

Texas
A
M &
University
N - M - R
Newsletter

No. 186

March, 1974

R. R. Ernst Signal Intensities in Fourier Spectroscopy	1
E. W. Randall A European E.N.C., 1974; International Meeting St. Andrews, 1975	5
R. H. Contreras and D. G. de Kowalewski Additivity Scheme in NMR Chemical Shifts of Disubstituted Pyridines	6
I. D. Blackburne, A. R. Katritzky and Y. Takeuchi Conformational Equilibria in Piperidines	8
S. Aime Multinuclear Studies of Phosphorus-Containing Compounds	11
J. Happe and B. E. Holder ^{35}Cl Relaxation by Mn(II) Chelates	15
Y. Takeuchi and N. Dennis Long-Range ^{13}C -H Coupling Constants in 2-Cyanopyridine	16
N. H. Werstiuk and B. G. Sayer The Deuterium Detective	20
I. D. Robb and R. Sallis Application of Fourier Transform Techniques to Problems in Colloid Chemistry	22
H. S. Gutowsky The Use of Shift Reagents and the Frequency Dependence of the Coalescence Temperature in Two-Site Chemical Exchange Studies	25
B. L. Shapiro Postdoctoral Fellowship Available	27
G. C. Pappalardo PMR Spectral Parameters of Diphenyl Disulphide	28
U. Henriksson and L. Odberg ^{13}C -Relaxation in Micellar Solutions	29
S. A. Knight and W. Wheatley Further Utilisation of a PDP8-I Computer for NMR Interferogram Operations	32
T. Fujito, H. Higuchi and M. Imanari ^{13}C High Resolution Study in Solid Adamantane	34

(Cont'd on p. (i))

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

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.

SPECTROSCOPIC RESEARCHERS...

HERE ARE 6 GOOD REASONS WHY IT PAYS TO STANDARDIZE ON WILMAD!

- **WORLD'S LARGEST SINGLE SOURCE.** We are the world's largest single source for glassware, accessories, and supplies for spectroscopic research.
- **MOST COMPLETE LINE.** Our line of glassware, accessories, and consumable supplies for spectroscopy now includes everything you need for your investigations . . . except the spectrometer.
- **NO SACRIFICE IN QUALITY.** Our operations are based on a policy of never sacrificing quality in order to meet a competitive price. No investigator wants to jeopardize accuracy, uniformity, stability, and repeatability just to save a few pennies.
- **MOST SAMPLE TUBES.** We have produced more sample tubes for spectroscopy than any other supplier in the world.
- **STANDARD OF EXCELLENCE.** Wilmad accuracy and precision in sample tubes have become the reigning standard of excellence in the industry. (Even the equipment manufacturers use Wilmad NMR sample tubes.)
- **A DESERVED REPUTATION.** With almost 20 years of pioneering in glassware, accessories and supplies for spectroscopic research, we have earned a reputation for reliability which supersedes monetary value.

**WRITE TODAY FOR
FREE CATALOGS**

If you don't have our two Catalogs covering the WILMAD line of Glassware, Accessories, and Supplies for spectroscopic research (NMR, EPR, IR and MS), write or call today. Wilmad Glass Company, Inc., U.S. Route 40 and Oak Road, Buena, N.J. 08310, U.S.A. Phone: (609) 697-3000.



WILMAD

PIONEERS IN ACCESSORIES AND SUPPLIES FOR SPECTROSCOPY

C. H. DePuy Deuterium NMR Study of a Reaction Mechanism	38
C. J. V. Scanio Position Available - Spectroscopist	41
D. Doddrell and N. V. Riggs Swept Audio-Sideband ^{13}C -N.M.R. Spectroscopy; Some Dielectric-Constant Effects on the Response of C.W. and PFT Probes	42
M. I. Levenberg and R. S. Egan Genie Automatic Magnet Turner-Onner	44
H. Durr, H. Kober and B. Ruge ^{13}C -NMR-Spectra of [1.2]-Spirenes	46

Deadline Dates: No. 187: 1 April 1974
No. 188: 6 May 1974

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.

SPONSORS:

Abbott Laboratories
Bruker Scientific, Inc.
JEOL, Inc.
Dr. R. Kosfeld, Abt. Kernresonanz, Inst. f. Phys. Chemie, TH Aachen (Germany)
The Lilly Research Laboratories, Eli Lilly and Company
The Monsanto Company
Unilever Research (U.K.)
Union Carbide Corporation
Varian, Analytical Instrument Division

CONTRIBUTORS:

The British Petroleum Co., Ltd. (England)
Eastman Kodak Company
E. I. DuPont DeNemours & Co.
International Business Machines Corp.
Nicolet Instrument Corporation
The Perkin-Elmer Company
The Procter & Gamble Company, Miami Valley Laboratories
Shell Development Company

ADVERTISERS:

Bruker Scientific, Inc.	- see p. 19
Electronic Navigation Industries	- see p. 10
JEOL, U.S.A., Inc.	- see inside back cover
Nicolet Instrument Corporation	- see p. 24
Nuclear Magnetic Resonance, Ltd.	- see p. 4
Perkin-Elmer Company	- see p. 14
Varian Instrument Division	- see outside back cover
Wilmad Glass Co., Inc.	- see inside front cover



EIDGENÖSSISCHE
TECHNISCHE HOCHSCHULE ZÜRICH

Laboratorium
für Physikalische Chemie

8006 ZÜRICH, 4 February, 1974
Universitätstrasse 22
Telefon (01) 32 62 11

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

SIGNAL INTENSITIES IN FOURIER SPECTROSCOPY

Dear Barry,

After having promoted Fourier spectroscopy for many years, it is time now to think also about its possible disadvantages. I would like to discuss here one major drawback of Fourier spectroscopy when applied to systems in a nonequilibrium state.

Two kinds of nonequilibrium states may be distinguished:

1. Nonequilibrium states of the first kind: The state may be described by a set of population numbers but which deviate from a Boltzmann distribution. The transverse magnetization is zero and the density operator commutes with the Hamiltonian.
2. Nonequilibrium states of the second kind: The density operator contains offdiagonal elements and does not commute with the Hamiltonian. Transverse magnetization may exist.

This state can not be described by population numbers.

Nonequilibrium states of the first kind occur in the course of many experiments like in saturation-, Overhauser- and CIDNP-experiments, in double resonance and during relaxation time measurements. The following comments will be restricted to this kind of a state.

In a slow passage low power experiment, the observed signal intensity $L_{jk}^{(SP)}$ is just proportional to the difference of the population numbers $P_k - P_j$ of the connected energy levels:

$$L_{jk}^{(SP)} \propto (P_k - P_j) \cdot |F_{yjk}|^2 \quad (1)$$

In a single-pulse Fourier experiment with the flip angle α , on the other hand, the corresponding signal intensity is given by

$$L_{jk}^{(FT)} = 2\text{Re} \left\{ \sum_r (e^{-iF_r \alpha})_{jr} (e^{iF_r \alpha})_{rk} F_{yjk} P_r \right\} \quad (2)$$

This formula shows that, in general, each intensity $L_{jk}^{(FT)}$ depends in a complicated manner on all population numbers P_r of the complete spin system. It can be shown that for a system in internal equilibrium, Eq. (2) simplifies to Eq. (1). For a system described by a Boltzmann distribution, the relative signal intensities in a Fourier spectrum are independent of the flip angle and are equal to those of a slow passage experiment. On the other hand, for a nonequilibrium state, the intensities strongly depend on the flip angle used. Particularly for a 90° pulse, completely unexpected intensities may occur, whereas for a sufficiently small flip angle, where the system may be treated in its linear approximation, the same intensities are obtained as in a slow passage experiment.

An example of a computed CIDNP Fourier experiment on a hypothetical AB_2 -system is shown in the following figure which well demonstrates the mentioned problems and calls for particular care in the treatment of nonequilibrium states. The computation has been done by Dr. A. Höhener. A detailed account will be published shortly in the Journal of Magnetic Resonance.

Sincerely yours,

Richard

Richard R. Ernst

FLIP
ANGLE

90.0°

80.0°

70.0°

60.0°

50.0°

40.0°

30.0°

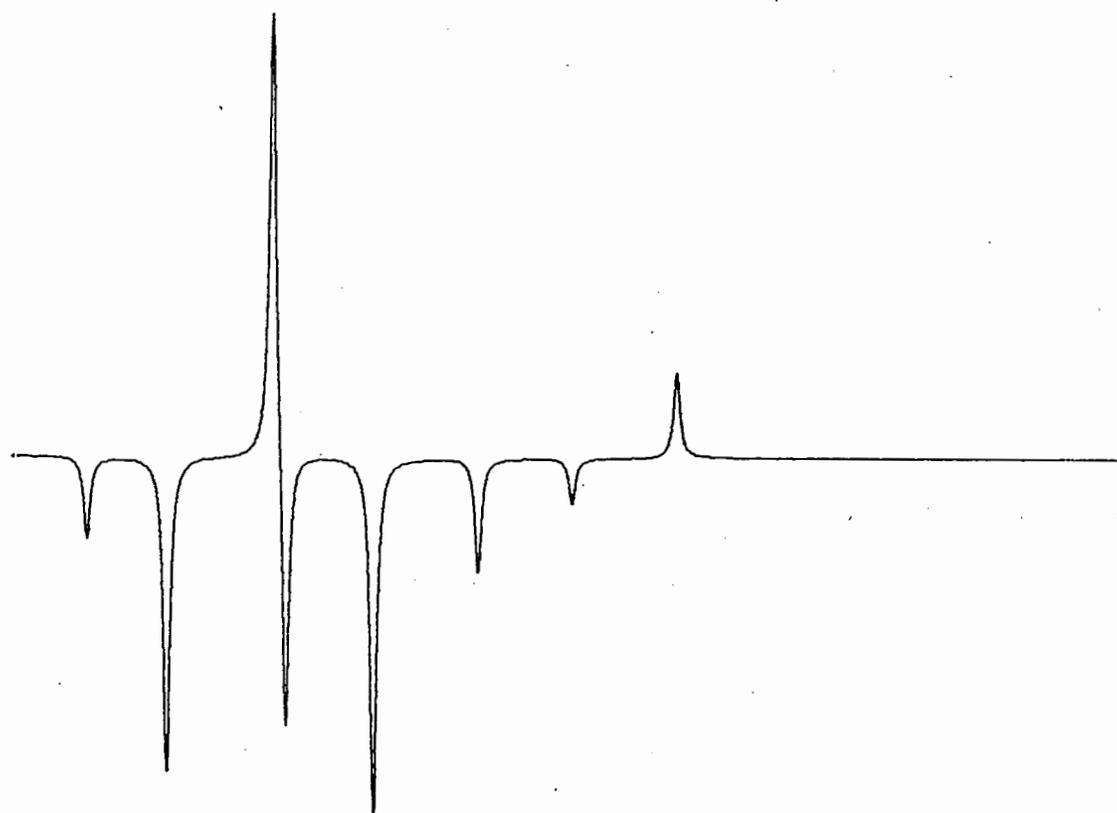
20.0°

FT-SPEKTREN

10.0°

DELTA = 6.770
AJ = 4.377
D = .646
DIF G = .00100
A1 = -40.000
B1 = 0.000
B2 = 0.000
B = 30.000

SLOW-PASSAGE



CIDNP-EXPERIMENT

**Deuterated Solvents
Reference Compounds
Chart Papers Etc:
Shift Reagents**



NUCLEAR MAGNETIC RESONANCE LTD.

MAGNETIC HOUSE/SCRUBBS LANE/BLEDLOW RIDGE/
HIGH WYCOMBE/BUCKS/HP14 4AF



QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

PRINCIPAL Sir Harry W. Melville, K.C.B., F.R.S.
 REGISTRAR R. P. Tong, O.B.E., J.P., M.A.

MILE END ROAD
 LONDON E.1
 Tel. 01-980 4811

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

8th January 1974

Dear Barry,

A European E.N.C., 1974;

International Meeting St. Andrews, 1975

The N.m.r. Discussion Group here (affiliated to the Chemical Society) is to have its next meeting at the University of Kent (April 8 - April 10th) with Experimental N.m.r. techniques as the theme. We have lengthened our usual one day meeting to two and a half days for the occasion, and we are inviting a large number of participants from other European countries. The objective is to see whether there is a need and a desire to initiate a cycle of such meetings in Europe, along the lines of the admirable E.N.C. in the United States. The response so far on this question has been very favourable. We are making the attempt to coordinate with other European Discussion Groups where they exist, notably the Aachen Conferences, the Dutch Discussion Group and the embryonic Swiss Group. The Dutch Group have already held a one day joint meeting with us (last year at Essex). 40 stalwart Lowlanders battled through high seas from the Hook of Holland to Harwich for the occasion. We hope one day to return the visit.

Our next next international meeting will be at St. Andrews (over-looking the Golf course) starting on July 7th, 1975. Golfers please note.

Lastly, let me mention that Ernie Cummins formerly of Perkin Elmer has resigned from the post of secretary/treasurer. He has been on the secretariat of the Group from its initiation in the early 1960's. We are all most grateful to him for his cool, calm, and cheerful services, and also to Perkin Elmer for the support they gave the Group in its formative years. Our new officers are Derek Shaw as Secretary, and Jim Feeney as treasurer. Additionally Peter Beynon has joined the committee.

With best regards

Ed

Dr. E. W. Randall.



UNIVERSIDAD DE BUENOS AIRES

FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Departamento de Física
Ciudad Universitaria
Pabellón 1
Buenos Aires-Argentina

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

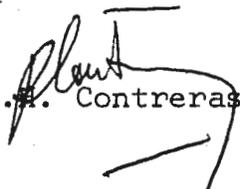
Additivity Scheme in NMR Chemical Shifts of
disubstituted Pyridines

Dear Professor Shapiro:

During the past few months we have tested in 11 disubstituted pyridines an additivity relationship for chemical shifts similar to that found in the literature for coupling constants. The chemical shifts of these disubstituted pyridines were measured in different solvents at different concentrations and extrapolated to infinite dilution.

In most cases, it was found that the extrapolated chemical shifts for disubstituted pyridines are in good agreement with those calculated using the additivity relationship. Only in a few cases it was found that the additivity scheme does not hold. These results are shown in the table.

Sincerely yours,


R. A. Contreras

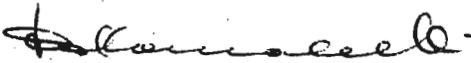

D.G. de Kowalewski

TABLE IV. Calculated and experimental chemical shifts (in Hz) for disubstituted pyridines

Substituents	Solvent	ν_3 Calc.	ν_3 Exp.	Diff.	ν_4 Calc.	ν_4 Exp.	Diff.	ν_5 Calc.	ν_5 Exp.	Diff.
2-NH ₂ -6-CH ₃	CH ₃ OH	1621.8	1621.7	+0.1	1565.2	1564.9	+0.3	1616.9	1617.5	-0.6
	CH ₃ NO ₂	1625.4	1624.4	+1.0	1566.8	1565.5	+1.3	1616.8	1616.3	+0.5
	CH ₂ Cl ₂ (x)	1631.7	1630.1	+1.6	1572.6	1570.1	+2.5	1621.3	1619.6	+1.7
2-CN-6-CH ₃	CH ₃ OH	1544.6	1545.1	-0.5	1531.6	1532.9	-1.3	1551.8	1552.3	-0.5
	CH ₃ NO ₂	1548.0	1547.4	+0.6	1533.3	1534.5	-1.2	1553.3	1554.2	-0.9
	CH ₂ Cl ₂ (x)	1553.5	1553.2	+0.3	1538.9	1539.9	-1.0	1559.3	1560.0	-0.7
2-OCCH ₃ -6-CH ₃	CH ₃ NO ₂	1539.3	1539.3	0.0	1536.8	1536.5	+0.3	1558.7	1559.1	-0.4
2-OCH ₃ -6-Cl	CH ₃ NO ₂	1599.9	1600.8	-0.9	1544.7	1545.4	-0.7	1586.5	1586.3	+0.2
2-6-di Cl	CH ₃ OH	1560.2	1560.0	+0.2	1536.4	1536.9	-0.5	1560.2	1560.0	+0.2
	CH ₃ NO ₂	1560.8	1560.8	0.0	1536.0	1536.7	-0.7	1560.8	1560.8	0.0
2-CHO-6-CH ₃	CH ₂ Cl ₂ (x)	1547.1	1543.0	+4.1	1537.6	1539.9	-2.3	1563.9	1563.4	+0.5
		ν_2 Calc.	ν_2 Exp.		ν_4 Calc.	ν_4 Exp.		ν_6 Calc.	ν_6 Exp.	
3-5-diBr	CH ₂ Cl ₂	1486.6	1488.9	-2.3	1525.0	1523.6	+1.4	1486.6	1488.9	-2.3
3-5-diCl	CH ₃ NO ₂	1495.3	1495.8	-0.5	1535.2	1533.8	+1.4	1495.3	1495.8	-0.5
		ν_4 Calc.	ν_4 Exp.		ν_5 Calc.	ν_5 Exp.		ν_6 Calc.	ν_6 Exp.	
2-3-diCl	CH ₃ OH	1533.2	1525.4	+7.8	1561.8	1561.4	+0.4	1506.1	1505.1	+1.0
	CH ₃ NO ₂	1535.6	1529.2	+6.4	1562.6	1562.7	-0.1	1506.9	1506.2	+0.7
2-NH ₂ -3-CH ₃	CH ₃ OH	1568.0	1565.8	+2.2	1615.6	1610.5	+5.1	1544.4	1539.1	+5.3
		ν_3 Calc.	ν_3 Exp.		ν_4 Calc.	ν_4 Exp.		ν_6 Calc.	ν_6 Exp.	
2-NH ₂ -5-CH ₃	CH ₃ OH	1615.8	1612.8	+3.0	1568.0	1566.0	+2.0	1541.8	1542.1	-0.3

(x) Values taken at a concentration Ca. 15% w/w.

From Professor A.R. Katritzky

School of Chemical Sciences
University Plain, Norwich NOR 88C
Telephone Norwich (0603) 56161
Telegraphic Address UEANOR

22nd January, 1974

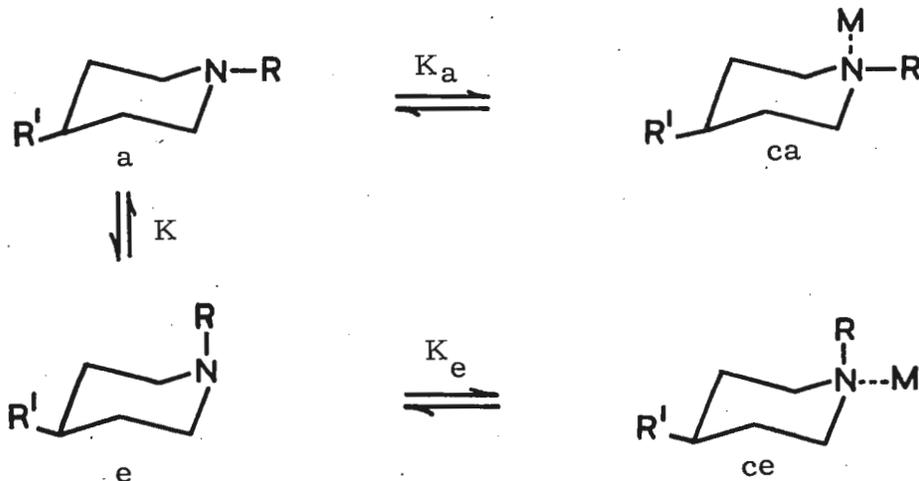
Dear Barry,

The conformational preference of piperidine has been extensively studied, and we believe that the reliable evidence now clearly demonstrates¹ the NH-equatorial conformer preferred by ca. 0.4 kcal. mole⁻¹. However, the case for NH-axial has also been cogently argued² and some recent papers³ have purported to demonstrate an NH-axial preference using Co(II)- and Ni(II)- bisacetylacetonate - induced shifts of the α -protons. Unfortunately, inherent in this last work is the assumption of equal complexing of the lone-pair - equatorial (e) and lone-pair - axial (a) conformers, a situation we hold to be most unlikely in view of other evidence such as rates of quaternisation.⁴

We have carried out a treatment for the situation outlined in the Scheme and derived the relationship:

$$\frac{(\Delta\nu^1)}{(\Delta\nu^2) \text{ obsd}} = \frac{P_e K_e (kg^1_{ce} + \nu^1_e) + (1 - P_e) K_a (kg^1_{ca} + \nu^1_a)}{P_e K_e (kg^2_{ce} + \nu^2_e) + (1 - P_e) K_a (kg^2_{ca} + \nu^2_a)}$$

$(\Delta\nu^1/\Delta\nu^2)$ obsd is the relative shift of any two observed protons for which a pseudocontact mechanism only is applicable, P_e , K_e and K_a are as indicated in the Scheme, g^1_{ce} etc. are the geometric factors of the observed protons for the equatorial or axial complexes, k is the proportionality constant of those factors to the induced shifts, and ν^1_{ce} , etc., are the shifts of the respective observed protons in the free base conformers. The relationship holds for low mole proportions of shift reagent.



R = H, Me or Et, R' = Ph

 P_e = mole fraction of e

We used the shifts of the phenyl protons induced by $M(AA)_2$ as a probe enabling two simultaneous equations for any two pairs of the ortho, meta and para protons to be set up. P_e , K_e , K_a and k are unknown but since K_e/K_a is the desired parameter it may be treated as a single variable and the equations solved for a range of P_e values. Uncertainty in the geometries of the complexes precludes precise determination of geometric factors and so our results are quoted as ranges.

For $R = Et$, we find that K_e/K_a is ca. 20 taking $P_e = 0.15$ for the conformational preference of N-ethylpiperidine. For $R = Me$ we find that K_e/K_a is ca. 11 for $P_e = 0.25$, and for piperidine itself with $R = H$, we find that K_e/K_a is ca. 2 taking $P_e = 0.4$, the value most widely accepted as defining the piperidine preference. The error of assuming $K_e = K_a$ is demonstrated by this work: complexation with bulky shift reagents does indeed perturb conformational equilibria.

This work will be published in more detail in J. A. C. S.

Yours sincerely,



I. D. Blackburne

A. R. Katritzky

Y. Takeuchi

1. cf. R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, J. Chem. Soc. (B), 1970, 127.
2. e. g. J. B. Lambert, D. S. Bailey, and B. F. Michel, J. Amer. Chem. Soc., 1972, 94, 2812.
3. T. Yonezawa, I. Morishima, and Y. Ohmori, J. Amer. Chem. Soc., 1970, 92, 1267.
4. R. P. Duke, R. A. Y. Jones, and A. R. Katritzky, J. C. S. Perkin II, 1973, 1553.

ENI

The world's leader in solid state rf power amplifiers

Once upon a time if you wanted broadband RF power, you had to settle for bulky tube-type power amplifiers. No more. Because ENI has developed a full line of all-solid-state Class A power amplifiers, covering the frequency spectrum of 10 kHz to 560 MHz, with power outputs ranging from 300 milliwatts to over 1000 watts. And there's more to come.

Driven by any signal generator, frequency synthesizer or sweeper, ENI's compact portable amplifiers, like the ones shown below, are versatile sources of power for general laboratory work, RFI/EMI testing, signal distribution, RF transmission, laser modulation, data transmission, NMR, ENDOR, ultrasonics and more.

Completely broadband and untuned, our highly linear units will amplify inputs of AM, FM, SSB, TV and pulse modulations with minimum

distortion. Although all power amplifiers deliver their rated power output to a matched load, only ENI power amplifiers will deliver their rated power to any load regardless of match.

We also designed our amplifiers to be unconditionally stable and failsafe—you need never fear damage or oscillation due to severe load conditions (including open or short circuit loads).

ENI instrumentation amplifiers come complete with an integral AC power supply and an RF output meter. Ruggedized amplifiers capable of operating under severe environmental conditions are available.

For a **complete** catalog of power amplifiers and multicouplers, write: ENI, 3000 Winton Road South, Rochester, New York 14623. Call 716-473-6900. TELEX 97-8283 ENI ROC.



40 WATT/ MODEL 240L

- 20KHz to 10MHz coverage
- More than 40w linear power output
- Up to 150w CW & pulse output
- Works into any load impedance
- Metered output

Extraordinary performance in a wide range of transducer drive applications. Deliver up to 150w into any load regardless of its impedance. Compatible with all signal and function generators, the 240L is a high quality laboratory instrument for ultrasonics, biological research & electro-optic modulation.

100 WATT/ MODEL 3100L

- 250 KHz to 105MHz coverage
- More than 100w linear output
- Up to 180w CW & pulse
- Works into any load
- Unconditionally stable

Designed to replace bulkier and less efficient tube type amplifiers, the Model 3100L will provide reliable and maintenance free operation. NMR, ENDOR, ultrasonics and laser modulation are just a few of the applications for this versatile source of RF energy.

20 WATT/ MODEL 420L

- 150KHz to 250MHz coverage
- 20 Watts power output
- Low noise figure
- 45dB \pm 1.5dB gain
- Class A linearity

The widest band solid state power amplifier available at its 20w power level, the ENI 420L is a truly state-of-the-art instrument. As a drive source for high resolution acousto-optic modulators and deflectors the Model 420L is invaluable. Its Class A linearity will amplify AM, FM, TV and pulse signals with minimum distortion.

.3 WATT/ MODEL 500L

- Flat 27dB gain 2MHz to 500 MHz
- 1.7MHz to 560MHz usable coverage
- Thin film construction
- 8dB noise figure
- Failsafe

This compact unit can deliver more than 300 milliwatts from 1.7MHz to 560MHz at low distortion. A thin film microelectronic circuit is the heart of this general utility laboratory amplifier. Extremely wide band response at a very modest price.



ISTITUTO CHIMICO

della

UNIVERSITÀ DI TORINO

Dr. S. Aime

10125 TORINO, January 1974

CORSO MASSIMO D'AZEGLIO, 48

Tel. 65 21 02 - 68 28 92 - 65 58 31 - 65 58 32

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

MULTINUCLEAR STUDIES OF PHOSPHORUS-CONTAINING COMPOUNDS

Dear Professor Shapiro,

This Institute has recently acquired a JEOL PS 100-FT spectrometer system here and we are building up NMR work, so we would like to join the mailing list for I.I.T.N.M.R.

As an initial subscription I want to describe some work carried out during ten months spent with Dr. Robin Harris at the University of East Anglia, Norwich, England, where I used a Varian XL 100 spectrometer system. The object of the work was to obtain NMR information about (C, P) and (P, P) coupling constants in some compounds containing several phosphorus atoms. In such cases the ^{13}C spectra are not, in principle, first order. For some compounds, notably those with $|J_{\text{PP}}| \gg |J_{\text{PC}} - J'_{\text{PC}}|$, a deceptively simple triplet is seen in the C-13 resonance, and full information cannot be obtained.

However, in other cases a five-line C-13 pattern can be seen, typical for the X part of an ABX spin system with $|\nu_{\text{A}} - \nu_{\text{B}}|$ very small. This occurs when $|J_{\text{PP}}| \approx |J_{\text{PC}} - J'_{\text{PC}}|$. The difference $|\nu_{\text{A}} - \nu_{\text{B}}|$ occurs solely as a result of differences in the isotopic effect of C-13 on the chemical shifts of the two phosphorus nuclei, and is normally only a few Hz. Therefore there are always two C-13

transitions very close to ν_x . There are also two C-13 lines separated by $|J_{PC} + J'_{PC}|$. In addition two weak lines with positions depending on J_{PP} , $\nu_A - \nu_B$ and $J_{PC} - J'_{PC}$ may be seen. When these are observed it is worth examining the C-13 satellites in P-31 resonance; these depend in principle on the same three parameters. In favourable cases J_{PP} , $\nu_A - \nu_B$ and $J_{PC} - J'_{PC}$ can all be obtained, though frequently it is best to assume

$\nu_A - \nu_B = 0$. If the C-13 satellites cannot be observed, prior knowledge of J_{PP} (e.g. from 1H work) may enable $J_{PC} - J'_{PC}$ to be obtained from the C-13 spectrum.

Some results are given below:

	Molecule	J_{PC}	J'_{PC}	J_{PP}	
I	$\begin{array}{c} \text{Me}_2 \text{ PP Me}_2 \\ \quad \\ \text{SS} \end{array}$	+48	+12	+18.7	
II	$\begin{array}{c} \text{Et}_2 \text{ PP Et}_2 \\ \quad \\ \text{SS} \end{array} \quad \text{-CH}_2$	+43	+10	53.5	
III	$\begin{array}{c} \text{nPr}_2 \text{ PP nPr}_2 \\ \quad \\ \text{SS} \end{array}$	α CH ₂	+41.9	+9.1	57.4
		β CH ₂	+1.5	+15.5	
IV	$\begin{array}{c} \text{Et} \quad \text{PP} \quad \text{Et} \\ \diagdown \quad \diagup \\ \text{Me} \quad \text{SS} \quad \text{Me} \end{array}$	α CH ₂	+46.5 ± 2	+9 ± 2	35.2 ± 1
		α CH ₃	+47 ± 2	+11 ± 2	
V	$\begin{array}{c} \text{Me} \quad \text{PP} \quad \text{Me} \\ \diagdown \quad \diagup \\ \text{Ph} \quad \text{SS} \quad \text{Ph} \end{array}$	CH ₃	+52.5	+13.5	+21
		C-1 AR	+69.7	+9.7	

The table indicates the most likely assignments; in the case of the compound III an assignment of ${}^2J_{\text{P-C-C}} = +1.5 \text{ H}_2$ and ${}^3J_{\text{PCC}} = +15.5 \text{ H}_2$ seems not very unlikely, since a small positive value correlates better with an expected negative value for ${}^2J_{\text{P-C-C}}$.

It must be outlined the positive sign of ${}^2J_{\text{CP}}$ through the linkage $\text{P}^{\text{V}}\text{P}^{\text{V}}\text{-C}$: ${}^2J_{\text{P}^{\text{V}}\text{C}}$ is well known to be negative in the $\text{P}^{\text{V}}\text{-C-C}$ and $\text{P}^{\text{V}}\text{-C-C}$ linkages and this change in sign seems to be in some relation with the passage from the first row to the second row in the periodic table of the atom between C and P.

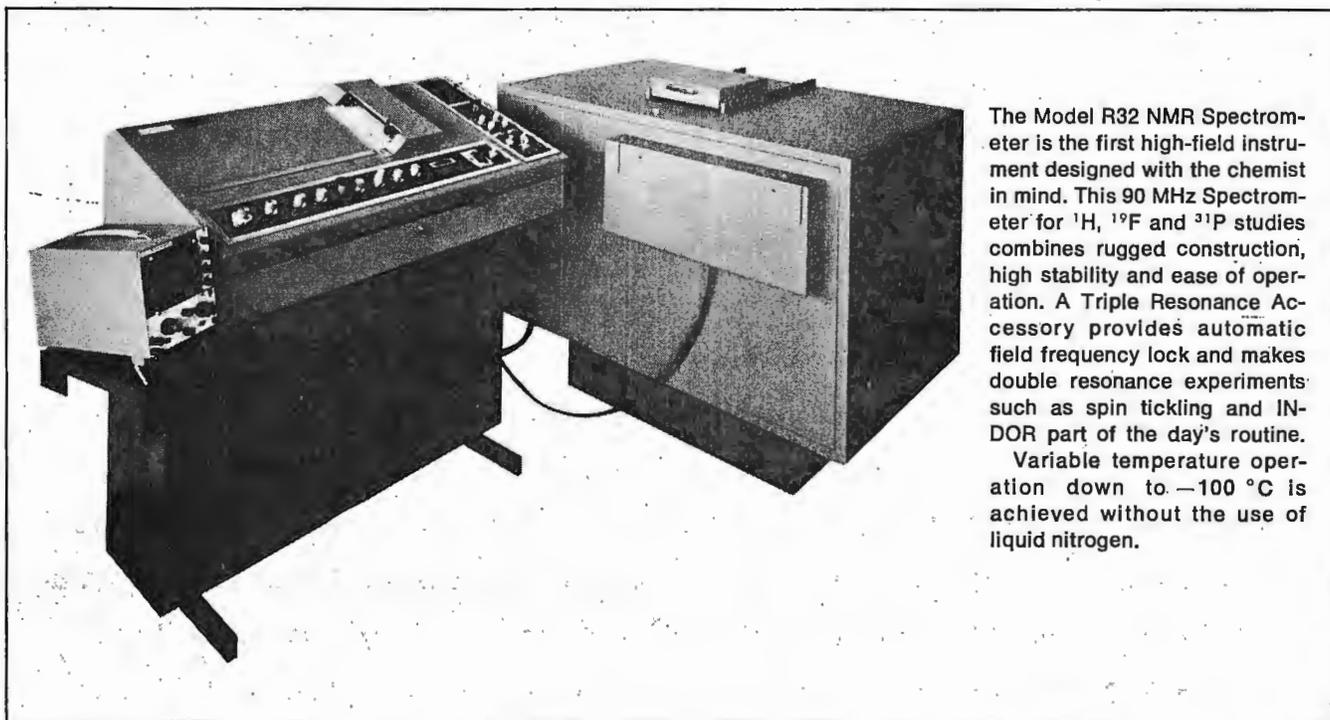
Of course C-13 and P-31 chemical shifts have also been obtained, but these will not be mentioned here. I hope this letter will suffice to put this Institute on your mailing list, and I look forward to receiving copies of I.I.T.N.M.R. - and later on, perhaps, your famous blue and pink letters.

Yours sincerely



S. Aime

A 100-watt bulb consumes as much power as the magnet in our NMR Spectrometers.



The Model R32 NMR Spectrometer is the first high-field instrument designed with the chemist in mind. This 90 MHz Spectrometer for ^1H , ^{19}F and ^{31}P studies combines rugged construction, high stability and ease of operation. A Triple Resonance Accessory provides automatic field frequency lock and makes double resonance experiments such as spin tickling and IN-DOR part of the day's routine. Variable temperature operation down to -100°C is achieved without the use of liquid nitrogen.



Model R24A. 60 MHz ^1H NMR Spectrometer. Digital sweep X-Y recording system. Best buy in low-cost field.

Since Perkin-Elmer's entire line of NMR Spectrometers employs *permanent* magnets, the only power required for the magnet is for thermostating and supplying the Golay coils*.

They need no troublesome cooling water and no noisy water refrigerator.

In fact, the savings in operating costs alone could pay for the cost of the instrument in as little as 7 years.

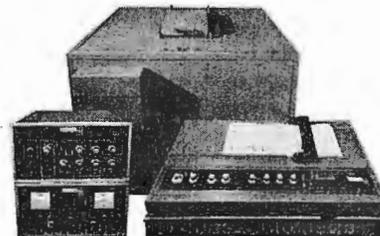
But economical operation is only one of the many benefits you get with our *permanent* magnet Spectrometers. Others are: unmatched resolution stability; amazing ease of set-up; and high throughput.

If you are planning to add to your current NMR capabilities or just getting into NMR, it will pay you to get more information on the entire Perkin-Elmer line of *permanent* magnet NMR Spectrometers.

Instrument Division, Perkin-Elmer Corporation, Main Avenue, Norwalk, Conn. 06856.

*Perkin-Elmer patent numbers 3,515,979 and 3,622,869.

Model R12. Versatile 60 MHz NMR Spectrometer. Can be equipped to solve the most demanding NMR problems.



PERKIN-ELMER

Committed to helping your samples tell you more.

UNIVERSITY OF TOKYO
 COLLEGE OF GENERAL EDUCATION
 DEPARTMENT OF CHEMISTRY
 KOMABA, MEGURO-KU
 TOKYO, JAPAN

February 7, 1974

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

"Long-range ^{13}C -H Coupling Constants in 2-Cyanopyridine"

Dear Professor Shapiro;

Most of the ^{13}C -H coupling constants have so far been obtained from the satellite peaks of proton nmr spectra. Hence information on the long-range (through more than two bonds) ^{13}C -H coupling constants is necessarily scarce. Recent development in ^{13}C -FT nmr spectrometer makes the measurement of proton-noise undecoupled ^{13}C nmr spectra, and hence the direct determination of long-range ^{13}C -H coupling constants feasible.

In Fig. 1 (next page) a part of the proton-noise undecoupled spectrum of 2-cyanopyridine is reproduced. Except for C_2 and C_{CN} , each carbon gives two peaks 160-180Hz apart from each other due to the one-bond coupling (^1J), and each peak is further split due to the long-range couplings. In the figure only one of the two peaks are given for C_3, C_4 and C_5 .

The assignment of the couplings was made with the aid of the reported value for benzene¹ and a few substituted benzenes² and of the non-decoupled spectra of other pyridines recorded by us. The results are summarized as follows.

Peak (a), C_4 : $^3\text{J}(\text{C}_4\text{-H}_6)$ 6Hz.

Peak (b), C_2 : $^3\text{J}(\text{C}_2\text{-H}_6)$ 12Hz, $^3\text{J}(\text{C}_2\text{-H}_4)$ 7Hz, $^2\text{J}(\text{C}_2\text{-H}_3)$ 2Hz,

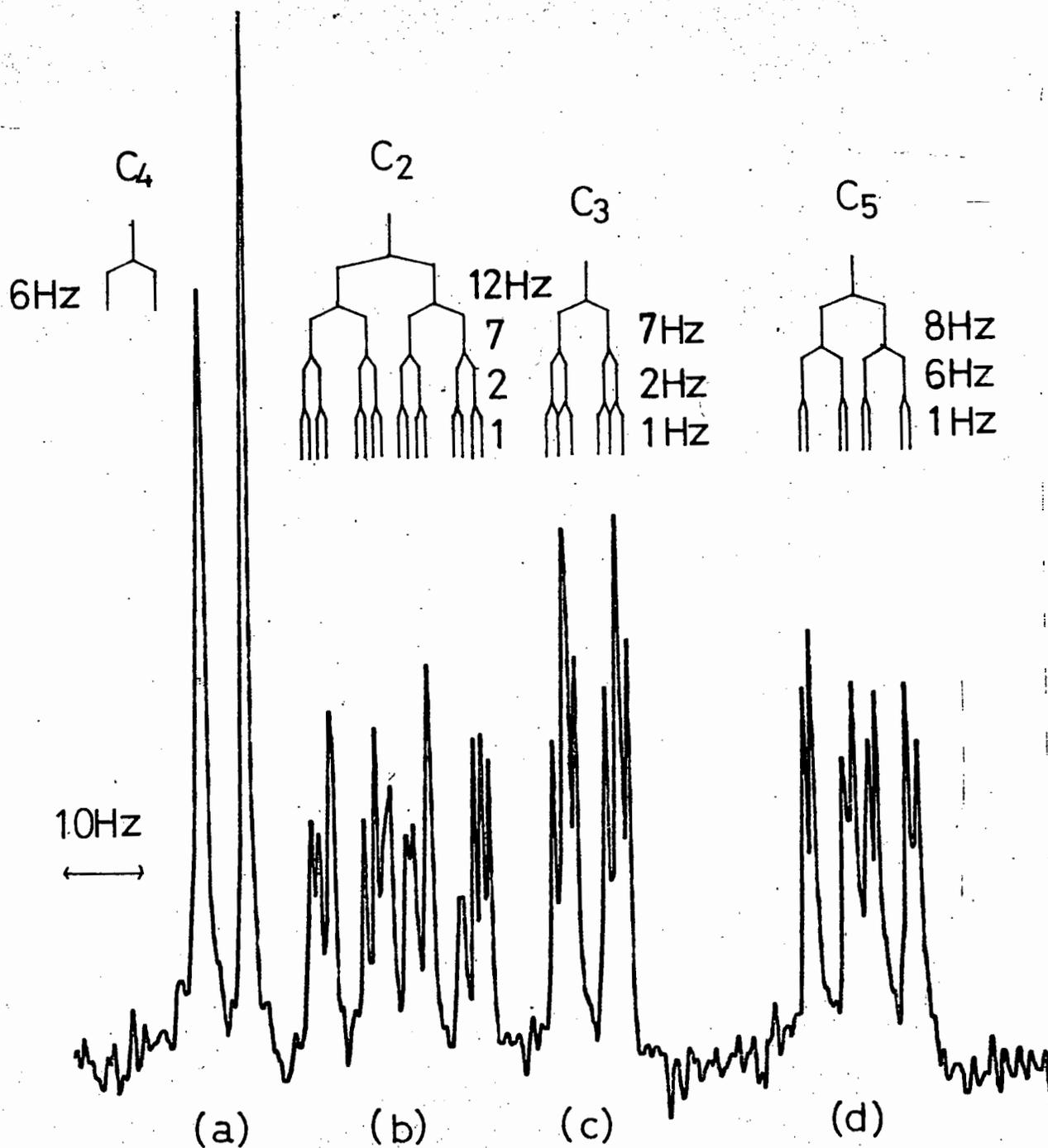


Fig. 1. A part of the proton-noise undecoupled spectrum of 2-cyanopyridine.

${}^4J(C_2-H_5)$ 1Hz.
 Peak (c), C_3 : ${}^3J(C_3-H_5)$ 7Hz, ${}^2J(C_3-H_4)$ 2Hz, ${}^4J(C_3-H_6)$ 1Hz.
 Peak (d), C_5 : ${}^2J(C_5-H_6)$ 8Hz, ${}^3J(C_5-H_3)$ 6Hz, ${}^2J(C_5-H_4)$ 1Hz.

It is noteworthy that (i) the three-bond coupling through nitrogen (${}^3J(C_2-H_6)$) is considerably enhanced, and that (ii), as a two-bond coupling, ${}^2J(C_5-H_6)$ is unexpectedly large. These are common to all pyridines investigated. Evidently the analysis of the fine splittings observed for the proton-noise undecoupled spectra would provide us with an unambiguous assignment of the chemical shifts.

The spectrum was obtained with Varian XL-100-FT spectrometer operating at 25.2MHz as a DMSO- d_6 solution. Pulse width, 10 μ sec; sweep width, 1000Hz; with 4096 memory points; no. of pulses accumulated, 2500.

- 1) F.J. Weigert and J.D. Roberts, J.Amer.Chem.Soc. 89, 2967(1967).
- 2) G. Govil, J.Chem.Soc.(A), 1420(1967).

Yoshito Takeuchi

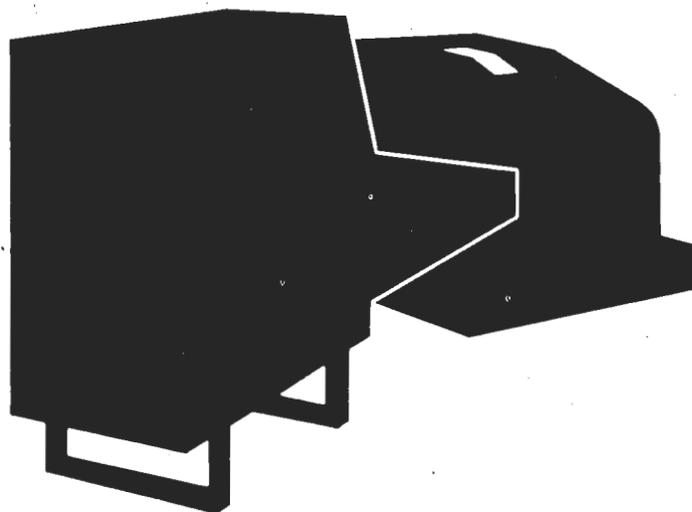
Yoshito TAKEUCHI
(University of Tokyo)

Nicholas DENNIS
(University of East Anglia)



WFP 60

The ultimate in low-cost
FT NMR Spectroscopy...



- Full multinuclear capability
- High resolution magnet for proton FT
- 10 mm variable temp for C¹³
- Superior sensitivity

FOR DETAILS, PLEASE CONTACT YOUR NEAREST BRUKER REPRESENTATIVE.

Bruker Scientific Inc.
One Westchester Plaza
Elmsford, N. Y. 10523
Tel. (914) 592-5470
Tlx. 13-1524

Bruker Magnetics Inc.
1 Vine Brook Park
Burlington, Mass. 01803
Tel. (617) 272-9250
Tlx. 94-9493

Bruker Research
1548 Page Mill Road
Palo Alto, Calif. 94305
Tel. (415) 493-3173
Tlx. 34-5533

Bruker Spectrospin Ltd.
84 Orchard View Blvd., Suite 101
Toronto, Canada
Tel. (416) 486-7907
Tlx. 02-2771

MCMASTER UNIVERSITY

HAMILTON, ONTARIO, CANADA

DEPARTMENT OF CHEMISTRY

February 13, 1974

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

THE DEUTERIUM DETECTIVE

Dear Barry:

In the development of a simple and quantitative method for the replacement of aromatic protons by deuterium (1), ^{13}C NMR has been used to establish the position and extent of deuterium exchange.

In the case of 85% deuterated chlorobenzene, ^1H and ^2H (2) NMR did not provide sufficient information to establish the site of deuterium incorporation. However, analysis of the ^{13}C spectrum indicated that the compound was essentially completely deuterated at the ortho position, almost fully deuterated at the para position and approximately 50% deuterated at the meta position.

Initially, to simplify interpretation it was necessary to predict the ^{13}C chemical shifts using shift parameters (3). Measurement of the extent of deuteration from ^{13}C spectra is possible under certain conditions (4). However, in the case of the proton decoupled spectrum B, caution is required due to intramolecular Overhauser effects and long range deuterium coupling (5). The intense signal in this spectrum indicates that the remaining protons are at the meta position.

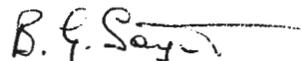
In the proton coupled spectrum A, the extent of deuteration at the meta position may be determined ($\pm 5\%$) by comparison of the area (x2) of the low field signal of the $\text{C}_{3,5}\text{-H}$ doublet (peak 1) with the area (x3) of the lowest field signal of the $\text{C}_{3,5}\text{-D}$ triplet (peak 2).

The spectra were obtained in the CW mode.

Yours sincerely,



N. H. Werstiuk

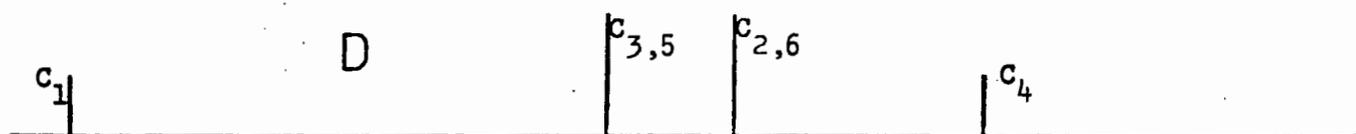
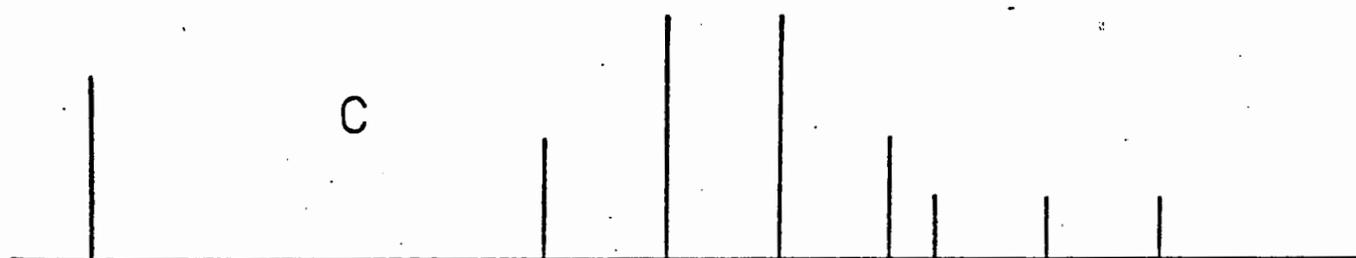
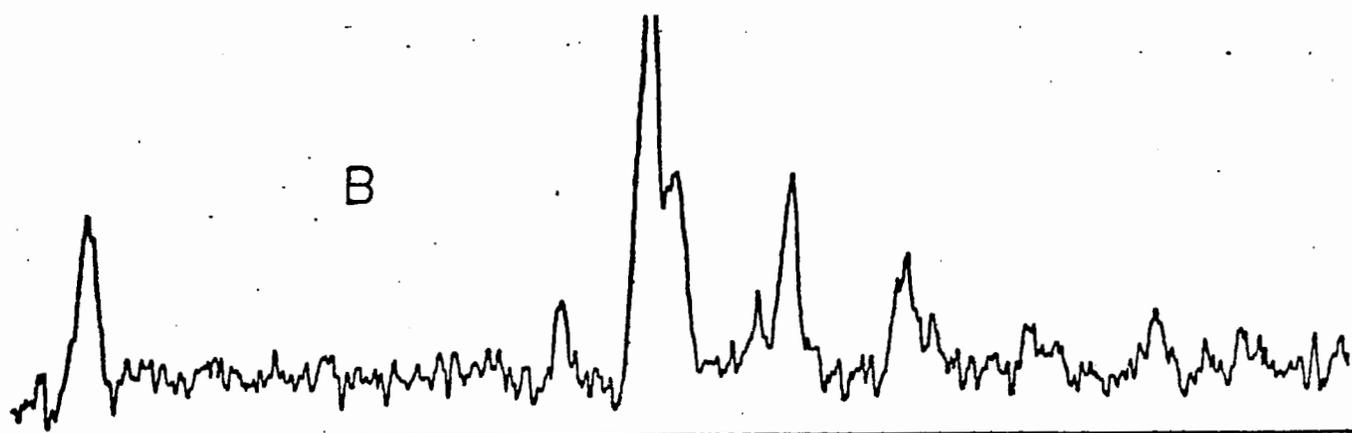
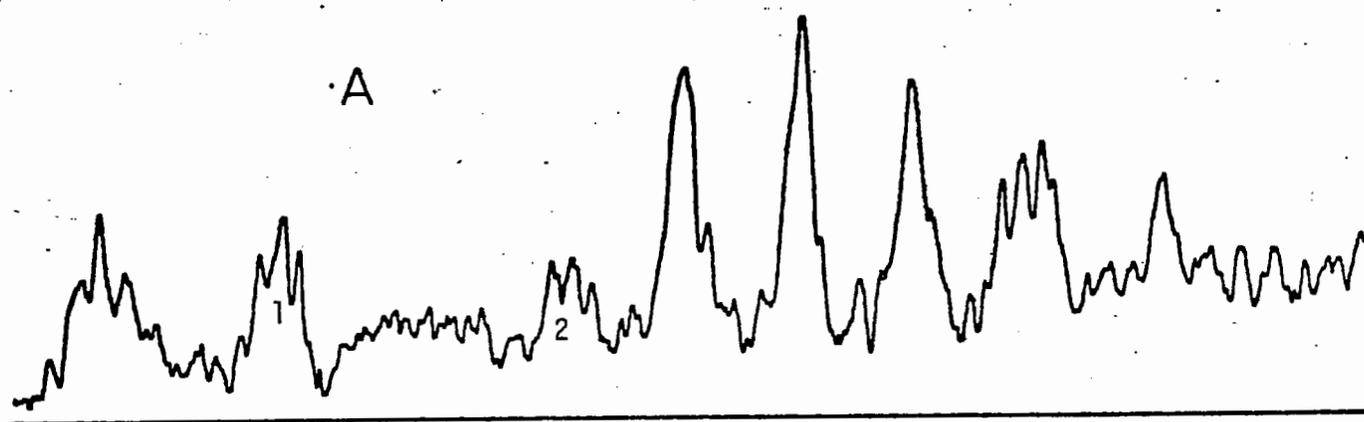


B. G. Sayer

/jff

References

1. N. H. Werstiuk, T. Kadai, Can. J. Chem. 51, 1485 (1973).
2. Courtesy of Professor J. Stothers, University of Western Ontario.
3. B. G. Sayer, TAMUNMR Newsletter 182 (p. 45).
4. G. L. Lebel, J. D. Laposa, B. G. Sayer, R. A. Bell, Analyt. Chem. 43, 1500 (1971).
5. R. A. Bell, C. L. Chan, B. G. Sayer, Chem. Commun. 67 (1972).



p.p.m., Benzene = 0

- A ^{13}C spectrum of 85% per Deutero Chlorobenzene (proton coupled)
B ^{13}C spectrum of 85% per Deutero Chlorobenzene (proton decoupled)
C Predicted ^{13}C spectrum of per Deutero Chlorobenzene
D ^{13}C spectrum of Chlorobenzene

Unilever Research

Port Sunlight Laboratory
Unilever Limited
Port Sunlight
Wirral Cheshire L62 4XN

Telephone 051-645 2000
Telex 627235



Prof B Shapiro
Dept of Chemistry
College of Science
Texas Aam University
College Station
TEXAS 77843
USA

APPLICATION OF FOURIER TRANSFORM TECHNIQUES TO PROBLEMS IN COLLOID CHEMISTRY

In recent months we have been utilising the greatly increased sensitivity of Fourier Transform techniques for investigations in the field of Colloid Chemistry.

One problem that n.m.r. could throw light on is the conformation of small molecules at the solid/liquid interface. The two major difficulties in using high resolution techniques are firstly low sensitivity, since there is a limited surface area of the colloid and secondly magnetic field inhomogeneities in the sample caused by the presence of solid colloidal particles.

About 1000 scans are usually sufficient to obtain adequate spectra for linewidth measurement and the magnetic field inhomogeneities can be minimised by using spherical polystyrene latex particles. Polystyrene has a similar magnetic susceptibility to water and provided the particles are not extensively aggregated magnetic field inhomogeneities are usually only about a cycle, as shown by narrow water resonances. So far we have studied the adsorption of nonionic surfactants onto polystyrene particles. The latex particles are prepared and dialysed against H_2O , freeze-dried, redispersed in D_2O and then small quantities of nonionic surfactant added. Measurements of the line broadening of the hydrocarbon and ethylene oxide resonances have been made.

Some results for $C_{8H_{17}}(OC_2H_4)_6-OH$ are shown in the accompanying diagram.

By assuming rapid exchange of the surfactant between two sites, the surface of the particle and the bulk of solution, it is possible to calculate the linewidth of the ethylene oxide and hydrocarbon portions on the interface. The relative populations in the two sites are given by the adsorption isotherm. The decrease in linewidth for the ethylene oxide indicate a change in conformation of the adsorbed molecules from one of lying flat in the interface to one of vertical orientation, where the mobility is greater.

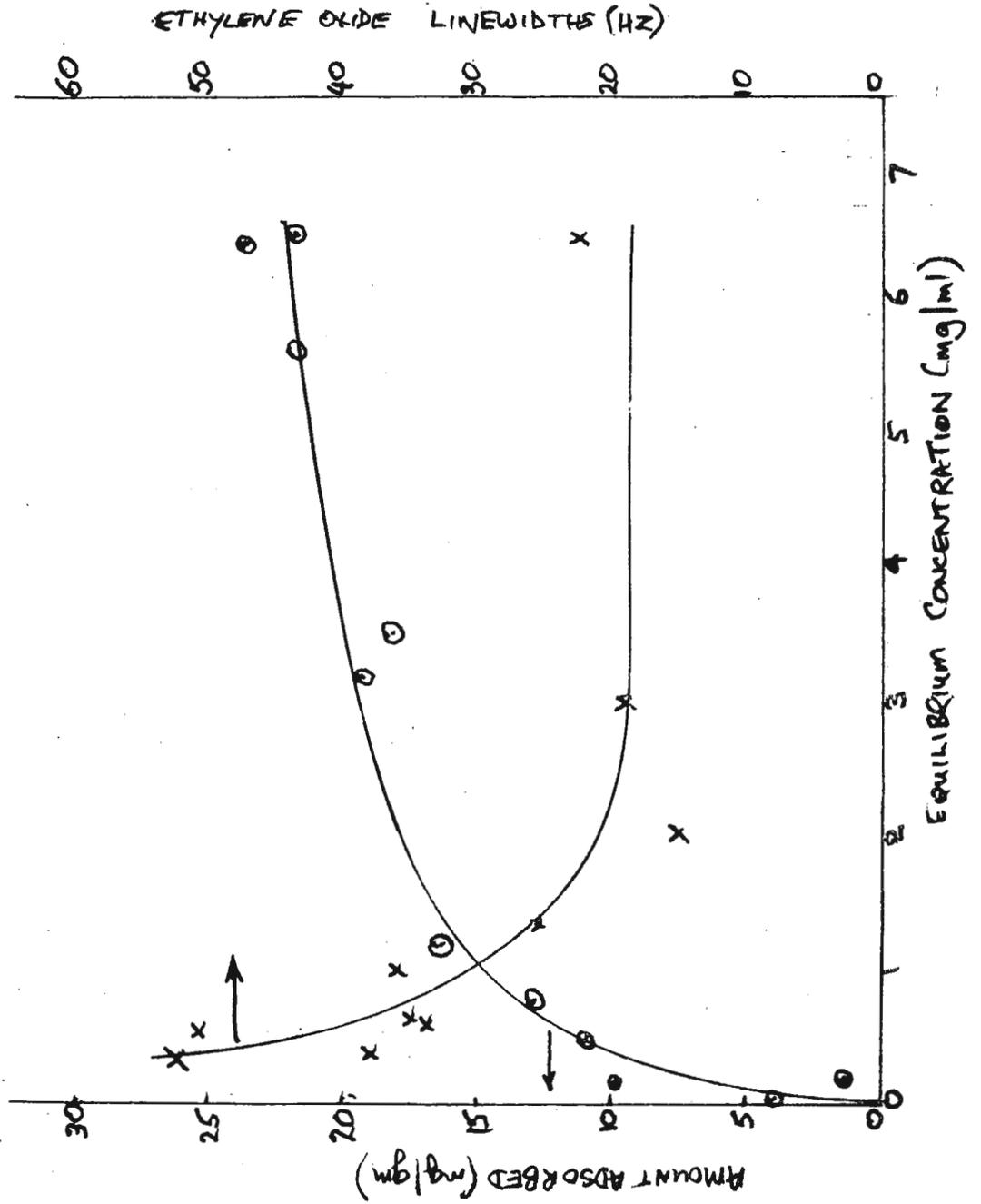
The accuracy and reproducibility of the linewidth measurements are clearly not as good as can be achieved with homogeneous solutions though quite adequate for showing major conformational changes.

I D Robb, R. Sallis.

I D Robb

R Sallis

ADSORPTION ISOTHERM OF NONIONIC C_8EO_6 ON POLYSTYRENE LATEX AND LINEWIDTH OF EO IN ADSORBED STATE.



UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *Urbana, Illinois 61801*

School of Chemical Sciences

DEPARTMENT OF CHEMISTRY

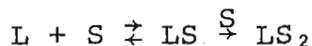
February 18, 1974

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

Dear Barry:

Re: The Use of Shift Reagents and the Frequency
Dependence of the Coalescence Temperature
in Two-Site Chemical Exchange Studies

A couple of years ago, Mr. H. N. Cheng (a current graduate student) and I reported to you on the use of lanthanide chemical shift reagents to adjust the chemical shifts of exchangeable nuclei and thereby facilitate the study of their exchange. That work [J. Am. Chem. Soc. 94, 5505 (1972)] has since been extended to include the nature and effects of the association between the lanthanide shift reagent (L) and the substrate molecule (S) in which the exchange occurs, using Pr(fod)₃ and dimethylacetamide (DMA) in 1,1,2,2-tetrachloroethane as a model system. In order to fit the chemical concentration and temperature dependences of the internal rotation and chemical shifts of DMA in this system, a two-step association is used:



The free energies of activation (ΔG^\ddagger) found on this basis for internal rotation in DMA are 18.35 kcal/mole for the free amide (S), 19.52 for the 1:1 complex (LS) and 19.32 for the 1:2 complex (LS₂).

Ancillary to the study of the association effects, we have investigated using measurements of the coalescence temperature at different resonance frequencies as a means of obtaining the temperature dependence of the exchange rate. The line-shape is most sensitive to the exchange rate at the coalescence point, which gives therefore the most accurate determination of the rate. Typical results are given in Tables I and II.

Table I. Frequency Dependence of Rate Parameters for Internal Rotation of Amides

		<u>A-60</u>	<u>HA-100</u>	<u>HR-220</u>
DMF	$\Delta\nu_\infty$ (Hz)	10.0	16.66	36.66
	T_C ($^\circ\text{C}$)	121.3	129.5	140.7
	ΔG^\ddagger (kcal/mole)	20.87	20.91	20.87
DMA	$\Delta\nu_\infty$ (Hz)	10.5	17.65	37.9
	T_C ($^\circ\text{C}$)	69.7	76.64	87.0
	ΔG^\ddagger (kcal/mole)	18.01	18.03	18.03
DMP	$\Delta\nu_\infty$ (Hz)	9.14	15.23	33.5
	T_C ($^\circ\text{C}$)	53.1	60.0	69.3
	ΔG^\ddagger (kcal/mole)	17.19	17.23	17.20

$$k_C = \pi\Delta\nu_\infty/\sqrt{2} = (kT_C/h) \exp(-\Delta G^\ddagger/RT_C)$$

The first of these lists the proton shifts for three dimethylamides (formamide, acetamide, and propionamide) in the absence of exchange ($\Delta\nu_\infty$), the coalescence temperature (T_C), and the free energy of activation (ΔG^\ddagger), obtained at 60, 100 and 220 MHz. Present instrumentation covers conveniently only a four-fold range in frequency, and in rates. However, this is sufficient to give quite accurate heats and entropies of activation as shown in Table II.

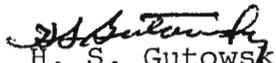
Table II. Activation Parameters from Frequency Dependence Data in Table I

Amide	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (e.u.)
Dimethylformamide	20.88 ± 0.02	0 ± 2
Dimethylacetamide	18.02 ± 0.01	0 ± 1
Dimethylpropionamide	17.21 ± 0.02	0 ± 2

The accuracy of the results obtained in this fashion is limited almost entirely by the accuracy of the temperature measurements, which has been a perennial problem with the spinning samples in conventional nmr probes. This use of the frequency dependence of the coalescence involves standard commercial instruments, and the

experiments and data analysis are relatively very simple compared to other methods of comparable accuracy. Moreover, with further development of superconducting solenoids, I expect it will be possible to cover a ten-fold frequency range in the not too distant future.

With best personal regards,


H. S. Gutowsky
Professor of Chemistry

HSG:cfh

POSTDOCTORAL FELLOWSHIP AVAILABLE

I have been asked to make known the availability *in a laboratory other than my own* of a postdoctoral fellowship. The candidate must not be a U.S. citizen. He or she must have no more than 3 years' postdoctoral experience, have a background in biochemistry, preferably a Ph.D. in protein chemistry or peptide synthesis, and be interested in NMR (proton and carbon-13). The fellowship is for a two year period, at an annual stipend in the range of \$7,000 to \$8,000.

Anyone interested in applying for this fellowship may contact me and I will put them in touch with the appropriate sponsor of this fellowship.

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

Phone: (713) 845-6944



ISTITUTO DI CHIMICA GENERALE

DELL'UNIVERSITÀ DI CATANIA

VIALE A. DORIA, 8 - 95125 CATANIA (ITALY)

CATANIA, 18th Febr., 1974
TEL. 330.533

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

Dear Professor Shapiro,

PMR spectral parameters of diphenyl disulphide

The 60 MHz spectrum of the title compound was of $[AB]_2C$ type. Full analysis was performed by using the LAME program. The parameters listed below were in CS_2 solution (10 mol%).

H-ortho 437.876 H-meta 421.919 H-para 417.781

$J_{om} = 7.673$; $J_{op} = 1.171$; $J_{om'} = 0.501$; $J_{oo'} = 1.945$;

$J_{mp} = 7.365$; $J_{mm'} = 1.566$. (rms 0.038)

All parameters are in Hz from TMS as internal standard.

The magnetic equivalence between chemically equivalent protons suggests free rotation about $C_{ar}-S$ bonds. The view is supported by disappearance of coalescence at -30° . Kinetic parameters cannot be determined owing to the complexity of the spin system dealt with.

Best regards.

Yours sincerely,

Dr. G. C. Pappalardo

DIVISION OF PHYSICAL CHEMISTRY
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

Stockholm, February 18, 1974

Cable address: Technology

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

Dear Professor Shapiro

^{13}C -RELAXATION IN MICELLAR SOLUTIONS

Since a rather long time we have in our laboratory been interested in micelle formation. During the last year we had a ^{13}C -channel installed at our Bruker pulse spectrometer. We have now started to investigate micelles and micelle formation by ^{13}C -NMR. In Fig. 1 we have plotted our ^{13}C -relaxation rates for the alkyl carbons in solutions of sodium n-hexanoate as a function of the inverse of the concentration. There is a clear break in the curve in the concentration range 1,6 - 1,7 M, which can be identified with the critical micelle concentration, CMC. The intercepts in Fig. 1 give the values for the relaxation rates in the micelle. As can be seen the relaxation rates are faster for the micelles than for the monomers. Furthermore the relaxation rates of the different alkyl carbons are more different in the micelles than in the monomers.

Presently we are trying to interpret our results along the

lines of Wallach¹ and Levine et al.². These studies will of course be extended to other surfactants.

Yours Sincerely



Ulf Henriksson



Lars Ödberg

- 1) Wallach, D., JCP 47, 5258 (1967)
- 2) Levine, Y.K., et al. Mol. Phys. 25, 497 (1973).

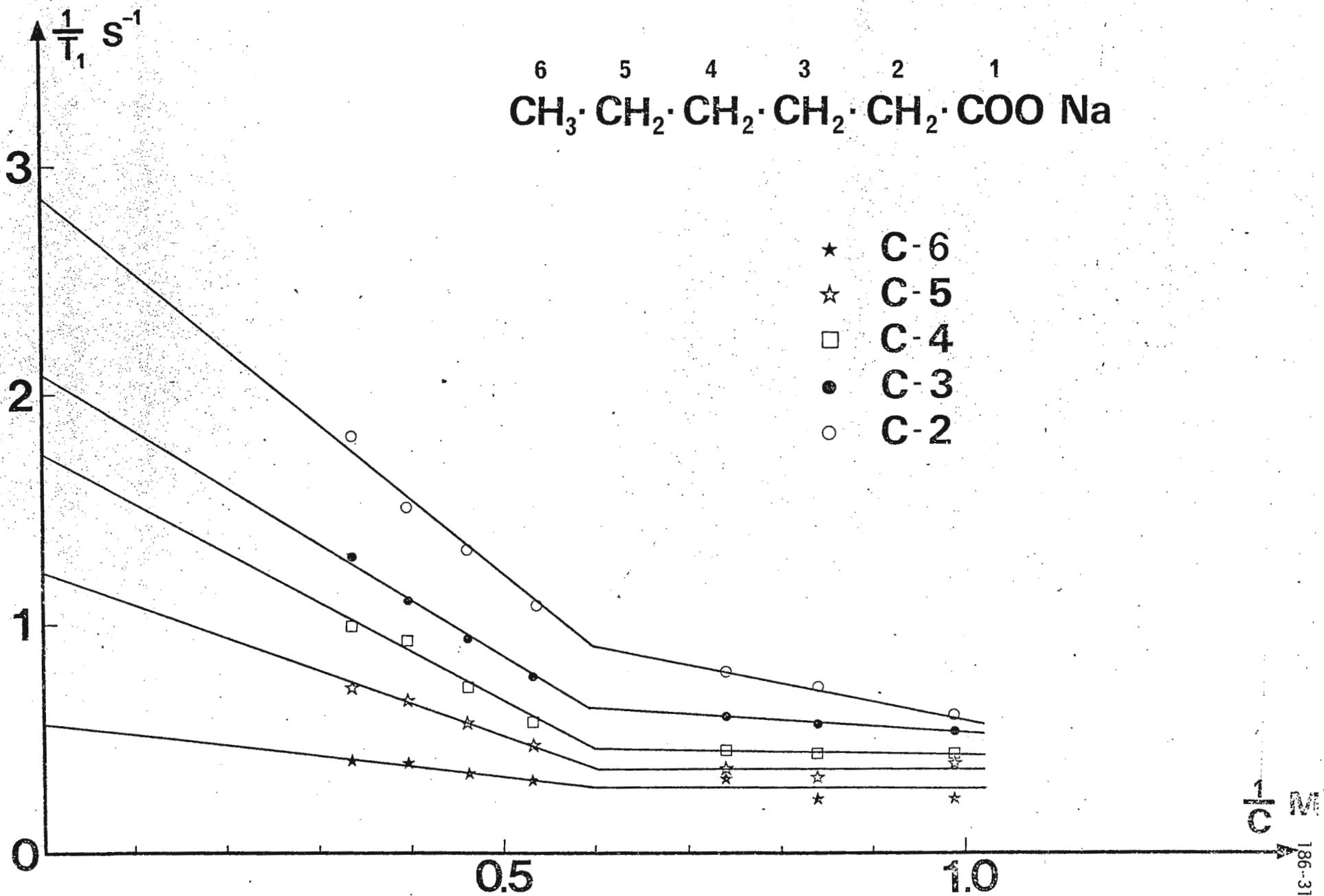


Fig. 1



BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND

FURTHER UTILISATION OF A PDP8-I COMPUTER
FOR NMR INTERFEROGRAM OPERATIONS

Part of our spectrometer system consists of a PDP8-I computer with two 4K memory blocks and a 1074 Nicolet (Fabritek) spectrum accumulator. For some time we have used only one block to store and utilise a fast Fourier transform (FFT) program. The second 4K memory block has been, until recently, only little used. However, in the software package sold by the manufacturer is a tape for compilation of the 'Focal, 1969' computer language. An additional 'patch' provided by Nicolet (Fabritek) enables access to and from the 1074 memory. Programs are fairly easy to write in FOCAL and we have written some to carry out useful operations on interferograms and spectra.

Large amplitude noise 'spike' removal from interferograms, exponential operation (resolution enhancement/filtering), 'off-set' (displacement) removal for interferograms and three point running average (spectrum noise reduction) are four small programs we have found particularly useful.

For operations the FOCAL compiler has to be put in field 0 of the computer and the FFT program in field 1. We enclose a copy of the programs for any interested ~~FAMU~~ newsletter-reader to use. Calculation times are slow-typically two minutes - but in an overall experiment time this is of little consequence.

Paper tape read-in times via teletype are also slow and we should be grateful for any details of an interface for either a Facit or an ICL high speed reader to the PDP8-I.

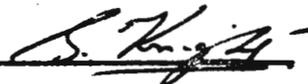
We should like to acknowledge the efforts of Mr M.A. Rothwell of our Applied Physics Branch who was responsible for writing the detailed programs.

Loading Procedure

Data Field 0	Inst. Field 0	Load Address (Octal)
Rim Loader		7756
Binary Loader		7756
"Focal, 1969" 4K Package		7777
Nicolet "FNEW PATCH" for "Focal, 1969"		7777
"Focal, 1969" Programs		200
Data Field 1	Inst. Field 1	
Fast Fourier Transform Program		7777
Extended Memory		7777

Operating Procedure

"Focal, 1969" Programs	1074 in READOUT mode, start address 200
>>Change value in a location	Type T FNEW (location number) press RETURN key
ØØ.1Ø SET S=Ø.Ø	
Ø1.2Ø FOR I=Ø,4Ø95; SET S=S+FNEW(I)	Type S X=FNEW (location number, new value) press RETURN key
Ø1.3Ø SET S=-S/4Ø96.Ø	
Ø1.4Ø FOR I=Ø,4Ø95; DO 2	
Ø1.5Ø QUIT	
>>Centring (Off-set)	Type GO 1.1 press RETURN key
Ø2.1Ø SET Y=FNEW(1)+S	
Ø2.2Ø SET X=FNEW(I,Y)	
>>Exponentiation	Type GO 3.1 press RETURN key (to change value of the time constant)
Ø3.1Ø SET C=-1.Ø	
Ø3.2Ø SET CN=C/4Ø96.Ø	
Ø3.3Ø FOR I=Ø,4Ø95; DO 4	Type Ø3.1Ø SET C = required value press RETURN key
Ø3.4Ø QUIT	
Ø4.1Ø SET X=FNEW(I)*FEXP(CN*I)	
Ø4.2Ø SET Y=FNEW(I,X)	
Ø5.1Ø SET R1=FNEW(Ø)	
Ø5.2Ø SET R2=FNEW(1)	
Ø5.3Ø FOR I=1,4Ø94; DO 6	
Ø5.4Ø QUIT	
>>Three point running average	Type GO 5.1 press RETURN key
Ø6.1Ø SET R3=FNEW(I+1)	
Ø6.2Ø SET X=Ø.25*(R1+R3)+Ø.5*R2	
Ø6.3Ø SET R1=R2	
Ø6.4Ø SET R2=R3	
Ø6.5Ø SET Y=FNEW(I,X)	
Ø7.1Ø FOR I=Ø,2ØØ; DO 8	
Ø7.2Ø QUIT	
Ø8.1Ø SET X=1ØØ*FRAN()	
Ø8.2Ø SET Y=FNEW(I,X)	
*	

S.A. Knight W. Wheatley 



JEOL LTD. 1418 Nakagami Akishima Tokyo 196 Japan
 Telephone: (0425)43-1111 Cable: JEMSCOPE TOKYO Telex: 0-2842-135

Dr. B.L. Shapiro
 Department of Chemistry
 Texas A&M University
 Collage station, Texas 77843
 U.S.A.

Dear Dr. Shapiro,

^{13}C high resolution study in solid adamantane

Recently, many excellent results of ^{13}C high resolution NMR spectra have been reported by Pines, Waugh et al. and the importance of T_1 measurement in order to investigate molecular dynamics was suggested. We also tried the observation of ^{13}C NMR in solid and T_1 measurement. T_1 measurement was carried out by a partially relaxed FT-NMR using the techniques of Pines-Waugh. The used pulse sequence in T_1 measurement is shown in Fig.1. Proton enhanced ^{13}C magnetization after the mixing pulse is turned from x' to $-z$ direction by the first $\pi/2(-y')$ pulse and recovers toward its thermal equilibrium value M_0 with the time constant T_1 . Magnetization $M(t)$ which is allowed to relax for a time t is observed by the second $\pi/2$ pulse and expressed as follows;

$$M(t) = M_0 \{ 1 - (1 + \alpha) \exp(-t/T_1) \}$$

where $\alpha = |M(0)/M(\infty)|$.

Semilogarithmic plot of above equation gives us T_1 as a inverse gradient ($\ln(M(0)-M(t))$ versus t). T_1 is also obtained from null method as $T_1 = t_0 / \ln(1+\alpha)$ when $M(t_0)=0$.

However, time t_0 depends on the enhancement factor which changes according to contact condition. So t_0 must be carefully measured in order to decide T_1 by null method.

In this letter, we would like to introduce the results of temperature dependence of signal intensity and T_1 at 30°C . Fig.2 shows a temperature dependence of ^{13}C signal intensity of solid adamantane. Signal intensity increases as lowering temperature, and suddenly falls below -50°C .

At last, signal disappears into noise level at about -60°C (transition point T_r). This phenomenon is explained as follows. Molecular motion becomes slower as decreasing temperature, so dipole-dipole interactions of C*H is increasing and enhancement comes to maximum about -50°C . Below T_r , however, dipolar interaction is too strong to be decoupled by proton irradiation power (about 10 gauss). Therefore, ^{13}C signals cannot be observed. Fig.3 shows a partially relaxed spectra of ^{13}C of solid adamantane at 30°C . T_1 value of methylene and methine carbon is 1.3 sec and 2.1 sec, respectively. This result suggests that the ^{13}C relaxation in solid is dominated by intramolecular C-H dipole-dipole interaction as same as in liquid.²⁾ So isotropic tumbling motion may occur in this molecule at this temperature. We are now undertaking T_1 measurement at various temperatures.

Yours sincerely,

T.Fujito, H.Higuchi, and M.Imanari

T. Fujito *H. Higuchi* *M. Imanari*

References

- (1) A.Pines, M.G.Gibby, J.S.Waugh ; J.Chem.Phys. 59 569(1973)
- (2) K.F.Kuhlman, D.M.Grant, R.K.Harris; J.Chem.Phys. 52 3439(1970)

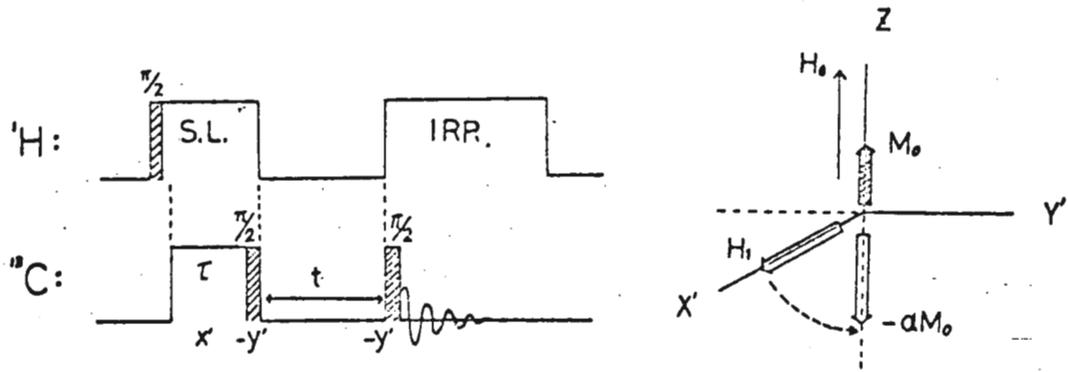


Fig.1 Pulse sequence for T_1 measurement

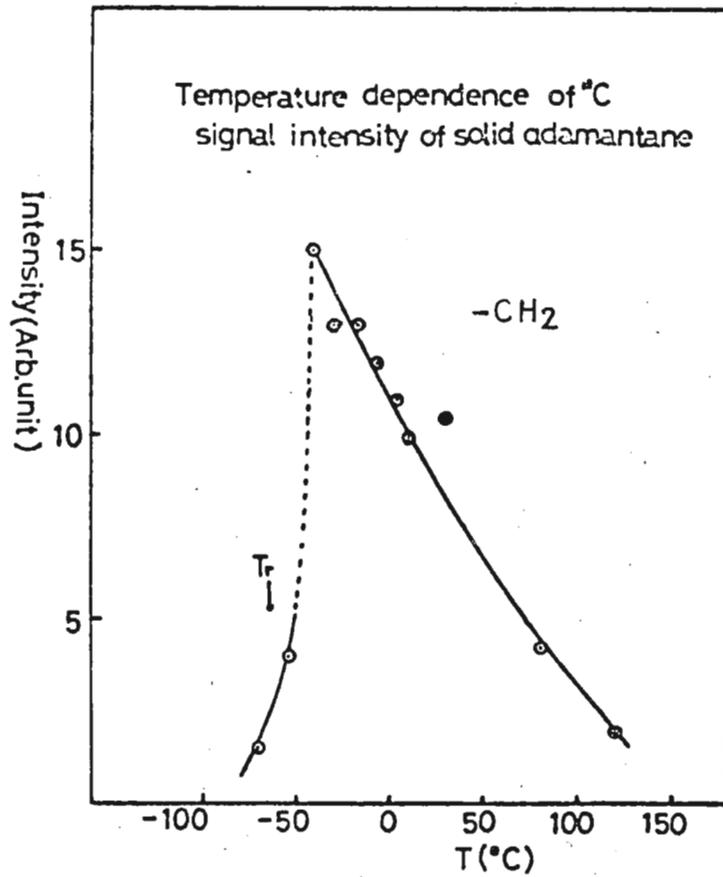


Fig.2

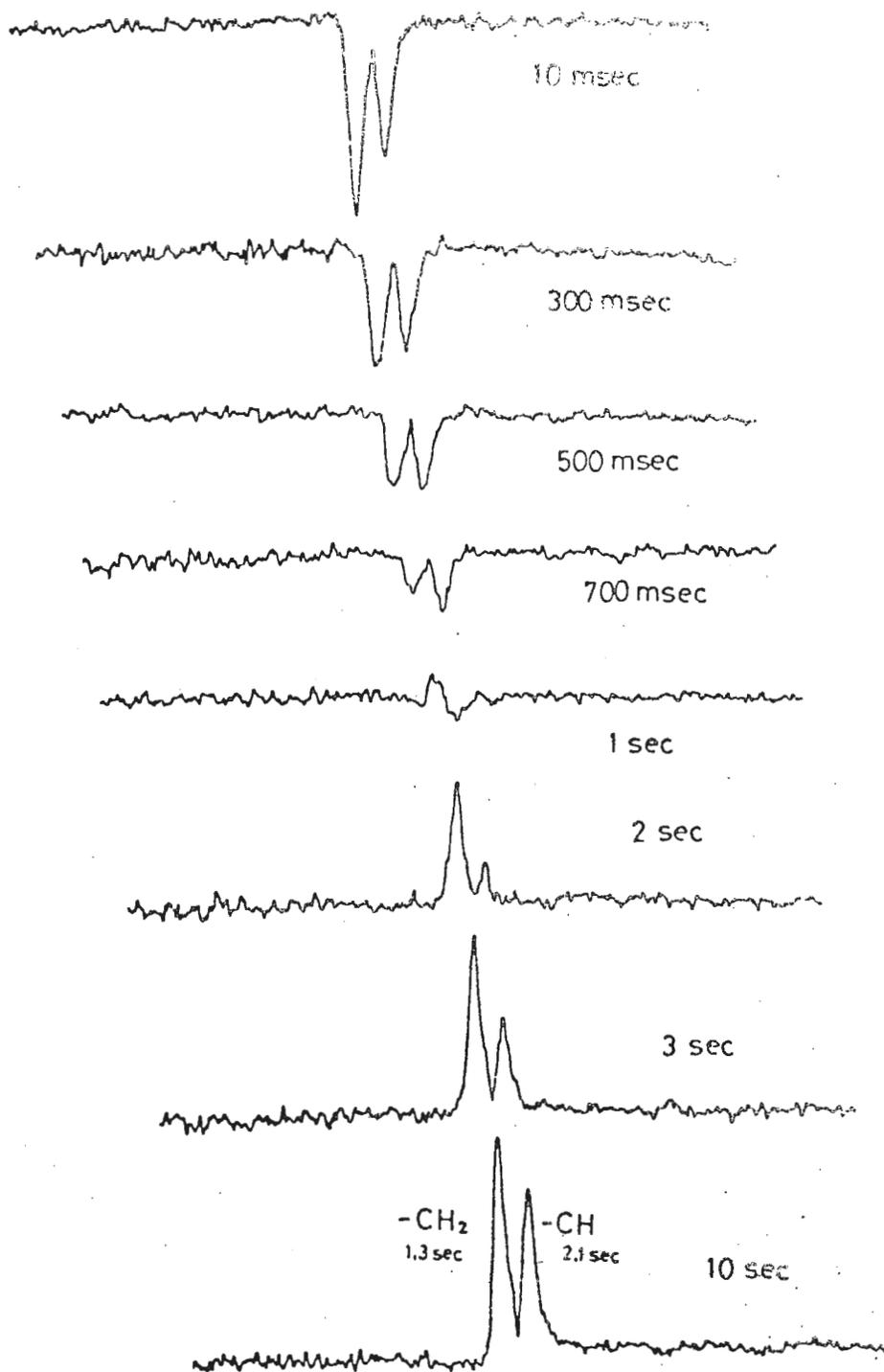


Fig.3 Spectra for T_1 measurement of solid adamantane

UNIVERSITY OF COLORADO

BOULDER, COLORADO 80302

February 21, 1974

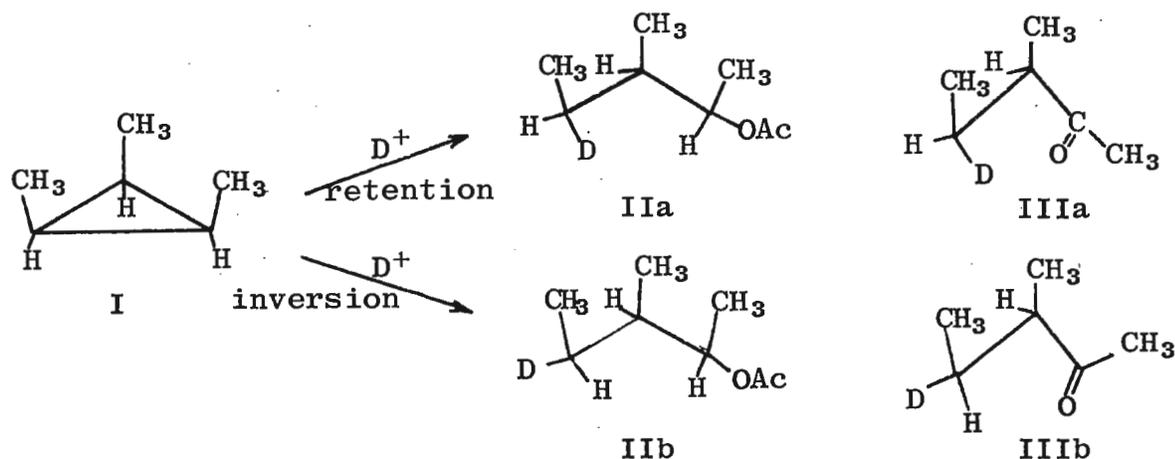
DEPARTMENT OF CHEMISTRY

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

Dear Barry:

Although a number of laboratories have the capability of determining deuterium magnetic resonance (dmr) spectra, the utility of this technique for studying organic reaction mechanisms still does not seem generally recognized. Since the relative chemical shifts of the various deuterons in a molecule are exactly the same as those for the corresponding protons, one does not have the problem of peak assignment so often encountered in cmr. In addition the relatively small J_{H-D} ($1/6.5 J_{H-H}$) serves to simplify the spectrum. We have found dmr to be extremely useful in some studies we have been carrying out on the stereochemistry of the ring opening of cyclopropanes.

Reaction of cis-1,2,3-trimethylcyclopropane (I) with acetic acid O-d gives a diastereomeric mixture of mono-deutereo acetate (IIa,b), which was converted into the corresponding mixture of ketones IIIa and IIIb.



Our problem was to determine the amount of deuterium in the erythro (IIIa) and threo (IIIb) positions of 4-deutereo-3-methyl-2-pentanone. In principle this can be done by analysis of the

pmr spectrum, since the two diastereotopic protons are clearly separated in the presence of shift reagent (Spectrum B) In practice, however, the results are not satisfactory because one proton is partially obscured by a methyl resonance, and also because of the the presence, in some experiments at least, of appreciable amounts of non-deuterated ketone (HX reacts faster than DX) which dilutes the spectrum and makes the integration inaccurate.

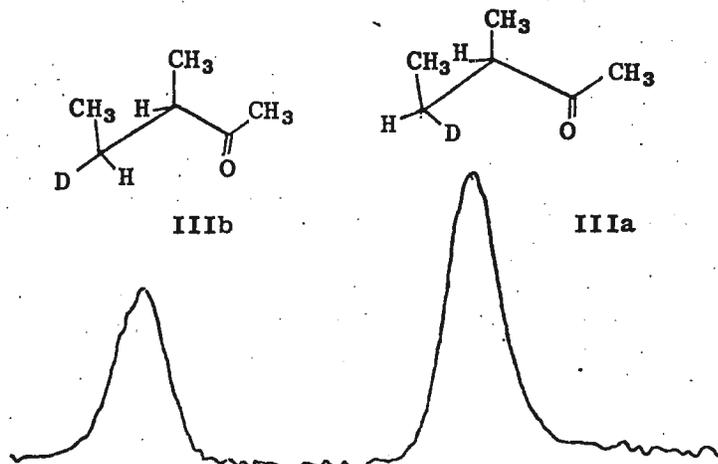
The dmr spectrum (Spectrum A) consists of only two peaks, one for the threo and one for the erythro deuterium atom. The methyl resonance no longer interferes for it contains no deuterium. We are looking here only at the product which actually reacts with a deutron; any diproteo species is irrelevant. We have found the integrations to be reproducible and known mixtures can be analyzed to within a few per cent. As this spectrum shows, the reaction occurs with predominant (68%) retention of configuration.

I wish to acknowledge the work of A. H. Andrist, P. C. Fünfschilling, and M. Ashley.

Sincerely yours,

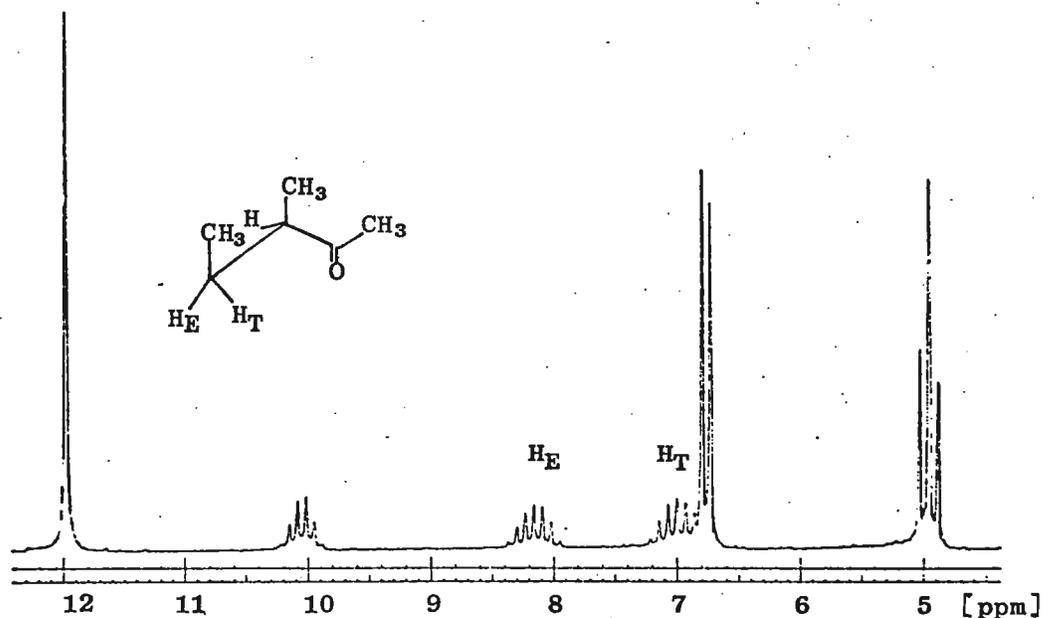


C. H. DePuy
Professor of Chemistry



A. DNMR spectrum of 4-deutero-3-methyl-2-pentanone [24 mg ketone + 120 mg $\text{Eu}(\text{fod})_3$ in 450 μl $\text{CCl}_4/\text{CFCl}_3$ 1:1]; mixture of the erythro isomer IIIa (68%) and the threo isomer IIIb (32%).

Instrument:	Jeol PFT-100
Frequency:	15.350265 M Hz
Pulse:	Single 45°
Width:	10.3 μsec .
Repetition:	5.3 sec.
Data points:	2048
Window Exp. T.C.:	-2.3
Mode:	Real
Spectrum width:	500 Hz
Filter:	500 Hz
Amplitude:	10.100
Number of scans:	2048
Lock (^{19}F):	94.09782 M Hz



B. 100 M Hz-PNMR spectrum of 3-methyl-2-pentanone [88 mg ketone + 345 mg $\text{Eu}(\text{fod})_3$ in 375 μl CCl_4 and 200 μl TMS].

**CENTRAL RESEARCH**PFIZER INC., EASTERN POINT ROAD, GROTON, CONNECTICUT 06340
203-445-5611

March 1, 1974

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

Dear Professor Shapiro:

I am enclosing a description of a position that we are anxious to fill within the month.

SPECTROSCOPIST

A permanent position is available for a suitable professional who will be responsible for setting up and overseeing a small research unit based on the acquisition of two recently authorized instruments - a 100 MHz FT $^1\text{H}/^{13}\text{C}$ NMR and a double focusing mass spectrometer with element map capabilities.

The successful applicant will have the following qualifications:

1. On-the-job experience in applying spectroscopic techniques in devising solutions to challenging structure and identification problems in organic chemistry based on effective day-to-day interactions with a large group of Ph.D.-level synthetic organic chemists and emphasizing the cooperative identification of problems and approaches to their solution.
2. Suitable instrumental maintenance experience.

Salary dependent on experience and qualifications. Interested and qualified candidates should immediately contact:

Dr. Walter T. Moreland
Executive Director
Medicinal Chemistry Research
Pfizer Inc.
Groton, Connecticut 06340

Very truly yours,

C. J. V. Scanio

/bb

IN REPLY PLEASE QUOTE
REF. NVR.RC

THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W. Australia.
DEPARTMENT OF ORGANIC CHEMISTRY.
5th February, 1974.

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

Dear Professor Shapiro,

- Subjects: (a) Swept Audio-Sideband ^{13}C -N.M.R. Spectroscopy
(b) Some Dielectric-Constant Effects on the Response of C.W.
and PFT Probes.

(a) Pulse and Fourier-transform (PFT) n.m.r. spectroscopy is now clearly the method of choice for most measurements of ^{13}C n.m.r. (c.m.r.) spectra, and construction of our own PFT system is now well advanced. During the past two years or so we have however successfully measured many hundreds of c.m.r. spectra by the swept audio-sideband c.w. method on a modified Varian HA60-IL spectrometer, designed basically to measure ^1H n.m.r. spectra at 60MHz (or, with appropriate transmitter, probe, and receiver retuning, ^{19}F n.m.r. spectra at 56.445MHz). Although it may appear old-hat, this represents the simplest and cheapest method of modifying the original (or similar) instrument for c.m.r. spectroscopy, and the system may readily be returned to its original uses; the conversion may therefore appeal to those who have such an instrument and wish to measure c.m.r. spectra but whose electronics-construction facilities and/or budget are limited. We can give appropriate details or advice within the limitations of our knowledge and experience to individuals or groups who request specific further information, but here we wish only to outline some important considerations in setting up such a system. One particular advantage of any c.w. method is that resolution may be easily improved by sweeping arbitrarily small spectral widths without filtering problems such as arise in PFT methods.

Amongst obvious requirements in addition to the basic instrument, for our system (14092 gauss magnet), Varian Associates supplied a V4311 RF transceiver unit and a V4336 probe operating at 15.086MHz (the latter double-tuned to accept also high-power RF at 60MHz for proton decoupling) and, to allow frequency sweeping, a Wavetek Model 111 VCO driven from a voltage ramp generated by a Varian 620/i 8K computer which also adds and stores the signals in 2660 discrete channels during multi-scan accumulations. (Other combinations of suitably stable VCO and/or signal-averaging systems such as a CAT1024 that provide a linear voltage ramp could be used). We have constructed our own proton-decoupling system: basically it consists of a crystal-controlled oscillator at 60MHz the output of which is modulated with a HP8057A noise-generator (bandwidth set typically to 300Hz) and amplified to ca. 20 watts of which ca. 10 watts is fed to the probe. To allow the centre frequency of the decoupling band to be set at an appropriate point in the proton spectrum or sufficiently outside it for off-resonance decoupling, the crystal oscillator can be "pulled" about 1kHz by a variable capacitor in series, but the actual range of centre frequencies required was determined by trial-and-error after the exact magnetic-field strength had been chosen as below.

The range of audio-sideband frequencies to be swept and the fixed locking frequency must be carefully chosen. A total range of 250 p.p.m. (3.75kHz at 15MHz) covers resonances from most "ordinary" organic compounds but, at the high RF power levels required (typically we use the full 0.5 watt output of the V4311 unit and sweep rates of 5-10Hz/sec), the baseline response may vary strongly with frequency over much smaller ranges. Our probe would be quite unuseable at frequencies below 12kHz, and the response of the standard HA60-1L detector circuits, falls off markedly beyond 18-20kHz, but most signals of interest lie in a reasonably flat-baseline region (13-16kHz) if the first upper sideband resonance of $^{13}\text{CH}_3\text{I}$ at a fixed frequency of 12.5kHz (obtained by mixing the outputs of two stable crystal oscillators at 200 and 212.5kHz) is used as lock signal; an adequately strong continuous signal is generated from a 1g. sample of 60% isotopically enriched $^{13}\text{CH}_3\text{I}$ in a sealed 5 mm tube mounted concentrically in the 10 or 12 mm sample tube. It was found advantageous to include a simple phase-shifting circuit in the analytical (swept) channel. Multi-scan accumulations on sweep-widths up to 25 p.p.m. (375Hz) usually show acceptably small baseline distortion, but substantial distortion may be observed for wider sweep-widths, especially at sweep frequencies beyond 14kHz in the olefinic-aromatic region. We have written a polynomial curve-fitting subroutine which effects major corrections rapidly (2 sec.), but numerical integration of our spectra, whether baseline-corrected or not and whether wide or narrow sweep, is not feasible; this has not proved a major disadvantage.

(b) Besides the paddles for minimizing transmitter-receiver leakage, a means of tuning the probe receiver coil for maximum signal response as provided on the Varian V4336 probe is essential if the best or even adequate signal-to-noise ratio (S/N) is to be achieved for any given sample mixture. For example, Mr. A. Marker found that, if the probe is tuned for maximum response with cyclohexane as sample (routinely used for homogeneity adjustment) and is not retuned for a sample of high dielectric constant such as a solution in DMF or DMSO, S/N may be so low that field-frequency lock on the 5 mm enriched $^{13}\text{CH}_3\text{I}$ sample cannot be maintained; with retuning however no such difficulty is experienced and high-quality c.m.r. spectra of such samples as 1M aqueous sucrose solution have been obtained. Although the Varian engineers were apparently aware of it, we have not seen this effect discussed in the literature. We are presenting a detailed theory and experimental results in a paper now being prepared for publication. Here we point out that, for $Q = 300$, a typical quality factor for the receiver coil of an n.m.r. probe, a change of 1% in the equivalent capacitance at resonance of the parallel resonant circuit concerned leads to a reduction of 70% in the rf energy admitted by the circuit. Fortunately the effect is less important for our transmitter coil; it is double-tuned for 15.1 and 60.0 MHz, and we should not care to tamper with it. For a single-coil PFT n.m.r. probe however the effect may be especially serious: for a particular probe, we have found 90° pulse-widths for $^{13}\text{CH}_3\text{I}$ to increase from 15 μsec to 23 μsec when the medium was changed from cyclohexane to formamide without retuning of the probe. If the pulse-width in the latter case were held at 15 μsec , the flip angle would be only ca. 59°, and S/N would thereby be reduced ca. 14%; as discussed above, receiver detuning would lead to further loss of S/N. Naturally the accuracy of any measurement that depends upon knowledge of the actual flip angle will be adversely affected if the experiment is set up without due regard to the above effect.

Yours sincerely,

D. DODDRELL.

N.V. RIGGS.

ABBOTT LABORATORIES, SCIENTIFIC DIVISIONS
NORTH CHICAGO, ILLINOIS 60064

February 11, 1974

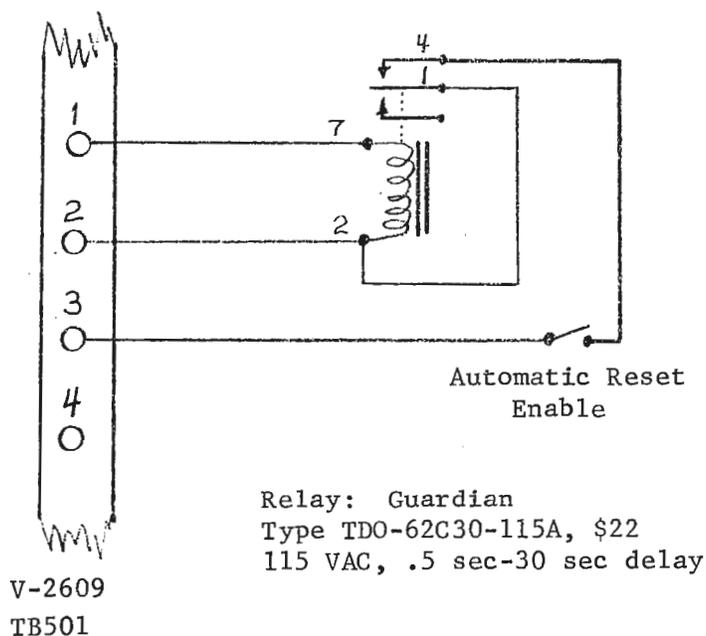
Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Genie Automatic Magnet Turner-Onner

Dear Barry:

In the Midwest we are blessed with frequent electrical storms in the spring and fall. These storms often result in momentary power blackouts which turn off the magnet on our HA-100. As this circuit in the V-2609 is held on by an electrically latched relay, it does not come back up when the power resumes. All too often this happens in the middle of the night and we come in to a cold magnet the next morning.

We have added a simple circuit to the HA-100 magnet power supply which will turn the magnet back on automatically after a power failure, but will not turn it on after it is pulled off by an over-temperature or a water safety shutdown. This last point is important to prevent damage to the system in the event of a malfunction either in the electronics or in the cooling system.



The relay coil is on a 115V line connected directly to the power mains. If this voltage fails, contacts 1 and 4 close to override the manual turn-on button. When the power comes back on, this immediately turns the magnet back on; however, after a few seconds this relay times out and will not hold the magnet on if a thermoswitch indicates a fault condition.

Your readers might also be interested to know that we have replaced the 1N1185A's in the main power bridge with 1N2130's which are rated at almost twice the current and hence run cooler. We have also provided extra tabs of #12 copper wire on the anodes of each diode for better heat dissipation.

Please credit this contribution to R. S. Egan. Thanks.

Sincerely yours,


Milton I. Levenberg


Richard S. Egan

msg

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

Dear Prof. Shapiro:

¹³C-NMR-Spectra of [1.2]-Spirenes

[1.2]-spirenes have been of considerable interest in connection with spiro-conjugation¹ and photochemical and thermal reactions¹ of these systems. The special properties of 1-4¹ as well as ring strain should also be reflected in the cmr spectra of these compounds. Chemical shifts (δ in ppm) for [1.2]-spirenes (1-4) are listed in table 1.

	<u>R¹ = R²</u>		<u>R³</u>
<u>1</u>	H	H	-CH ₂ -CH ₃
<u>2</u>	Cl	Cl	CO ₂ CH ₃
<u>3</u>	Ph	Ph	CO ₂ CH ₃
<u>4</u>	o-phenylene		CO ₂ CH ₃

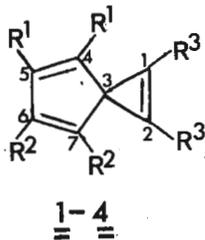


Table 1: CMR-Spectra of [1.2]-Spirenes in CDCl₃ (chemical shifts relative to TMS)

compound	$\delta(1/2)$	$\delta(3)$	$\delta(4/7)$	$\delta(5/6)$	$\delta_{C=O}$	δ_{-CH_3}
(δ in ppm)						
<u>1</u>	119.5	41.0	139.9	129.0		12.5 20.0(CH ₂)
<u>2</u>	118.8	49.6	128.6	128.1	155.7	53.7
<u>3</u>	124.9	40.2	143.9	135.5	157.9	52.9
<u>4</u>	120.7	44.5	144.5	140.7	158.1	52.9
<u>5</u>	31.9	43.1	129.8	127.7	164.6	52.7

Table 1 shows that in the [1.2]-spirenes 1-4 the spiro-carbon C-7 is at highest field (δ : 40.2-49.6 ppm). The higher ring strain in 2 compared to the spirane 5 is borne out by a downfield shift of +6.5 ppm. If fluorene (sp³-C: 38.1 ppm) and tetraphenyl-cyclopentadiene (sp³-C: 45.5 ppm) are compared one notices the expected downfield shift (+6.4 ppm) for C-3 for 4. In 3 however the C-3 resonance experiences an upfield

shift of -5.3 ppm. In the fluorene moiety of 4 the spirene double bonds are buried in the aromatic system. Therefore the upfield shift in 3 might be attributed to spiro-conjugation.

Financial support of the Deutsche Forschungsgemeinschaft as well as the Verband der Chemischen Industrie is gratefully acknowledged.

(H. Dürr)

(H. Kober)

(B. Ruge)

¹ H. Dürr and B. Ruge, Angew. Chem. 85, 616 (1973);
H. Dürr and L. Schrader, Chem. Ber. 103, 1334 (1970).

AUTHOR INDEX

Aime, S.	11
Blackburne, I. D.	8
Contreras, R. H.	6
Dennis, N.	16
DePuy, C. H.	38
Doddrell, D.	42
Durr, H.	46
Egan, R. S.	44
Ernst, R. R.	1
Fujito, T.	34
Gutowsky, H. S.	25
Happe, J.	15
Henriksson, U.	29
Higuchi, H.	34
Hořder, B. E.	15
Imanari, M.	34
Katritzky, A. R.	8
Knight, S. A.	32
Kober, H.	46
de Kowalewski, D. G.	6
Levenberg, M. I.	44
Odberg, L.	29
Pappalardo, G. C.	28
Randall, E. W.	5
Riggs, N. V.	42
Robb, I. D.	22
Ruge, B.	46
Sallis, R.	22
Sayer, B. G.	20
Scanio, C. J. V.	41
Shapiro, B. L.	27
Takeuchi, Y.	8
Takeuchi, Y.	16
Werstiuk, N. H.	20
Wheatley, W.	32



This is the turning point in FT NMR research.



Introducing the JEOL EC-100. It's the first commercial real-time NMR data reduction system.

Now, simply by touching a button and turning the single parameter vernier control, accurate and reliable analysis can be accomplished in real-time.

Such functions as vertical expansion or shift, horizontal expansion or shift and real-time phase correction have been simplified as never before. Not only has data manipulation been advanced, data display is more complete. Results are provided in real-time CRT display, on direct frequency shift display, by digital printout, and through traditional plotting methods.

The EC-100 is a joint development of our computer engineers and analytical research staff. They set about designing a system that would be fast, accurate and reliable. They also sought to create a computer system that virtually anyone in the lab can utilize. The result is the EC-100, a system for truly practical research. Practical in capability, operation and price.

Currently, the EC-100 is being utilized with all models of JEOL FT NMR systems. In the near future it will encompass applications on all appropriate JEOL systems and will offer retrofitting packages for many non-JEOL products.

You should learn more about it. Simply write JEOL, Analytical Instruments Division, 235 Birchwood Ave., Cranford, N.J. 07016. Tel. (201) 272-8820.



JEOL

INSTRUMENTATION: Scanning Electron Microscopes / Electron Microscopes / X-ray Microprobes / NMR Spectrometers / Mass Spectrometers / ESR Spectrometers / Laser Raman Spectrophotometers / Gas Chromatographs / Laboratory Computers / X-ray Diffractometers / Amino Acid Analyzers / Sequence Analyzers / Electron Beam Apparatus.
WORLDWIDE: 16, Avenue de Colmar, 92 Rueil-Malmaison (Paris) / Grove Park, Edgware Road, Colindale, London N.W.9 / 3-3-1 Marunouchi, Chiyoda-ku, Tokyo 100 / 477 Riverside Avenue, Medford, (Boston) Massachusetts 02155 / Australia and New Zealand, Austria, Benelux, Brazil, Canada, Colombia, Germany, Italy, Scandinavia and Finland, South Africa, Spain and Portugal, Switzerland, Venezuela.

Varian has an NMR system for every application...

for instance, the new CFT-20 for Carbon-13

Varian, world leader in magnetic resonance spectroscopy, offers a complete selection of NMR spectrometers, from low-cost instruments designed to solve the typical problems of industrial and academic laboratories to the ultimate in research systems.

EM-300X

World's lowest priced, high resolution NMR system. A really economical thermostatted 30-MHz permanent magnet system that produces highly informative spectra on a wide variety of compounds. Like higher performance proton spectrometers, it uses 5-mm samples, contains a built-in integrator, has a homogeneity adjust circuit for fast tune-up, and includes a flatbed recorder with precalibrated chart paper. Its ruggedness, small size, low weight and easy operation make it ideal for routine analyses and teaching applications.

EM-360

A legend in its own time. Reaction from hundreds of scientists who have seen it in operation has been unanimous: with its resolution (0.6 Hz), its sensitivity (18:1), and most of all, its extremely low price, the 60-MHz EM-360 is being hailed as one of the most outstanding contributions to the field of NMR to come along in years. And it's available with a lock/decoupler accessory.

T-60A

A brand new, old reliable spectrometer. The old, reliable part of the T-60A is a heritage of fine workmanship and dependability inherited from the renowned System T-60.

The brand new aspect includes a wide range of improved features—sensitivity in excess of 30:1; resolution better than 0.3 Hz; resolution stability of 0.5 Hz per day; more sweep widths; and more sweep times. Yet even with all this improved capability, the T-60A costs no more than the System T-60 before it.

CFT-20

Varian's newest instrument, the first low-priced NMR spectrometer specifically designed for ^{13}C spectroscopy. Its low impedance electromagnet is double-thermally insulated for excellent long-term stability. And the magnetic field is so homogeneous, the CFT-20 can accommodate 10-mm sample tubes for room temperature experiments and 8-mm sample tubes over the temperature range of -80°C to $+200^\circ\text{C}$. The operating console houses a keyboard for entering operating parameters and experimental commands; an oscilloscope that can display alphanumeric characters or spectral data; an X-Y plotter; and a built-in 620L-100 minicomputer with 8,192 words of memory. If that's not enough, the CFT-20 also features: internal pulsed deuterium lock; continuous wave, noise modulated and gated decoupling; Autoshim™; and a built-in read only magnetic tape cassette for loading programs. Best of all is the price. Ask about it. You'll be surprised.

XL-100

The industry standard. A pulsed-Fourier transform or frequency swept high resolution 23.5-kG spectrometer. It features observing capability from 7 to 100 MHz and decoupling range from 2.9 to 58 and 94 to 100 MHz for continuous wave, noise decoupling or INDOR experiments. The availability of homo- or heteronuclear internal lock on ^1H , ^{19}F , and ^2H , and external lock on ^1H and ^{19}F provides locking flexibility. Fourier transform operation, T_1 measurements, homonuclear decoupling and solvent elimination techniques are also routine XL-100 operations. The XL-100 can be tailored to meet single purpose or multi-departmental NMR needs.

SC-300 and SC-360

For the highest performance in commercially available high resolution NMR spectrometers. The SC-300 (300 MHz) and SC-360 (360 MHz) spectrometers are engineered for use in applications requiring the highest magnetic field strengths—liquid crystal, biological, biopolymer, and biochemical studies. Accessories are available for observation of other nuclei in both continuous wave and Fourier transform modes.

If you'd like more information on any of these systems, see your local Varian representative or write Varian Instrument Division, 611 Hansen Way, Palo Alto, California 94303.

varian instruments 

Brand names: ANASPECT™ • CARY® • MAT • VARIAN®
VARIAN AEROGRAPH® • VARIAN TECHTRON

CFT-20

