into two subspectra P_{α} and P_{β} (one for each polarization of the phosphorus spin). The difference of the two subspectra agrees with the experimental two-dimensional spectrum (see (a) and (d) on the previous page).



The multiplet pattern is quite sensitive to variations of $J_1'_2'$ and $J_2'_3'$. The spectra in the figure above on the right were calculated for two typical "rigid nucleotide" conformations of the ribose. The solution state spectrum arises from a rapid averaging of the ribose between several different conformations.

This technique could be used to study the conformation of a phosphate containing substrate bound to an enzyme. Such information is not normally available since the proton signals of the enzyme obscure those of the substrate. Our spies, however, conveniently ignore the enzyme while dutifully reporting conformational information about the substrate.

1. A. A. Maudsley and R. R. Ernst, Chem. Phys. Lett., <u>50</u>, 368 (1977).

2. G. Bodenhausen and R. Freeman, J. Mag. Res., 28, 471 (1977).

Yours.

Geoffey Belakerien

Geoffrey Bodenhausen Chemistry Department University of California, San Diego La Jolla, California 92093 Philip Bolton

Philip Bolton
Pharmaceutical Chemistry Department
University of California, San Francisco
San Francisco, California 92143

Please credit this letter to Tom James' account.



The University of Sydney

N.S.W. 2006
Department of Organic Chemistry

IN REPLY
PLEASE QUOTE:

TELEPHONE: 692 1122.

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

November 13, 1978

Dear Barry,

Van der Waals radii from oriented NMR spectra

We have recently published the results of a study of conformation of a number of biphenyl derivatives in nematic phase. This work has now been extended, especially by the analysis of the oriented spectrum of the fluoro derivative (Figure 1, X=F, Y=Br) and it is clear that a very significant relationship (Fig. 1) exists between the Bondi van der Waals radius of X and the dihedral angle Ø defined in the projection shown in Figure 2.

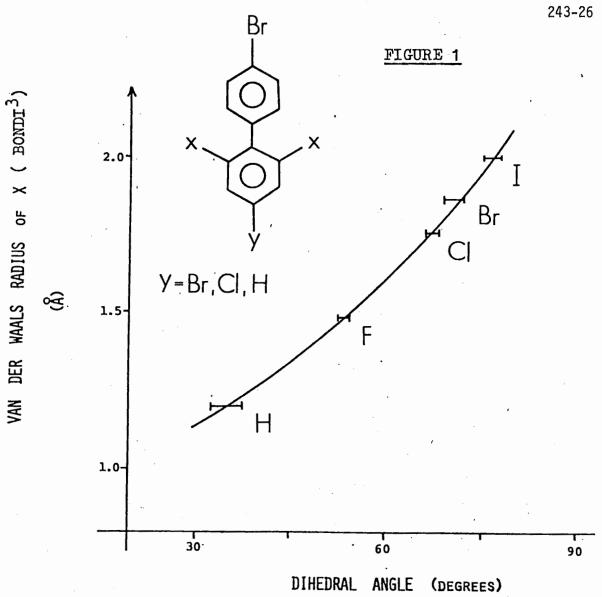
This prompted us to interpret the results in the reverse fashion: assuming that the conformation ¹ of the biphenyl is that shown in projection in Figure 2, ie. with hydrogen and X at their distance of closest approach, one can independently derive a set of apparent van der Waals radii (column 3 of Figure 2). It can be seen that they are comparable with the usually accepted values (column 4 of Figure 2) and, although agreement is not accurate, we consider the results significant because they are derived from an experimental procedure ² which is entirely independent of diffraction data. ³

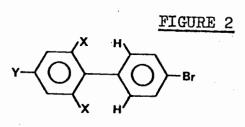
Yours sincerely

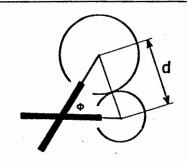
S. Sternhell

L.D. Field

- 1. Field, Sternhell and Tracey, JACS 99, 5249 (1977).
- Emsley and Lindon, "NMR Spectroscopy using liquid crystal solvents", Pergamon Press, 1975.
- 3. Bondi, "Physical Properties of Molecular Crystals, Liquids and Glasses", Wiley 1968







x	Φ (degrees)	Internuclear Distance (Å)	Apparent van der Waals Radius (Å)	van der Waals Radius (literature values) (Å)	φ (predicted)
H	33 ± 3	2.16 ± 0.06	1.08 ± 0.03	1.0 - 1.2	25 - 45
F.	49 ± 1.5	2.50 ± 0.04	1.42 ± 0.07	1.47	48 - 55
Cl	69 ± 2	3.12 ± 0.06	2.04 ± 0.09	1.75	56 - 63
Br	71 ± 2	3.23 ± 0.06	2.15 ± 0.09	1.85 - 2.01	59 - 65
I	78 ± 2.5	3.46 ± 0.07	2.38 ± 0.1		
			2.55	1.98 - 2.06	61 - 70



University of Strathclyde

Department of Pure and Applied Chemistry

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

21st November, 1978.

Professor B. L. Shapiro, Texas A and M University, College of Science, College Station, Texas, 77843. U.S.A.

Dear Barry,

Conformational Effects in Spectra of Ketone Peroxides

In connection with work on ketone peroxides being done in this department by Drs. D. C. Nonhebel and K. J. McCullough, we had occasion to look at the proton and carbon spectra of the compounds 1, 2, and 3, under varying temperature conditions. The results for the thermodynamics of the flipping process of the peroxide ring are shown in the table and are in line with literature values for similar compounds.

Two interesting phenomena were observed in the course of this work. Firstly, the di-p-tolyl ketone peroxide (2) showed at low temperature in the proton spectrum, the expected two methyl signals, together with two A₂B₂ patterns (effectively AB) for the aromatic protons. On warming up, the methyl signal collapses to a single line as expected. Moreover the aromatic peaks also collapsed to a single line (still broad at 80°) and not to the (at first sight) expected single A₂B₂ pattern. What this means is that in one of the two conformational positions of the benzene rings, the ortho protons are at lower field than the meta protons, while in the other site of the benzene ring the reverse is true (see structure).

Secondly in the case of the <u>trans</u> ethyl p-tolyl ketone peroxide which is thought to have the conformation shown (4) and would not be expected to show ring flipping, the methylene signal of the ethyl groups is a rather broad hump at room temperature. This signal sharpens up to the expected quartet both on raising the temperature to +80° or on cooling to -30°. The remaining signals are unchanged in appearance and show only small changes in chemical shift throughout this temperature range. Some sort of rotation process involving the ethyl groups must be present but I can think of no simple explanation. We would welcome any ideas from readers.

Yours sincerely.

Patra Real

Ring Flipping in Ketone Peroxides

	R ¹	R²	Ea	ΔG	ΔН	ΔS	Resonance used	тс
1.	-CH ₂ Ph	-CH ₂ Ph	9.5	14.0	8.95	-17.1	1H(CH2)	278
2	-C ₆ H ₄ Me(p)	-C ₆ H ₄ Me(p)	10.8	15.8	10.2	-18.1	1 H (CH3)	313
3	-(CH ₂) 5-	8.6	14.2	8.05	-21,1	¹³ C(aC)	290

Units: E_a , ΔG , ΔH , $kcal.mol^{-1}$; ΔS , $cal.mol^{-1}K^{-1}$; T_c ; K.

$$R''$$
 R''
 R''
 R''

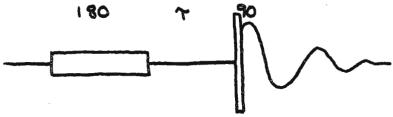
Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Title: Selective T₁ Inversion Recovery

Dear Barry:

During one of our recent development endeavors we have added a new ^IH experiment to our arsenal of capabilities. The response by other visiting scientists to use this experiment has been good and so I thought that other potential users should be made aware of this capability.

The new experiment is a variation of the standard T_1 inversion recovery scheme where the 180° pulse is a long weak pulse for selective inversion, <u>i.e.</u>,



The amount of power for the 180° pulse is variable continuously from 0-3 watts. Typical 180° pulses are 22 m sec. and the pulse power is confined to a region within \pm 30 Hz of the carrier. The experiment is performed routinely without any hardware adjustments by calling up the experiment from the data system.

We have included an example of the experiment to demonstrate its performance. The resonance irradiated is $^{1}\mathrm{H}_{3}\mathrm{C}$ of Blenoxane (12.5 mM in D $_{2}\mathrm{O}$) in the dimethyl sulfonium moiety.

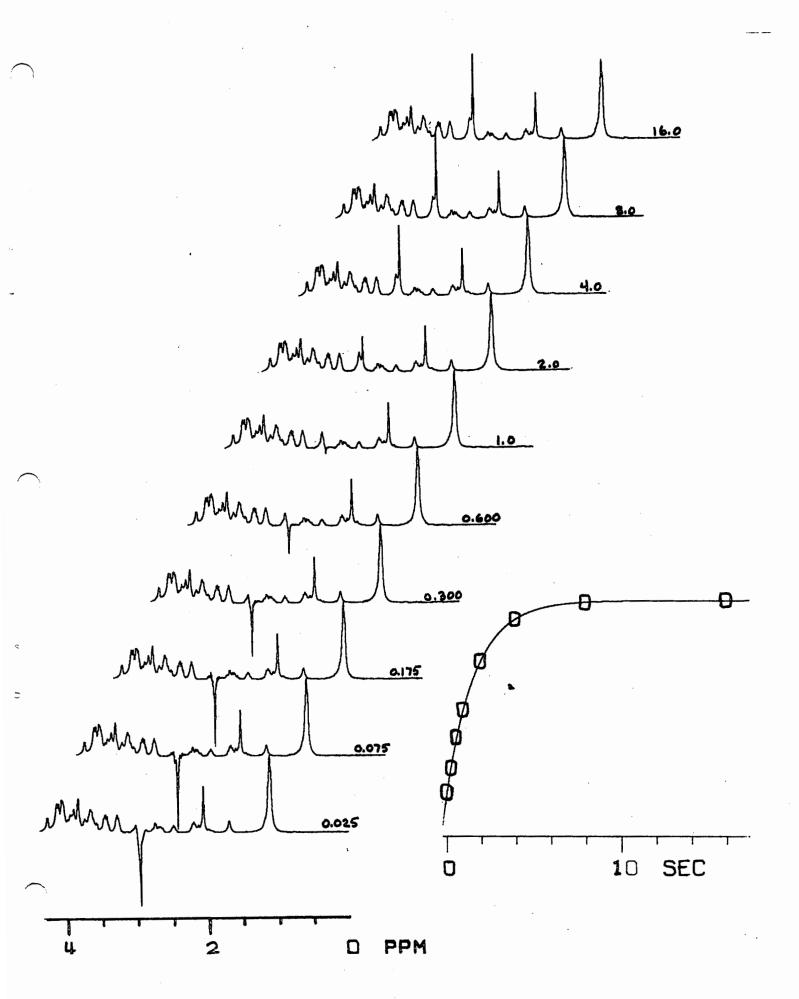
This experiment as well as a variety of other experiments involving combinations of low power and high power pulses are available to users. Interested users should contact Jerry Dallas for details (317-749-2438). We are currently considering the extension of this capability to selective simultaneous excitation of more than one resonance.

Yours truly,

Jerry 1. Dallas Operations Manager

JD:1n





THE INSTITUTE FOR CANCER RESEARCH

7701 BURHOLME AVENUE

FOX CHASE-PHILADELPHIA, PENNSYLVANIA 10111
(215) 342-1000-CABLE ADDRESS: CANSEARCH
November 6, 1978

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

Title: DIPOLAR CORRELATION TIMES FOR DETERMINATION OF Mn²⁺-SUBSTRATE DISTANCES ON ENZYMES

Dear Barry:

An important parameter needed for determining metal-substrate distances and metal-water coordination numbers on enzymes is the correlation time (τ_c) .

For paramagnetic ions such as Co $^{2+}$ with short electron-spin relaxation times ($^{\tau}_{S}$) the dipolar correlation time ($^{\tau}_{C}$) is dominated by $^{\tau}_{S}$. This permits an estimation of $^{\tau}_{C}$ for calculating metal-substrate distances from the frequency dependence of the longitudinal relaxation time ($^{\tau}_{Lp}$) of water protons in the same complex. For macromolecular complexes of Mn²⁺ the similarity of $^{\tau}_{C}$ values determined from $^{\tau}_{Lp}$ of water protons and of substrate nuclei ($^{1}_{H}$, $^{13}_{C}$, $^{31}_{P}$) at magnetic fields ranging from 2 - 52 K gauss (Table) indicates this to be a reasonable approximation as well. Hence a common mechanism ($^{\tau}_{S}$) may modulate all Mn²⁺-nuclear dipolar interactions in macromolecular complexes. A 2-fold uncertainty in $^{\tau}_{C}$ yields a 2-fold uncertainty in the number of water ligands but only a 12% uncertainty in the calculated Mn²⁺-substrate distances.

Mn ²⁺ -Complex	τ _c (H ₂ 0)(nsec)	τ _C (Substrate)(nsec)
Pyruvate Kinase-Mn ²⁺ -Pyruvate-Pi	5.5 + 1.0	$3.5 \pm 1.5 {}^{(13)}_{(1H)}, 3.2 \pm 1.0 {}^{(13)}_{(1H)}, 4.5 \pm 1.0 {}^{(13)}_{(1H)}$
Pyruvate Carboxylase-Mn ²⁺ -Pyruvate	6.5 + 2.0	$3.2 + 1.0 (^{1}_{1}H), 4.5 + 1.0 (^{13}C)$
Phosphoglucomutase-Mn ²⁺ -CH ₃ PO ₃	3.6 + 1.0	$3.5 + 1.0 (^{1}_{7}\text{H})$
Xylose Isomerase-Mn ²⁺ -Xylose ³	0.35 ± 0.15	$0.4 + 0.2 (\frac{1}{1}H)$
RNA Polyr rase-Mn ²⁺ -ApU	2.9 + 1.0	$1.8 + 1.2 (^{1}_{4}H)$
Fnolase-Mn ²⁺ -CH PEP	0.8 ± 0.2	$2.1 \pm 1.7 (_{1}^{\perp}H)$
Carbonic Anhydrase-Mn ²⁺ -pNO ₂ phenol	3.8 + 0.4	$5.5 + 0.6 (^{\perp}H)$
Aldolase-Mn ²⁺ -Acetol-P	2.1 ± 0.5	$2.0 \pm 0.6 (^{31}P), 0.9 \pm 0.5 (^{1}H)$

Sincerely yours,

Albert S Mildyan

Gary Smith

Rai K. Gupta

A hot performer at a cool 4.2°K

Varian introduces: The XL-200 superconducting FT NMR spectrometer

In a cost- and resource-conscious world, the new XL-200 with 47-kG superconducting magnet makes a lot of sense. To begin with, its high-field performance and advanced design come in a truly affordable package. And economy characterizes the XL-200 spectrometer in other ways, too—such as the low-loss dewar unit, which lets the system operate over three months on only 25 liters of liquid helium!

The basic instrument is designed for ¹H (200 MHz) and ¹³C (50.3 MHz) observation, but it will accommodate a host of other nuclei with the optional 20-80 MHz broadband accessory.

The XL-200's data management system tops all conventional concepts of versatility and convenience. There are two processing units working in tandem—one 32 bits wide and very fast for data acquisition, the other programmed in a high-level language and extremely flexible for data manipulation. Both operate continuously and, together with the XL-200's full complement of built-in I/O devices, offer you unique multi-tasking capability and high sample throughput.

And that's only the beginning of a long list of features which could read like your own NMR wishlist:

- 47-kG Nb-Ti superconducting magnet with 50-mm bore
- 25 liters liquid He dewar capacity; 3-month refill interval
- 35 liters liquid N₂ dewar capacity; 14-day refill

interval (45 days with optional refrigerator)

- 5- and 10-mm samples standard; other sample sizes optional
- Broadband probes covering 20-80 MHz and 188-212 MHz ranges
- Flexible mix/match RF system with fixed-frequency sources such as ¹H, ¹³C, ¹⁹F, and ³¹P
- Compatible with RF synthesizer for broadband multinuclear operation
- 50-kHz spectral widths with quadrature phase detection
- Automatic ²H internal field/frequency stabilization with exclusive AutoLockTM circuit
- ¹H homo/heteronuclear decoupler for a wide variety of gated modes
- Programmable 32K CPU for data processing and multitasking
- Independent 32-bit parallel processor with dedicated random-access memory for spectrometer control and data acquisition
- Built-in I/O devices include solid-state keyboard;
 5M-word moving-head disk with dual platter (one removable); high resolution raster scan storage/display oscilloscope; 32-column line printer; 500 x 240 mm

oscilloscope; 32-column line printer; 500 x 240 mm X-Y recorder.

If you would like the balance of the features to compare with your wishlist, write Varian Associates, Inc., Box D-070,611 Hansen Way, Palo Alto, CA 94303.

Varian Sales Offices

CALIFORNIA

9901 Paramount Boulevard Downey, CA 90240 Phone: (213) 927-3415

375 Distel Circle Los Altos, CA 94022 Phone: (415) 968-8141

COLORADO

4665 Kipling, Suite 1 Wheatridge, CO 80033 Phone: (303) 425-0413

GEORGIA

6650 Powers Ferry Road Suite 100 Atlanta, GA 30339

Phone: (404) 955-1392

ILLINOIS

205 W. Touhy Avenue Park Ridge, IL 60068 Phone: (312) 825-7772

KENTUCKY

Executive Park, Suite 110 Louisville, KY 40207 Phone: (502) 897-0171

MARYLAND

4701 Lydell Drive Cheverly, MD 20781 Phone: (301) 772-3683

MASSACHUSETTS

400 Totten Pond Road Waltham, MA 02154 Phone: (617) 890-8430

NEW JERSEY

25 Hanover Road Florham Park, NJ 07932 Phone: (201) 822-3700

NEW YORK

6489 Ridings Road Syracuse, NY 13206 Phone: (315) 437-6464

OHIO

25000 Euclid Avenue Euclid, OH 44117 Phone: (216) 261-2115

TEXAS

Plaza Southwest 5750 Bintliff Drive, Suite 202 Houston, TX 77036 Phone: (713) 783-1800

WASHINGTON

300 120th Avenue Bldg. 2, Suite 230 Bellevue, WA 98005 Phone: (206) 454-2910



Instrument Division sales offices and representatives are located in: Algeria, Argentina, Australia, Austria, Benelux, Brazil, Canada, Chile, China, Colombia, Costa Rica, Denmark, Eire, Finland, France, Germany, Great Britain, Greece, Holland, Hong Kong, Iceland, India, Iran, Israel, Italy, Japan, Korea, Lebanon, Malaysia, Mexico, Morocco, New Zealand, Norway, Pakistan, Peru, Philippines, Puerto Rico, Portugal, Scandinavia, South Africa, Spain, Sweden, Switzerland, Thailand, Turkey, United States, Venezuela.



UNIVERSITY OF UMEA
Department of Organic Chemistry

1978-11-09

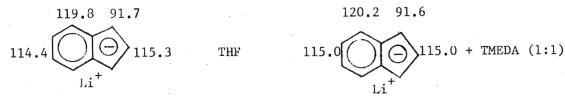
Professor B.L. Shapiro Department of Chemistry Texas A & M University College Station, Texas 77843 U.S.A.

Dear Barry,

Title: TMEDA as a Complexation Agent; Steric Hindrance to Cation Solvation

Tetramethylethylenediamine (TMEDA) is a solvent known for its capability to disaggregate alkali carbanion systems. This behaviour is explained by an effective coordination to the alkali cation. However, this coordinating ability does not nessecarily parallel the solvating ability as could be seen from the following, very preliminary ¹³C NMR study:

120.6 91.8
116.4
$$\bigcirc$$
 114.5 DEE 115.7 \bigcirc 114.8 + TMEDA (1:1)



Using the indene system we have shown that a change of solvent from diethylether (DEE) to tetrahydrofuran (THF) causes a change of the ion pair equilibrium to solvent-separated ion pairs and the accompanying increase of the anion-cation distance induces a diminished m-polarization to the fivemembered ring. After addition of TMEDA to the samples we noted a low-field shift of the TMEDA methyl groups, indicating that TMEDA substitutes DEE and THF in the cation solvation shell. A decreased anion π -polarization due to the spread of the positive charge is thus expected in both cases. As could be seen this expectation was just met in the DEE case. In THF, a low-field shift was observed for the remote C,5,6 positions. Obviously, the increased spread of the cationic charge resulted in a change of the equilibrium toward contact ion pairs, thus decreasing the anion-cation distance. This is in analogy with the equilibrium change induced when we changes the size of the cation radius (Na+, K+). The bulky TMEDA agent also efficiently prevents THF in acting as a good solvating medium.

Best regards

tuf
Ulf Edlund

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO



SANTA BARBARA • SANTA CRUZ

DEPARTMENT OF CHEMISTRY, B-014 LA JOLLA, CALIFORNIA 92093

27 November 1978

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

Two-Dimensional Spin Echoes from Liquid Crystalline Samples

Dear Barry,

The infamous pink notice arrived roughly simultaneously in our laboratory with an Oxford Instruments widebore (73 mm) 58 kgauss high resolution superconducting magnet. As of this writing we have obtained deuterium spectra using a homebuilt 10 mm probe with a sideways (nonspinning) solenoid single coil, and have achieved the expected ~ 8.5 fold increase in sensitivity over operation at 14.1 kgauss. However, there is nothing meaty enough here to serve as a subscription renewal. Instead, we offer the two-dimensional Carr-Purcell spin echo experiemnt shown in Figure 1.

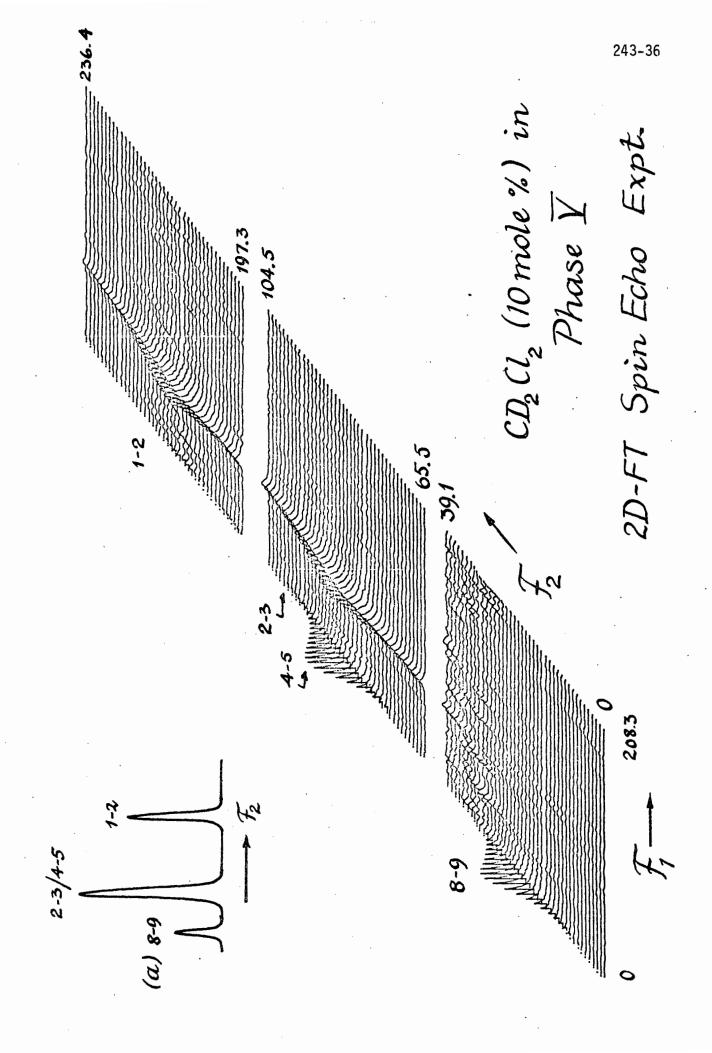
The sample consists of ~ 10 mole % dichloromethane-d₂ in Merck Phase V at 30.0° C. There is a quadrupole splitting of ~ 14 kHz at this temperature, and well resolved fine structure due to ²H-²H dipolar interactions. The pulse sequence 90-\frac{1}{2}t1-180-\frac{1}{2}t1AC (AC means acquire data) was applied selectively to the half spectrum shown in the inset. The echo decay is modulated because the semiselective refocussing pulse mixes lines 12 and 23. Thus, a single FT (with respect to acquisition time t2) yields an unmodulated decay (as a function of t1) for line 89 but both 23/45 and 1-2 are amplitude modulated. The second Fourier transform (with respect to t_1) is needed to analyze the decay rates of the modulated components. Linewidths in the F1 domain provide T2 values, without dephasing due to static field inhomogeneity or to a thermally induced distribution of quadrupolar splittings.

The alert reader will note that Figure 1 shows a magnitude spectrum, with phase information suppressed. In addition, the lineshapes of peaks at F1=0 are distorted because of the one sided Fourier transform algorithm. This can be conveniently avoided by introducing a progressive, frequency independent phase shift into successive spectra in the (t₁,F₂) domain, thereby moving lines 89 and 45 away from the edge of the plot.

We are presently engaged in using the results of this experiment, together with measurements of double quantum decay rates and various kinds of T1 measurements, to determine all six spectral densities which characterize quadrupolar relaxation of a D2 spin system in an ordered medium.

Sincerely, Gille

R.L. Vold, R.R. Vold and G. Bodenhausen





U.S. Department of Energy Laramie Energy Technology Center P.O. Box 3395, University Station Laramie, Wyoming 82071

November 27, 1978

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

Dear Barry:

13C NMR Identification of Olefins in Shale Oil 21st Annual Rocky Mountain Conference

Thank you for the reminder. I didn't realize it is that time of year again.

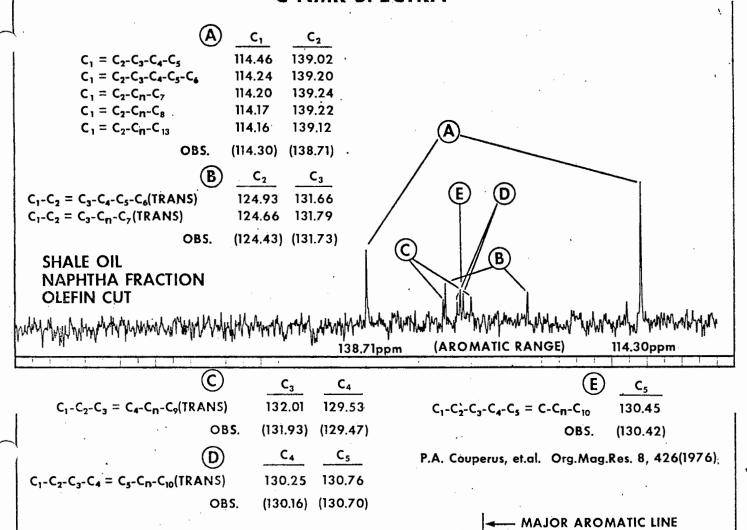
One of the projects at the Center is the identification of olefins in shale oil. Both mass spectrometry and $^{13}\mathrm{C}$ NMR are being used extensively in this regard. Since shale oil can have an aromaticity value up to 30 percent, the olefinic carbons are masked by the aromatic carbons in a C spectrum. Using a suitable separation procedure, the olefinic carbons can be separated from the aromatic carbons. The attached figure shows the olefinic cut from both a shale oil naphtha fraction and a light distillate fraction. It is trivial to distinguish the location of the double bond. The observed chemical shifts values were compared to the values obtained by P.A. Couperus, et al. for a series of olefins. Though not the best spectrum, the naphtha fraction shows five different types of olefinic carbons. The hydrocarbon chain length has not been ascertained from the aliphatic carbon region of the spectrum and the spectrometer was not optimized for quantitative work in this case. Mass spectral data give the relative amounts of the mono and di olefins, chain length but not the position of the double bond. According to mass spectral analysis, the sample contains only monoalkenes and no dialkenes. The monoalkenes are divided nearly equally between normal and branched. Chain lengths range from C_8 to C_{12} with C_{10} being most dominant. The lower spectrum in the figure is the olefinic cut of the light distillate fraction. The major aromatic line is in reference to the main aromatic resonance which would result from poor separation of the olefin and aromatic cuts. Further details of this work and related studies will be published in the near future.

1. P. A. Couperus, et. al., Org. Mag. Res. 8, 426 (1976).

Sincerely,

Daniel A. Netzel

"C NMR SPECTRA



LIGHT DISTILLATE FRACTION

OLEFIN CUT

AND THE PROPERTY OF THE

21st Annual Rocky Mountain Conference (July 30-August 1, 1979, Denver CO)

SHALE OIL

Again, as last year, the Rocky Mountain Conference will have symposia on NMR of Macromolecules (solid state NMR, polymers, biopolymers, fossil fuels) and EPR. Those who are interested are invited to submit intent of oral or poster presentation to Dr. Gareth Eaton, Dept. of Chemistry, University of Denver, Denver, CO., 80208 for EPR papers and to me for NMR papers.

FACHBEREICH CHEMIE DER PHILIPPS-UNIVERSITÄT

Dr.Stefan Berger

Fachbereich Chemie - Lahnberge - D-3550 Marburg 1

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

Lahnberge Postfach 1929 D-3550 MARBURG 1

Telefon (0 64 21) 28 ... 5.5-2Q-

Telex: 482372

den 1:11.1978

¹³c¹³C Spin Coupling Constants Additive Or NOT ?

The current interest in vicinal ¹³C¹³C spin coupling constants in the literature prompts me to communicate the following result. We have measured the bridgehead bridgehead ¹³C¹³C spin coupling constant in 4-methyl-bicyclo(2.2.2)-octane-1-carboxylic acid ethyl ester labelled at bridgehead 4 with ¹³C:

By simply adding the spin coupling constants transmitted via identical pathways¹⁾ one would have expected 17.4 Hz²⁾. That the experimental value lies significantly below that expected from theory cannot be due to substitution in the sense of Wray³⁾ or Barfield⁴⁾. Since "multiple impinging rear lobes" are now questionable^{3,4)} we interpret this effect as NMR evidence for through space interaction between the bridgehead carbon atoms in the bicyclo(2.2.2) system as shown by ESR by Schleyer⁵⁾ and Kawamura⁶⁾.

Sincerely yours

Selan bergo

- 1) J.L.Marshall, TAMU <u>235</u>,33
- 2) M.Barfield, I.Burfitt and D.Doddrell, J.Amer. Chem. Soc. 97,2631 (1975)
- 3) V.Wray, ibid. 100,768 (1978)
- 4) M.Barfield, TAMU <u>239</u>,27
- 5) P.J.Krusic,T.A.Rettig and P.v.R.Schleyer,J.Amer.Chem.Soc. 94,995 (1972)
- 6) T.Kawamura, M.Matsunaga and T.Yonezawa, ibid. 100,92 (1978)

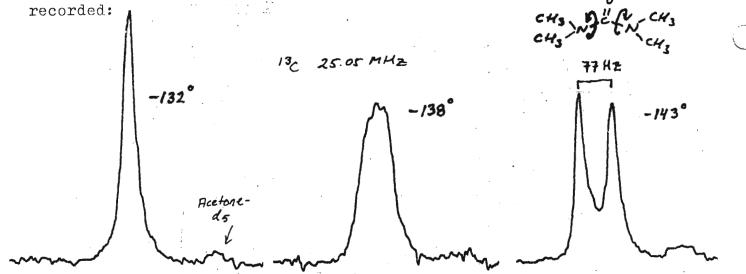
Cont'd. from p. 243-41

- 1) J. Phys. Chem., 75 (1971) 1901. 2) Acta Chem. Scand., 25 (1971) 2635
- 3) Tetrahedron, <u>91</u> (1971) 4583 4) <u>Ibid.</u>, <u>93</u> (1973) 2269
- 5) Thesis, Lund 1974 6) J. Magn. Resonance, <u>31</u> (1978) 55.

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

Dear Professor Shapiro,

My doctoral research concerned hindered internal rotation in ureas and various aspects of their adduct formation with metal halides, especially SbCl₅ (1-5 and references therein). A problem which was unresolved at the time was the height of the barrier to internal rotation in tetramethylurea. Reaxamining the problem with the aid of ^{13}C $T_{1\rho}-$ measurements (6) led to an estimated ^{13}C &v of c:a 95 Hz at 25 MHz and a ΔG^{\neq} of 6.1 $^{\pm}$ 0.1 kcal/mole, corresponding to a ^{13}C T_{c} of \approx -150 $^{\circ}\text{C}$. Since our low-temperature setup has lately been improved, it was of course interesting to confirm this through bandshape studies. In a 10 % solution in 4:1 CHFCl₂/Acetone-d₆ the following ^{13}C spectra were



They correspond to a ΔG^{\neq} of \approx 6.3 kcal/mole at - 138 °C. Although there is a slight difference between the T_{1p} - and bandshape-based data, the agreement is quite satisfactory, considering difficulties in accurately measuring differences between $1/T_{1p}$ and $1/T_{1}$ when $1/T_{1}$ is large (6), as in the present case. - Interestingly, the increase in barrier height upon SbCl₅ adduct formation (\approx 5 kcal/mole) is almost the same for a trisubstituted urea (2,3) as for the tetrasubstituted urea (3,6), suggesting that steric interactions between SbCl₅ and the methyls are not severe.

Yours sincerely,
Pelu Shu

Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

.212) 570-5666

November 15, 1978

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

Dear Dr. Shapiro:

Beginning 1 January 1979 a postdoctoral position will be available in my laboratory. Our research focusses on applications of naturalabundance 15N NMR spectroscopy to organic and bioorganic structure elucidation. Areas of current interest include characterization of alkaloids and other pharmacologically important materials; structure - chemical shift relationships in model compounds; and characterization of molecular electronic effects on chemical shifts of saturated and unsaturated nitrogen compounds. We are especially interested in exploring the utility of 15N NMR in establishing molecular geometries, particular the geometry of ring fusion at nitrogen.

NMR spectra are determined with a JEOL PFT-100 spectrometer which is optimized for $^{15}\mathrm{N}$ operation. In addition, a proposal is pending before NSF for a superconducting system which, if funded, is expected to be in operation by next fall.

A solid background in organic chemistry, some experience with FT NMR, and familiarity with principles of NMR chemical shifts are important attributes expected of interested individuals. The salar which is derived from grant funds, is \$10,800 - \$12,000 per year depending on level of experience, and liberal fringe benefits are provided. Interested applicants should send a curriculum vitae, publications list, and two-three letters of recommendation to me at the above address. Hunter College is an affirmative action-equal opportunity employer.

Sincerely yours,

Robert L. Lichter Associate Professor

Robert Lichter

Chairman

RLL: jd

GRUPPO LEPETIT 500

anno di fondazione 1868
sede in Milano : capitale sociale L. 29.363.000.000
trib Milano N. 22049 : C.C.I.A. Milano 95669
Research Laboratories
Via Durando, 38
20158 Milano, Italy

20124 Milano . Via R. Lepetit, 8 telefoni: 2777 . interurb.: 279735.6.7 telegrammi: Lepetit . Milano telex. 32054 Lepetit . Milano conto corrente postale N. 3 12064 casella postale 3698 . 20100 Milano

REGISTERED
SPECIAL DELIVERY

destinatario:

Professor B.L. SHAPIRO Department of Chemistry Texas A&M University College Station TEXAS 77843 - U.S.A.

nostro riterimento. Department of Physical Chemistry

Milano, November 24,1978

Title: IONIZATION OF 3 AND 4-SUBSTITUTED RIFAMYCINS BY 1H NMR SPECTROSCOPY

Dear Professor Shapiro,

We have been investigating the conformation and physical behavior of some rifamycins in non polar and polar media using PFT 1 H NMR at 270 MHz and the results of this study will appear in the literature $^{(1)}$. Here we want to anticipate an interesting result obtained on rifampicin (1) and 4-N-dimethylamino-4-deoxy rifamycin SV (2) whose structures are reported in the figure.

The ionization constants pKa_1 and pKa_2 in water solution of 1 are 1.7 and 7.9 and are attributed to 0H at C-8 and N-4 of piperazine, respectively the values for 2 are 0 and 10.8 and are attributable to 0H at C-8 and N at C-4. Both 1 and 2 exist in water solution as the zwitterions.

In the table are reported the chemical shifts of 1 and 2 in CDCl $_3$ and D $_2$ 0. Comparison of the data in the two solvents shows a similar trend for most of the protons and will be rationalized ⁽¹⁾. However, it is noteworthy in 1 the paramagnetic shifts of N-CH $_3$ and CH $_2$ -3',5' by passing from CDCl $_3$ to D $_2$ 0. This does not occur in 2 for the two non equivalent methyls of N(CH $_3$) $_2$. These data show that in D $_2$ 0 both 1 and 2 exist as internal salts, whereas in CDCl $_3$ 2 but not 1 exists as internal salt.

These conclusions are in agreement with what found by infrared $^{(3)}$ and can be rationalized by the higher ΔpKa value between the two functions in 2 than in 1.

Yours sincerely,

E. Martinelli P. Gironi

References

1) E.Martinelli, P.Gironi, G.G.Gallo, to be published.

2) C.R.Pasqualucci, A.Vigevani, P.Radaelli and N.Maggi, Farmaco, Ed.Prat., 24, 46 (1969).

3) P.Ferrari and G.G.Gallo, Farmaco Ed.Sci., 30, 676 (1975).

Table - 1 H NMR data of rifamp cin (1) and 4-N-dimethylamino-4-deoxy rifamycin SV (2) at 270 MHz in CDCl $_{3}$ and D $_{2}$ 0 at pD = 6 , (conc. 10^{-3} M).

PROTON	1		2			1		2	
	CDCI3	D ₂ 0	CDC13	D ₂ 0	PROTON	CDCI3	D ₂ 0	CDC I 3	D ₂ O
NH	12.00	_	8.40	_	H-26	1.37	1.21	1.4	n d
OH-I	n.d.	· .	n.d.	_	H-27	3.48	3.55	3.38	n.d. 3.51
OH-4	n.d.	-	n.d.	-	H-28	5.10	5.14	5.25	5.35
0н-8	n.d.	-	n.d.	-	H-29	6.20	6.37	6:18	6.33
H-13	1.80	1.81	1.83	1.86	H-30	2.07	2.04	2.08	2.04
H-14	2.22	2.10	2.13	2.07	H-31	0.88	0.93	0.85	0.95
H-17	6.42	6.50	6.23	6.4	H-32	1.02	0.96	1.05	0.95
н-18	6.60	6.98	6.43	6.4	H-33	0.60	0.61	0.57	0.45
H-19	5.92	6.21	6.02	6.08	H-34	-0.30	-0.24	-0.08	-0.04
H- 20	2.33	2.40	2.4	2.3	H-36	2.05	2.04	2.00	2.07
H-21	3.78	3.83	3.70	3.78	H-37	3.05	3.05	3.10	3.09
OH-21	3.43	-	3.66	-	CH=N	8.28	7.90	= .	=
H-22	1.72	1.88	1.75	1.9	H-2;6'	3.1	3.2	=	=
H-23	3.03	3.12	3.03	3.11	H-3;5'	2.5	3.2	2	=
OH-23	3.60	- '	3.66	-	NCH ₃	2.33	2.92	· =	=
H-24	1.55	1.38	1.75	1.9	H-3	=	=	8.80	8.44
H-25	4.93	5.09	4.92	5.02	N(CH ₃) ₂	=	=	3.07;3.1	9 3.28;3.

n.d. = not determined.

 $(\)$

6 . .



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE NATIONAL INSTITUTES OF HEALTH BETHESDA, MARYLAND 20014

Building 2, Room B2-02

November 29, 1978

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

Dear Professor Shapiro:

As the owners of a Varian HR-220 superconducting solenoid, we have been concerned with the helium boil-off rate and the annual cost of keeping the system running. We have talked to representatives of Oxford Instruments and Nicolet/Cryogenics Associates about the possibility of building a new dewar for the Varian magnet and changing the leads and protective circuits to a more modern design. The objective is to reach a boil-off rate such that no more than one monthly fill of 25 1. of helium would be required, in addition to a nitrogen fill every two weeks. The cost of such a modification is estimated to be between 10 and 14 k\$.

The purpose of this letter is to inform all owners of Varian HR-220 and HR-300 magnets of our discussions and to ascertain their interest in such a conversion. By combining some of these conversions we may be able to get a better deal on dewars and spread the initial engineering cost over several systems.

We would appreciate hearing from interested individuals, with the following information:

- 1. Type of system
- 2. Serial Number
- 3. Present He consumption
- 4. Present N consumption
- 5. Degree of interest in such a conversion
- 6. At what point in time
- 7. Comments

We are interested in making arrangements for conversion of our own magnet soon, so we would appreciate prompt replies by mail or phone (301-496-1024) to Rolf Tschudin.

Sincerely.

Edwin D. Becker, Rolf Tschudin Laboratory of Chemical Physics National Institute of Arthritis, Metabolism and Digestive Diseases



DIVISIONE PETROLCHIMICA CENTRO RICERCHE BOLLATE VIA S. PIETRO 50 20021 BOLLATE (MILANO)

CASELLA POSTALE 80 TELEFONO (02) 3501201/2/3/4/5 TELEX 31679 MONTEDIS

DATA 3.11.78

VS. RIF.

Prof. B.L. SHAPIRO
Texas A. & M. University
College of Science
College Station, TEXAS 77843

NS. RIF.ES/nd

Object: Quantitative F.T. Hnmr determination of end groups in polycarbonates from Bisphenol A (BPA)

Dear Prof. Shapiro,

Polycarbonates are usually prepared by interfacial polycondensation. The process is carried out in two stages: 1. the phosgenation stage with production of oligomers; 2. the polycondensation stage. The chemical groups usually present as chain ends are the following ones¹⁾:

1, - 0C00
$$\bigcirc$$
 $\stackrel{\underline{\underline{H}}}{\bigcirc}$ OH; II) - 0C00 \bigcirc \bigcirc \bigcirc 0C0C1

III) - 0C00
$$\leftarrow$$
 0C00 \leftarrow 0C00 \leftarrow R = H R = C \leftarrow CH₃)₃

The hydroxyl group (I) is due to the unreacted phenoxide or to hydrolysis of chloroformates; the chloroformate group (II) is due to the reaction of phenoxide with phosgene and the last one (III) is due to the reaction of the chain regulator (usually phenol or t.butylphenol). For all these groups ($R \equiv C-(CH_3)_3$) we have performed nmr quantitative methods which have good sensibility and reliability. In fact the resonance position of t.butyl group is slightly different (0.35 ppm upfield, with CDCl₃ as solvent) from that one of the methyls of BPA ($\delta = 1.67$ ppm).

FOGLIO N.

The underlined protons of structure I give absorbance in the region 6.6.8 ppm as high field part of a complex AB pattern, well separated from the broad complex band centered at 7.2 ppm of the aromatic protons of the chain. The quantitative determination of chloroformate end group is done indirectly taking into account the amount of the OH group before and after hydrolysis.

A very simple method of hydrolysis of the chloroformate has been defined, just using DMSO as a cosolvent with CDC1₃ It is well known²) that DMSO promotes nucleophilic reactions, particulary hydrolysis. We have used this catalytic ability of DMSO (in presence of water) in alternative to the conventional water solution hydrolysis catalized by amines, in order to achieve the quantitative UV determination of OH and OCOC1 groups.

On the other hand we have found that the well known reaction of ArCOCl group with DMSO can be advantageously used for the quantitative measure of the chloroformate group.

In fact, in absence of water, the arylchloroformates react exothermically in a few seconds, according to the following path:

The final result in both cases (with and without water) is the production of the OH group. The esteric linkages in the polymer chain are not affected. This reaction gives the possibility of a fast determination of phenolic and chloroformate groups on the same nmr sample, simply adding DMSO-d6. The quantitative results via nmr are favourably compared with the data obtained by indipendent measurements such as those by UV and by potentiometric titration of Cl after hydrolysis of the OCOC1 group. The sensivity of the nmr methods is quite good. One t.butyl phenyl and one OH group can be estimated over more than 700, 300 ripetitive BPA units, respectively. The OCOC1 group has a lower sensitivity as it is determined from the difference of two OH values. The nmr methods let us to obtain reliable determination of the amount of the different terminal groups in the two stages of the process. The values of number average molecular weight M determined by this way are more accurate than those obtained by other physical-chemical methods (osmometry and gel permeation chromatography). The \overline{M}_n values of a set of

FOGLIO N

experimental products compared with $\overline{\mathbf{M}}_{\mathbf{w}}$ data obtained from gel permeation chromatography measurements, give a ratio \vec{M}_w/\vec{M}_n in the range 1.5+1.7. This value is clearly lower than typical data found in literature³⁾ for polycarbonates $(\overline{M_W}/\overline{M_D} > 2)$.

Yours sincerely,

E. Santoro, F. Campadelli, F. Visani

References

- 1) Z. Dobkowski, Z. Wielgosz and B. Krajwski "Angew.Makr. Chemie" 39 (1974), 7.
- 2) S.W. Jacob, E.E. Rosenbaurn and D.C. Wood "Dimethylsulphoxide" Vol. 1 Marcel Dekker (N.Y.) 1971.
- 3) K.B. Abbas "ACS Polymer Preprint" Vol. 18 nº 2 (Aug. 1977) pag. 231.

HOWARD UNIVERSITY



DEPARTMENT OF CHEMISTRY

November 13, 1978

We have recently been funded for a Nicolet NT-200 NMR spectrometer at Howard. We will be replacing the HA-100 that we currently use with the new system. If anyone is interested in purchasing all or part of the HA-100 we are interested in any offers.

Sincerely yours,

Carlyle B. Storm

NT-150 A WIDE-BORE, FT-NMR SYSTEM FROM NICOLET





For routine NMR and state-of-the-art techniques such as:

- 31P experiments on living organs.
- Cross-polarization studies on solids.
- 13C studies of high molecular weight polymers.
- Two-dimensional FT-NMR.

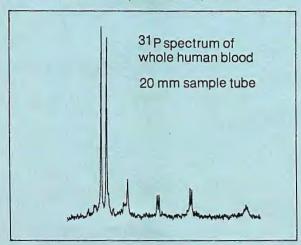
FEATURES INCLUDE:

- 3.5T superconducting magnet with 10 cm room-temperature bore.
- · Straight-through access to sample area.
- Quick-disconnect probes for rapid changeover.
- 5, 12 and 20 mm sample tubes as standard, 30 mm optional.
- Quadrature phase detection as standard.
- Computer-controlled audio filter from 100 Hz to 51,100 Hz in 100 Hz steps.
- Nicolet 1180 data system with simultaneous acquisition, processing and plotting.
- Digital plotter with plot lengths selectable from 1 cm to 900 cm.

OPTIONS INCLUDE:

• NT-150 MF: broad-band multi-nuclei observe for 4 to 60 MHz.

• NT-150 CP: optimized system for Waugh-Pines cross-polarization studies.



For more information or to discuss your applications, please telephone or write.



145 East Dana Street Mountain View, California 94041 Phone: 415/969-2076

While you're working in the foreground *... your FX is working in the background*

examples:

fourier transformation data massage basic programming T₁/T₁ calculation plot/print/CRT display spin simulation



* Foreground/Background system



235 Birchwood Ave., Cranford, NJ 07016 201-272-8820

The FX60Q, FX90Q & FX100 features:

\$

- (DQD) DIGITAL Quadrature Detection System
 Multi-Frequency TUNEABLE Probe observation
 Dual Frequency probes
 4-channel DIGITAL phase shifters (DPS)
 Comprehensive auto-stacking system
 Foreground/Background system
 Computer based pulse programmer with
 Multiple Pulse Sequence Generator
 CPU Expandable to 65K words (MOS)
 2-channel 12 bit AD/DA
 T₁p/spin locking system
 Disc storage systems

 - Disc storage systems
 Multi-Mode HOMO/HETERO decoupling capabilities
 Programmable Variable Temperature Unit
 Simplex Y/Curvature gradient controller