Texas A & M University N-M-R Newsletter

No. 217

October, 1976

G. E. Hawkes
^{15}N NMR of Polymixin B and ^{15}N-(^{1}H) Off-Resonance. 1

H. Shindo
Sensitivity Improvement in High Resolution C-13 NMR at 68 MHz 4

B. R. Appleman
Fluorine Shielding Anisotropies in Trifluoromethyl Systems. 7

A. Ripamonti and E. Martinelli
^{13}C NMR Spectrum of Tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octanedione-d_3)-europium(III), Eu(FOD)$_3$-d_{27}. 10

A. Briguet, J. Delmau and J. C. Duplan
Transistorisations sur Spectromètre HA 100: II Replacement de l'USA 3. 13

K. L. Servis and K. G. Sharp
A Remarkably Small Geminal F-F Coupling in a Fluorosilane. 14

J.A.G. Drake, D.W. Jones and H. Pakdel
Solvent Shifts in 220 MHz ^{1}H Spectra of Dibenz [b,f] oxepin. 17

V. J. Kowalewski
Consumer Report: Nicolet NMR-812. 19

I. C. P. Smith
A Comprehensive Review of Deuterium NMR in Chemistry, Physics and Biology. 21

H. Günther
Postdoctoral Position Available. 21

S. E. Ulrich
Low Temperature Studies on a JEOL NMR Spectrometer 24

B. D. Sykes
T_2 Measurements at 270 MHz 25

P. D. Ellis
A Multinuclear 18mm Probe, ^{113}Cd NMR of Metalloproteins; Postdoctoral Position Available. 28

R. A. Komoroski
Detailed Interaction of Aqueous Salts with Random Coil Polypeptides. 31

C. P. Beeman and K. L. Williamson
"High Speed" Optical Paper Tape Reader . .33

H. Dürr and K. H. Albert
^{13}C NMR Studien an Bicyclen. 35

J.P.C.M. van Dongen, C. Masters and A.D.H. Clague
Measurement of ^{195}Pt NMR Parameters in Pt_2Cl_4 (Pn-Bu_3)$_2$ 42

K. Takahashi, C.A.G. Haasnoot, C. Erkelens and J. Lugtenburg
Modification of the JEOL DP-1 Pulse Programmer 45

A. de Bruyn and M. Anteunis
Conformation and Remarkable High Coupling Values of the 2,5-cis-disubstituted tetrahydrofuran Ring in NONACTIN-Potassium Complex. 47

T. Nakashima
Homemade ^{13}C Micro Insert for HFX-90's . .49

J. A. den Hollander
Rate Constants from CIDNP Enhancement Factors. 51

R. D. Knapp
Temperature Effects on Dextran ^{13}C NMR . .53

L. T. Muus
NATO Advanced Study Institute on "Chemically Induced Magnetic Polarization", Urbino, Italy, April 17-30, 1977 54

S. Barcza and J. H. Eckhardt
Nuclear Magnetic Resonance Spectrometer Probe Protection 55

N.M. Szeverenyi, R.R. Vold and R.R. Vold
A Ubiquitous Impurity in Our ^{14}N NMR Spectra. 57

S. Barcza
Position Available: Organic NMR 58

A. S. Mildvan and R. K. Gupta
Notice of Position Available 59

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All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
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AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 217

Albert, K. H. 35
Anteunis, M. 47
Appleman, B. R. . . . 7
Barcza, S. 55
Barcza, S. 58
Beeman, C. P. 33
Briguet, A. 13
de Bruyn, A. 47
Clague, A. D. H. . . 42
Delmau, J. 13
van Dongen, J.P.C.M. 42
Drake, J.A.G. 17
Duplan, J. C. 13
Durr, H. 35
Eckhardt, J. H. . . . 55
Ellis, P. D. 29
Erkelens, C. 45
Gunther, H. 21
Gupta, R. K. 59
Haasnoot, C. A. G. . 45
Hawkes, G. E. 1
den Hollander, J. A. 51
Jones, D. W. 17
Knapp, R. D. 53
Komoroski, R. A. 31
Kowalewski, V. J. 19
Lugtenburg, J. 45
Martinelli, E. 10
Masters, C. 42
Mildvan, A. S. 59
Muus, L. T. 54
Nakashima, T. 49
Pakdel, H. 17
Ripamonti, A. 10
Servis, K. L. 14
Sharp, K. G. 14
Shindo, H. 4
Smith, I. C. P. 21
Sykes, B. D. 25
Szeverinyi, N. M. 57
Takahashi, K. 45
Ulrich, S. E. 24
Vold, R. R. 57
Vold, R. R. 57
Williamson, K. L. 33

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

26th August, 1976

^{15}N N.M.R. of Polymixin B and ^{15}N-(^{1}H) Off-Resonance.

Dear Professor Shapiro,

As part of our continuing work on ^{15}N at natural abundance I want to show a problem and a solution, although the two are not directly related.

First the problem - the ^{1}H noise-decoupled ^{15}N spectrum of Polymixin B sulphate. This represents an over-night run on the Bruker WH-180 in Karlsruhe-Forchheim (thanks to Bill Hull for his assistance). The sample was ca. 3.3 g. in 20 ml. H_2O in 25 mm o.d. tube; 5 mm concentric D_2O for lock. The molecule comprises only four types of amino-acids: α,γ-diaminobutyric acid (6 units), threonine (2 units), phenylalanine (1 unit), and leucine (1 unit). However we observe all eleven amide nitrogens - the peak marked * showed a small splitting in a subsequent spectrum. Thus our long term problem is to assign this, and other, peptide spectra where differential conformational, solvation, and sequence effects are influencing the shifts. Our only assignment so far is the lowest frequency resonance (11.8 p.p.m.) is due to the side-chain $-NH_3^+$ groups and the highest frequency peak (105.4 p.p.m.) is due to Phe.

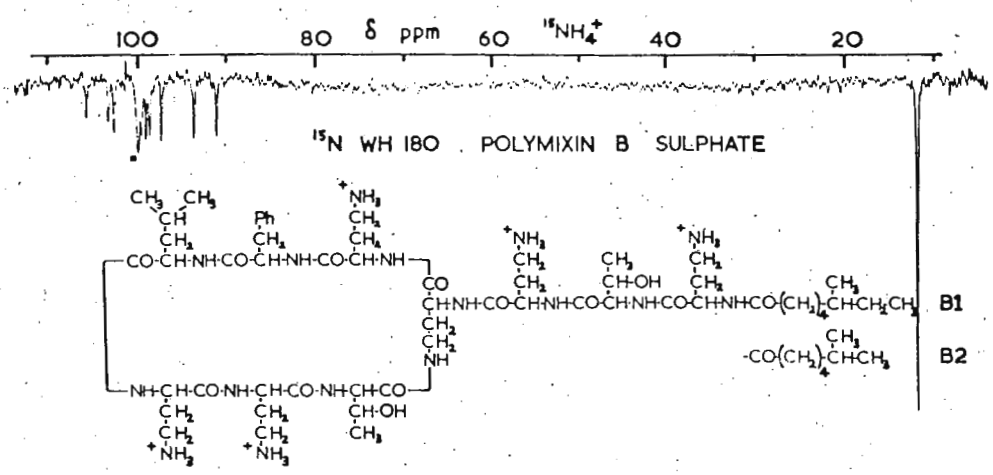
Next a solution - we have not yet seen any other reports on the use of off-resonance ^{1}H (CW) decoupling as an assignment aid in nitrogen n.m.r., so I present two examples. The spectra were run at 9.12 MHz on the HFX-13 here at QMC. The upper trace is from isopropylurea (2M in DMSO); the doublet and triplet make the assignment unambiguous. The lower trace is from hydantoin (2M in DMSO); the expected pair of doublets was not found. Obviously the imide proton is exchanging sufficiently fast to wash out the residual splitting. The amide nitrogen however shows the doublet splitting. Interestingly the resonances in both spectra are inverted by the ^{15}N-(^{1}H) NOE, in spite of the off-resonance character of the ^{1}H irradiation.

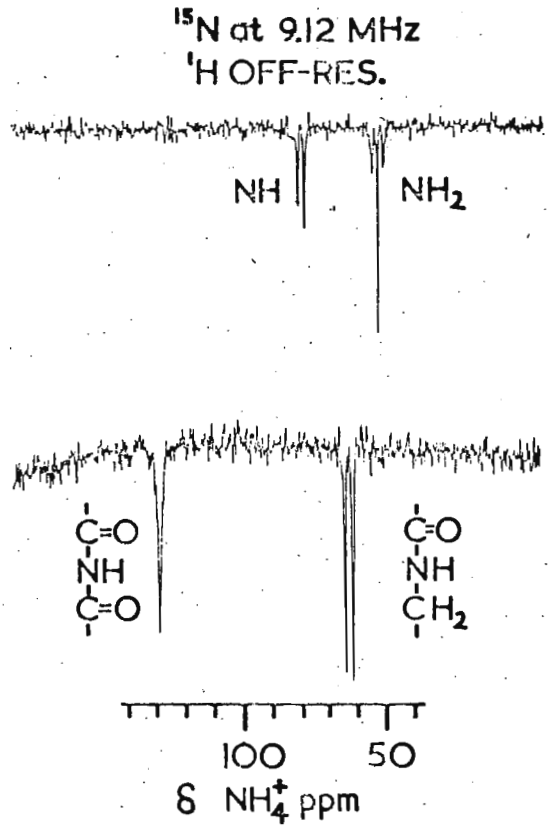
Best wishes from Ed Randall, and please credit this contribution to his group.

Yours sincerely

Geoff Hawkes

Dr. G.E. Hawkes


100
80
δ ppm
60
$^{15}NH_4^+$
40
20
^{15}N WH 180 POLYMIXIN B SULPHATE
B1
B2


^{15}N at 9.12 MHz
^{1}H OFF-RES.
NH
NH_2
C=O
NH
C=O
C=O
NH
CH_2
100
50
δ NH_4^+ ppm

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Building 2, Room B2-08E

September 1, 1976

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

Dear Professor Shapiro:

Sensitivity Improvement in High Resolution C-13 NMR at 68 MHz

For the last year we have been studying ^{13}C at 68 MHz with a homemade spectrometer (NIH-270) and a Bruker superconducting magnet and probe. We have found the dispersion provided by the high field to be essential for many studies in biochemical systems, and some of our successful results are reported elsewhere.[1,2] Sensitivity and temperature control while decoupling have constituted the principal problems for our studies. We have now achieved some improvement by designing and building a new probe, patterned after the Bruker probe, but with two important modifications: (1) provision for a 12 mm OD sample tube, rather than the standard 10 mm OD; (2) separation of the nitrogen flow used to control sample temperature from air used to cool the decoupling coil. This latter result was achieved by using a small dewar as the coil bobbin, with the ^{13}C coil wound on the inside of the dewar and the decoupling coil on the outside. This probe is superior to the Bruker probe in sensitivity by a factor of at least 2. It promises to provide better low temperature performance, but we have yet to make modifications in nitrogen flow to achieve such an improvement. Resolution is better than 0.5 Hz at 68 MHz, and effective decoupling power, $\gamma H_2/2\pi$, is about 2.3 kHz with 10 W input. (We can increase the decoupling power, if necessary.) An illustration of the improved sensitivity of our probe is provided in the attached polysaccharide spectra.

I am also attaching a table showing an interesting comparison of integrated sensitivity with a few spectrometers and probes at different field strengths.[1] As pointed out elsewhere,[3] superconducting systems generally do not achieve the theoretically predicted improvement in sensitivity over low field, iron core magnet systems; nevertheless, as the table shows, there is a distinct improvement at high field. Since some instruments (including our own probe) achieve better sensitivity by virtue of a larger sample volume, it is important to consider a sensitivity normalized for this factor, as well, for instances where the total amount of sample is fixed. Such a normalized sensitivity is given also in the table.

Tom Clem and Rolf Tschudin, at NIH, have made major contributions to the development of our ^{13}C NMR instrumentation.

Sincerely yours,

Heisaburo Shindo

Heisaburo Shindo
Reproduction Research Branch
National Institute of Child
Health and Human Development

1. H. Shindo and J. S. Cohen, P.N.A.S. USA, 73, 1979 (1976).
2. W. Egan, H. Shindo and J. S. Cohen, Ann. Rev. Biophys. Bioeng., in press.
3. D. I. Hoult and R. E. Richard, J. Mag. Res., in press.

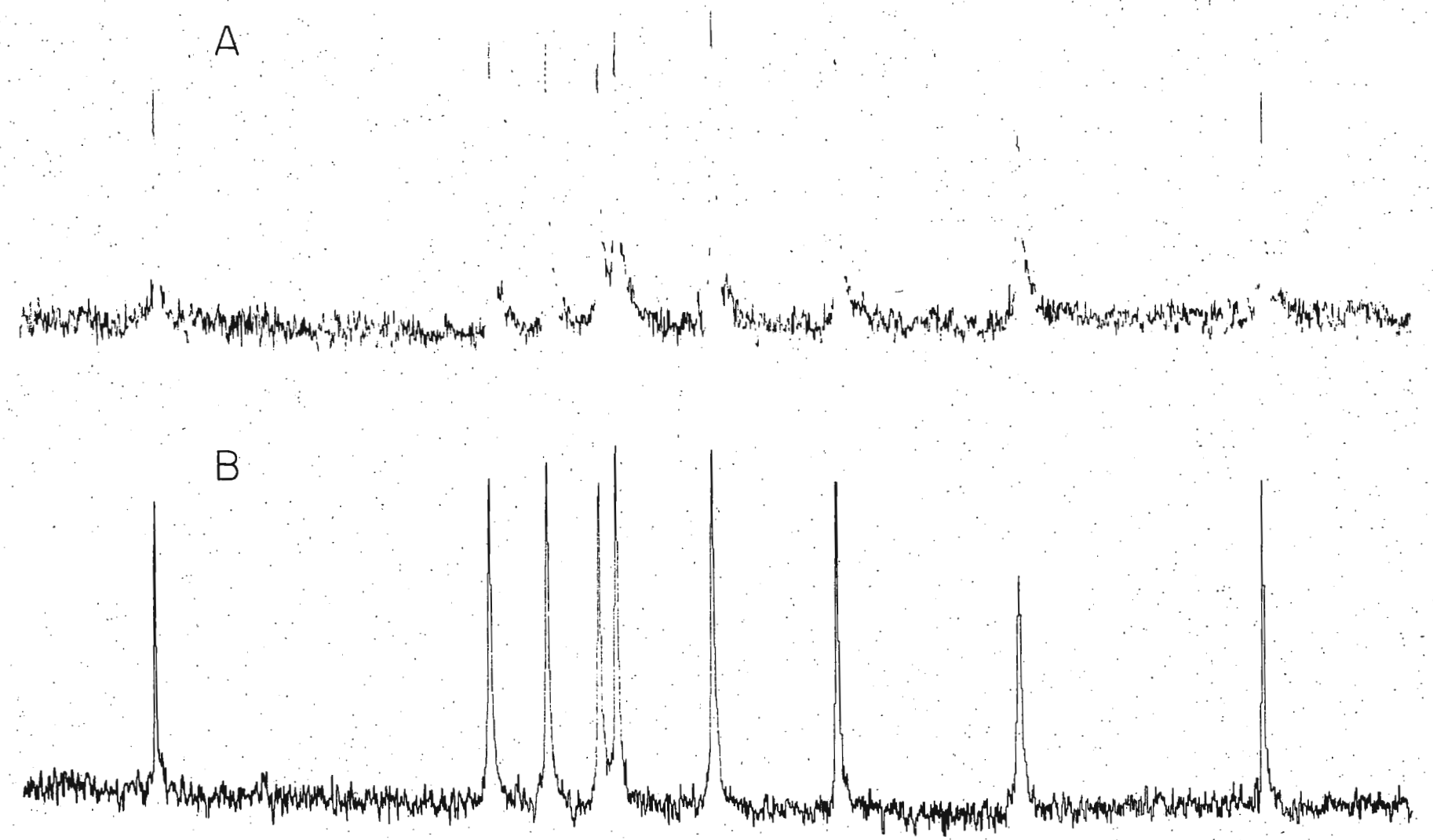


Fig.1. Carbon-13 NMR spectra(at 68 MHz) of anomeric and aliphatic regions of N.Meningitidis Serogroup B polysaccharide(conc.24 mg/ml) at 35°C. Trace A; use of NIH 12mm Probe, 15 kHz sweep width and audio filter,16 k data points in time domain,0.54 sec delay, 2 Hz line broading,4096 accum., Trace B; use of Bruker 10mm probe,the same conditions except for accum. numbers 16384.

Table I. Integral Signal to Root Mean Square Noise Ratio (S/N)[a] for Ethylene Glycol-$\underline{d}_2$ at Differing Magnetic Field Strengths.

Spectrometer	Observing Frequency (MHz)	Sample Volume[b] (ml)	I_s/I_n [c]	Normalized[d] Relative S/N Ratio[e] Obs.	$\underline{H}_o$ [e]	$\underline{H}_o^{3/2}$ [e]
FX-60	15	0.95	1.6	1.0	1.0	1.0
TT-14	15	10.0	4.0	0.77		
TT-14 (home-built probe)	15	1.5	3.0	1.5		
FX-100	25	0.95	3.0	1.9	1.7	2.2
NIH-270 (Bruker magnet & probe; home-built spectrometer)	68	1.2	6.5	3.6	4.5	9.6
NIH-270 (Bruker magnet & home-built probe and spectrometer)	68	1.9	15.0	6.6		

a The sample used for measuring the S/N ratio was neat ethylene glycol-$\underline{d}_2$. Eight acquisitions were collected with a 4 kHz sweep width and audio filter. The signal intensity, I_s, is given by integration of the Fourier transformed signal; the rms noise, I_n, is given by the integral value of the power spectrum of the noise component over 1024 data points.

b Estimated effective sample volume.

c Either crystal filtering or quadrature phase detection was used in all cases.

d The standard S/N ratio was based on an effective volume of 1 ml at a 15 MHz observing frequency for the FX-60 spectrometer.

e Theoretical values assuming the S/N ratio to vary either linearly or with the 3/2 power of the applied magnetic field strength.

367 Old Bay Ridge Rd.
Annapolis, Maryland 21403

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

August 30, 1976

Fluorine Shielding Anisotropies in Trifluoromethyl Systems

Dear Professor Shapiro:

The use of smectic liquid crystals has made possible the preparation of solutions of relatively high solute ordering. This feature has in turn led to more accurate determinations of chemical shielding anisotropies. Recently we have measured the fluorine chemical shielding anisotropies of several trifluoromethyl compounds. The experiments were done at Columbia University using a JEOL PFT-100 NMR spectrometer described previously (1). Much of the experimental work, including smectic liquid crystal syntheses (2) were done by Anthony Montana.

The NMR liquid crystal experiment provides the quantities

$$\sigma_{avg} = \frac{1}{3}\mathrm{Tr}\,\underline{\underline{\sigma}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \qquad \text{and}$$

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = \sigma_{zz} - \tfrac{1}{2}(\sigma_{xx} + \sigma_{yy}) ,$$

using the axis system depicted below. A single fluorine anisotropy is obtained for each molecule because each of the 3 fluorines on a given molecule has identical values of $\sigma_{\parallel} = \sigma_{zz}$ and $\sigma_{\perp} = \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$. However, the values of σ_{xx} and σ_{yy} will be different for each fluorine, and these quantities are not obtained from the experiment. Furthermore, in the axis system chosen, each fluorine has at least one off-diagonal shielding component. Therefore any attempts to transform the shielding anisotropy require approximations and assumptions, which are often unjustified (2).

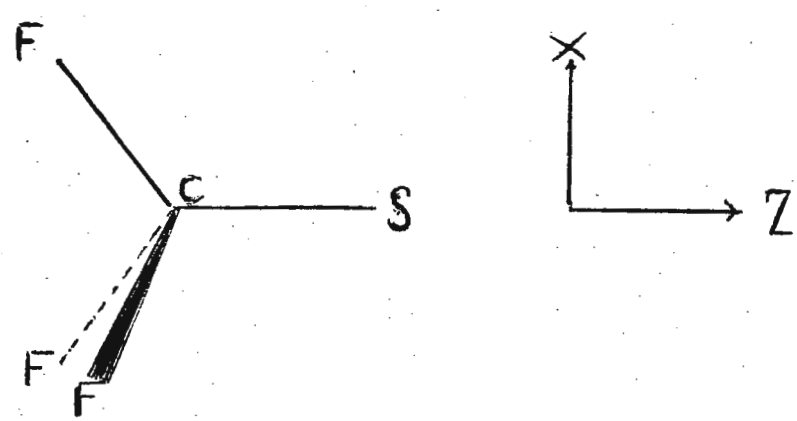


Figure 1 (S = substituent)

Knowledge of the anisotropic and isotropic chemical shielding allows the determination of the individual shielding components, $\sigma_{\parallel}$ and $\sigma_{\perp}$, which are tabulated below.

Fluorine Shielding in CF_3 Molecules

Molecule	$\sigma_{\parallel} - \sigma_{\perp}$	$\sigma^{a}_{average}$	$\sigma_{\parallel}$	$\sigma_{\perp}$
CF_3Cl	-13.3 ± 0.5	222 ± 10	213 ± 11	226 ± 10
CF_3Br	2.7 ± 0.3	210 ± 10	212 + 10	209 ± 10
CF_3I	16.7 ± 0.2	194 ± 10	205 ± 10	188 ± 10
CF_3CCl_3	-72.9 ± 0.7	271 ± 10	222 ± 11	295 ± 11

a. Absolute fluorine shielding scale (3).

It is observed that the quantity $\sigma_{\parallel}$ remains relatively constant among this series of trifluoromethyl compounds. If this trend is assumed to be valid for the molecule CF_4, the quantity $\sigma_{\perp}$ and the anisotropy, $\sigma_{\parallel} - \sigma_{\perp}$, can be derived from the known isotropic chemical shift of CF_4, $\sigma_{avge} = 255 \pm 10$ ppm.

For CF_4 the fluorine shielding tensor possesses C_{3V} symmetry and is completely determined by the 2 quantities, $\sigma_{\parallel}$ and $\sigma_{\perp}$. Thus for fluorine # 4, (S in Figure), $\sigma_{\parallel} = \sigma_{zz}$ and $\sigma_{xx} = \sigma_{yy} = \sigma_{\perp}$.

The values of the principal fluorine shielding tensor components can be combined with semi-empirical atom-dipole calculations of the diamagnetic shielding (3) to yield the paramagnetic shielding and the spin-rotation contribution to the shielding. Then using the relation

$$\sigma^{sr}_{ii} = 2.082\text{x}10^{33}\ C_{ii}\ I_{ii}\ ,$$

the fluorine spin-rotation constants, $C_{\parallel}$ and $C_{\perp}$, can be determined for CF_4. The results are shown below.

Fluorine Shielding & Spin Rotation Data for CF_4

$\sigma_{\parallel}$	215 ± 20	$\sigma_{\perp}$	275 ± 25	ppm
$\sigma_{\parallel}^{d}$	549.9	$\sigma_{\perp}^{d}$	671.3	ppm
$\sigma_{\parallel}^{sr}$	-115 ± 20	$\sigma_{\perp}^{sr}$	-264 ± 25	ppm
$I_{\parallel}$	145.9 x10^{-40}	$I_{\perp}$	145.9 x10^{-40}	g cm^2
$C_{\parallel}$	-3.8 ± 0.9	$C_{\perp}$	-8.7 ± 0.9	kHz
C_{avge}	-7.1 ± 0.9	ΔC	4.9 ± 1.8	kHz

These values agree within experimental uncertainty with spin-rotation constants obtained by 1) gas-phase spin-lattice relaxation studies (4)

$$C_{avge} = -6.41 + 0.12 \text{ kHz}; \quad |\Delta C| < 5 \text{ kHz},$$

and 2) molecular-beam studies (5)

$$C_{avge} = -6.85 + 0.35 \text{ kHz}; \quad |\Delta C| < 17 \text{ kHz}.$$

The latter results gave little precision regarding the anisotropic contributions.

Sincerely,

Bernie Appleman

Bernard R. Appleman

1. Appleman,B.R. & Dailey,B.P., J. Magn. Reson. 16,265(1974); Bhattacharyya,P.K. & Dailey,B.P., Mol. Phys. 26,1379(1973).
2. Montana,A.J., Appleman,B.R., & Dailey,B.P., J. Chem. Phys. 66,xxxx(1977).
3. Appleman,B.R. & Dailey,B.P., Advan. Magn. Reson. 7,231(1974).
4. Dong,R.Y. & Bloom,M., Can. J. Phys.48,793(1970).
5. Ozier, I. , Crapo,L.M. & Lee,S.S., Phys. Rev. 172,63(1968).

GRUPPO LEPETIT

Lepetit Research Laboratories
Via Durando, 38
20158 Milano, Italy

destinatario

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

Department of Physical Chemistry - Milano, September 2, 1976

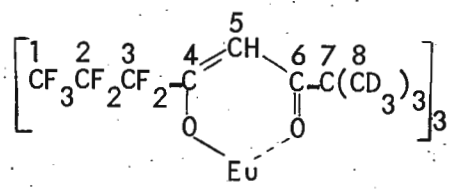
Subject : ^{13}C NMR Spectrum of tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-d_6-4,6-octanedione-d_3)-europium (III), $Eu(FOD)_3$-d_{27}

Dear Prof. Shapiro,

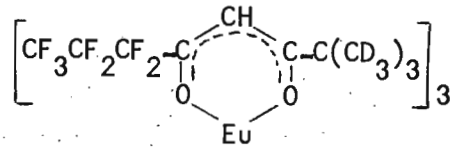
During the use of $Eu(FOD)_3$-d_{27} as a shift reagent for ^{13}C NMR of organic substrates, we realized that, owing to the relatively high concentrations used, the ^{13}C signals of the shift reagent itself were clearly visible in the spectra. Thus, we thought it interesting to have the spectrum assigned. To do that, we recorded also the ^{13}C spectrum of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, FOD, and the two spectra are shown in the figure. The ^{13}C chemical shifts, the corresponding $\Delta\delta$ values, and the J_{CF} couplings are reported in the table.

It can be seen that striking differences are observed between C-4, C-5, C-6 and especially C-7 of $Eu(FOD)_3$-d_{27} and FOD. While the $\Delta\delta$ values of C-4 and C-6 can be accounted for because of the asymmetry of FOD, the strong diamagnetic shifts of C-5 and C-7 upon complexation appear difficult to explain.

Whatever the explanation may be, our results indicate that the structural formula of $Eu(FOD)_3$-d_{27} should be more correctly written



instead of the usually reported



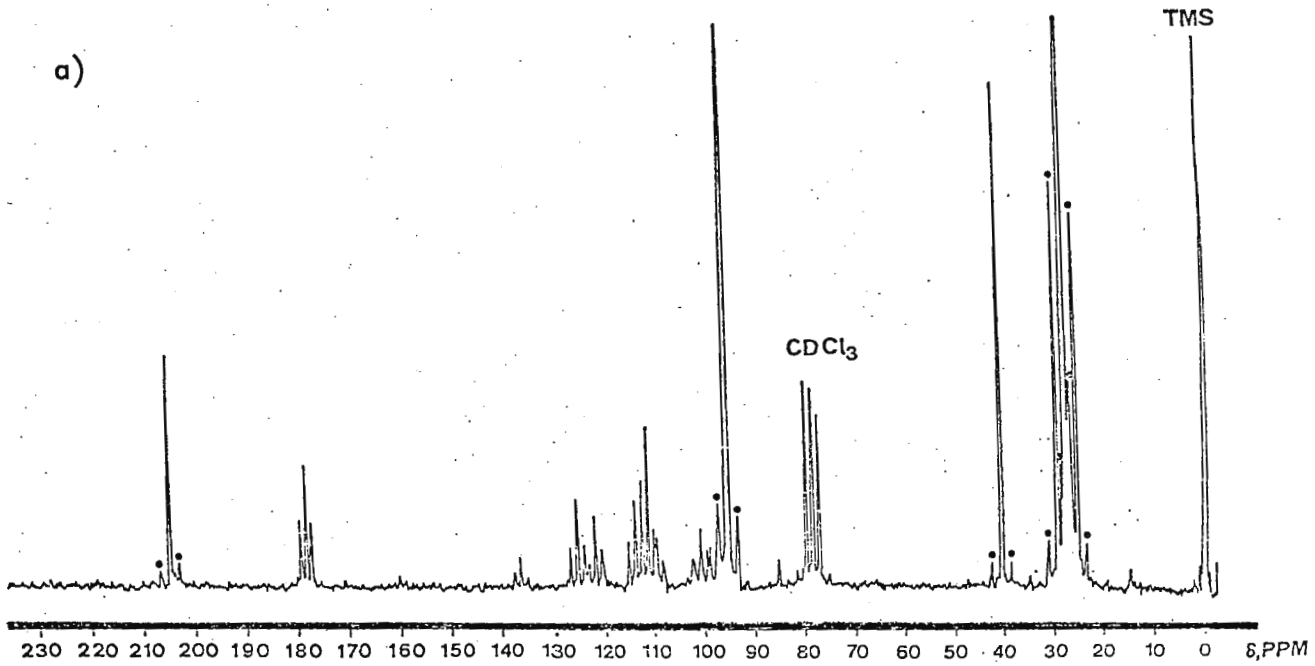
Yours sincerely,

Ambrogio Ripamonti Edoardo Martinelli

Table - ^{13}C NMR data of $Eu(FOD)_3$-d_{27} and FOD in $CDCl_3$ with TMS as internal reference .

Carbon	δ $Eu(FOD)_3$-d_{27} ppm	J_{CF}, Hz	δ FOD ppm	J_{CF}, Hz	Δδ $Eu(FOD)_3$-d_{27}-FOD ppm
1	116.5	J_{C_1F} = 288 $J_{C_1C_2F}$ = 34.8	118.8	J_{C_1F} = 288 $J_{C_1C_2F}$ = 33.7	- 2.3
2	107.2	J_{C_2F} = 263 $J_{C_2C_3F}$ = 39	108.8	J_{C_2F} = 263 $J_{C_2C_3F}$ = 31.7	- 1.5
3	109.6	J_{C_3F} = 263	109.6	J_{C_3F} = 263	0.0
4	162.7[a]	n.d.	177.7	$J_{C_4C_3F}$ = 26.2	-15.0
5	53.4	-	93.9	-	-40.5
6	216.0[a]	-	204.2	-	+11.8
7	8.2	-	40.2	-	-32.0
8	29.4	-	27.1	-	+ 2.3

(a) the signals are broadened by shortening of T_1 due to electron-nuclear relaxation. This effect significantly diminishes in the presence of a substrate.



. Spinning side bands

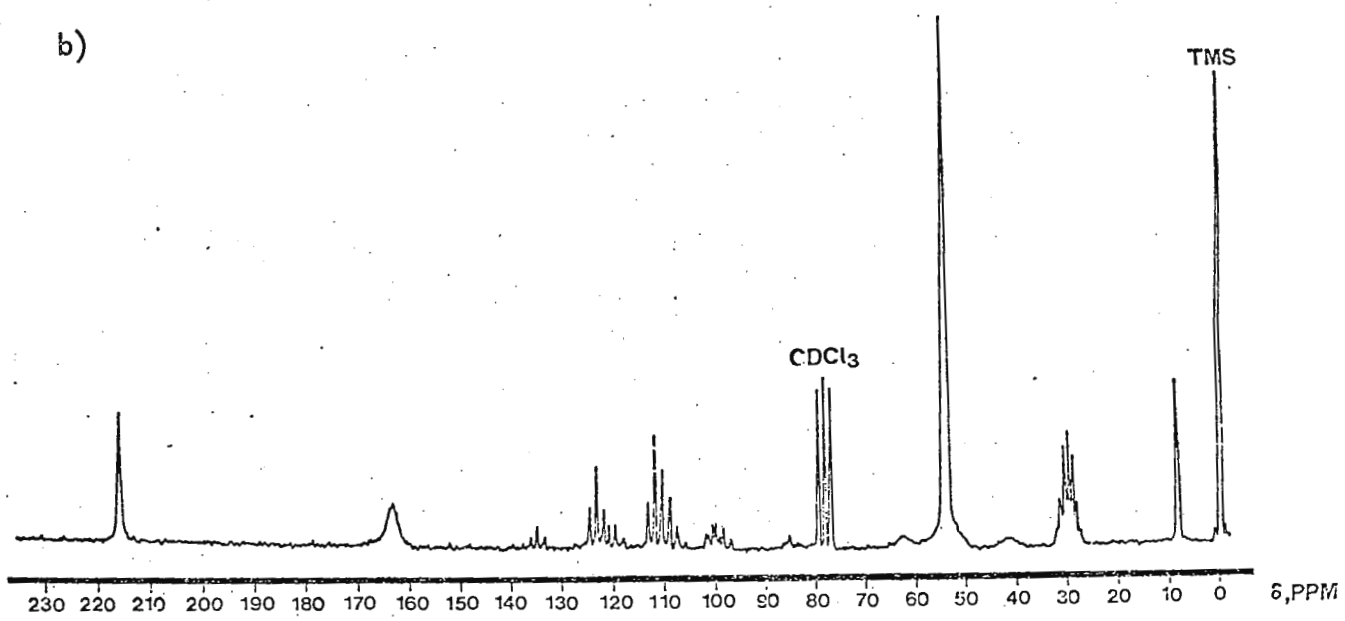


Figure - ^{1}H noise decoupled ^{13}C spectra at 25.2 MHz in $CDCl_3$ of a) FOD, conc. ~1 M ; b) $Eu(FOD)_3$-d_{27}, conc. ~ 0.35M. No apparent variations of ^{13}C δ's are observed in the concentration range 0.2-1M.

UNIVERSITÉ CLAUDE BERNARD, LYON I

LABORATOIRE DE SPECTROSCOPIE ET DE LUMINESCENCE

43, Bd DU 11 NOVEMBRE 1918
69621 VILLEURBANNE – FRANCE

TÉL. (78) 52.07.04

Villeurbanne, 21 Septembre 1976

Cher Professeur SHAPIRO,

Transistorisations sur Spectromètre HA 100 : II Remplacement de l'USA 3

Après la transistorisation de l'alimentation V2100B (1), le remplacement du préamplificateur (2) Cf V4333A, nous avons poursuivi l'implantation de circuits solides sur notre HA 100. Le remplacement de l'amplificateur D.C. USA 3 par des circuits solides a déjà été évoqué par J.E. PAGE (3) et les plans d'un montage nous ont été aimablement transmis par A.C. PARKER et P.C. LOUGHERY (Glaxo Res. Ltd, Greenford, Middlesex). Le dispositif réalisé à partir de ces informations s'est avéré excellent une fois porté remède à deux inconvénients rencontrés initialement :

- Il apparaît un décalage en tension de sortie (donc en ligne de base), lors du passage de la position "Scope" à la position "Spectrum" sur l'unité V 3521 A du fait de la différence entre les résistances d'entrée de l'amplificateur pour ces deux positions. Nous avons remédié à cet inconvénient en modifiant le "bouclage" de l'amplificateur (cf V-3521 A Integrator Decoupler Schematic Pub N° 87-101-702, Rev. G666).
- L'utilisation des tensions ± 300 V préexistantes pour alimenter l'étage de puissance à transistors, dans la modification apportée, nécessite une protection de la sortie contre les court-circuits avec la masse.

Bien qu'ayant atteint un âge respectable (10 ans), notre HA 100 fonctionne toujours de façon satisfaisante moyennant, bien sûr, des ménagements et certaines réparations inévitables (c'est ainsi qu'il a fallu réaliser un nouvel échangeur de température V 3520)

Néanmoins nous voyons arriver avec inquiétude le moment où les bobines de l'aimant vont nous lâcher. Face à cette éventualité nous aimerions savoir si un laboratoire serait susceptible de nous céder des bobines de HA 100 et sous quelles conditions...

Cordialement à vous.

BRIGUET DELMAU DUPLAN TÉTU

(1) A. BRIGUET, J. DELMAU et J.C. DUPLAN Texas AMU NMR News Letters 169, 24 (1972)
(2) F.K. DAVIES and B.C. MANNING Rev. Sc. Instrum. 44, 1513 (1973)
(3) J.E. PAGE, R.A. FLETTON and G.F.H. GREEN Texas AMU NMR New Letters 180, 1 (1973)

UNIVERSITY OF SOUTHERN CALIFORNIA
UNIVERSITY PARK
LOS ANGELES, CALIFORNIA 90007

DEPARTMENT OF CHEMISTRY
(213) 746-2780

September 10, 1976

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

A Remarkably Small Geminal F-F Coupling in a Fluorosilane

Dear Barry,

We have observed what we believe to be the first two-bond fluorine-fluorine coupling constant for silicon bonded fluorine atoms. The ^{29}Si satellites in the ^{1}H decoupled ^{19}F nmr spectrum of 1,2-dimethyltetrafluorodisilane can be analyzed as a slightly second-order AA'XX' pattern.

With the reasonable assumption that $J_{AA} - J_{XX}$ is zero, the values of J_{AX}, J'_{AX}, and $J_{AA} = J_{XX}$ can be approximated from a first order analysis of the spectrum. Using only the eight most intense lines in each half of the spectrum, iterative calculations with LAOCOON III provided best-fit parameters for the coupling constants (Table I). With this procedure, two sets of parameters gave equally good spectral fits. (See Figure 1). The low intensity lines appear to be in better agreement with the set of parameters in which all coupling constants are of the same sign. Since the vicinal F-F coupling constant, $1/2\ (^{3}J_{FF} + {}^{3}J'_{FF})$, can be reasonably assigned a positive value[1], the geminal F-F coupling would then also be of positive sign.

Since geminal F-F coupling constants are also positive in fluoroalkanes[2], the sign of the geminal F-F coupling constant in the fluorosilane is perhaps not surprising. What is most definitely surprising, however, is the magnitude of the coupling constant. Geminal F-F coupling constants in fluoroalkanes range from ca. 150 to 270 Hz. In 1,2-dimethyltetrafluorodisilane the magnitude is only 5 Hz.

Sincerely yours,

Ken Sharp

Kenneth L. Servis
Associate Professor
of Chemistry

Kenneth G. Sharp
Assistant Professor
of Chemistry

References:

(1) K.G. Sharp, S.Li and R.B. Johannesen, Inorg. Chem. 15, 0000 (1976).

(2) K. Hirao, H. Nakatsuji, H. Kato & T. Yonezawa, J. Amer. Chem. Soc., 94, 4078 (1972).

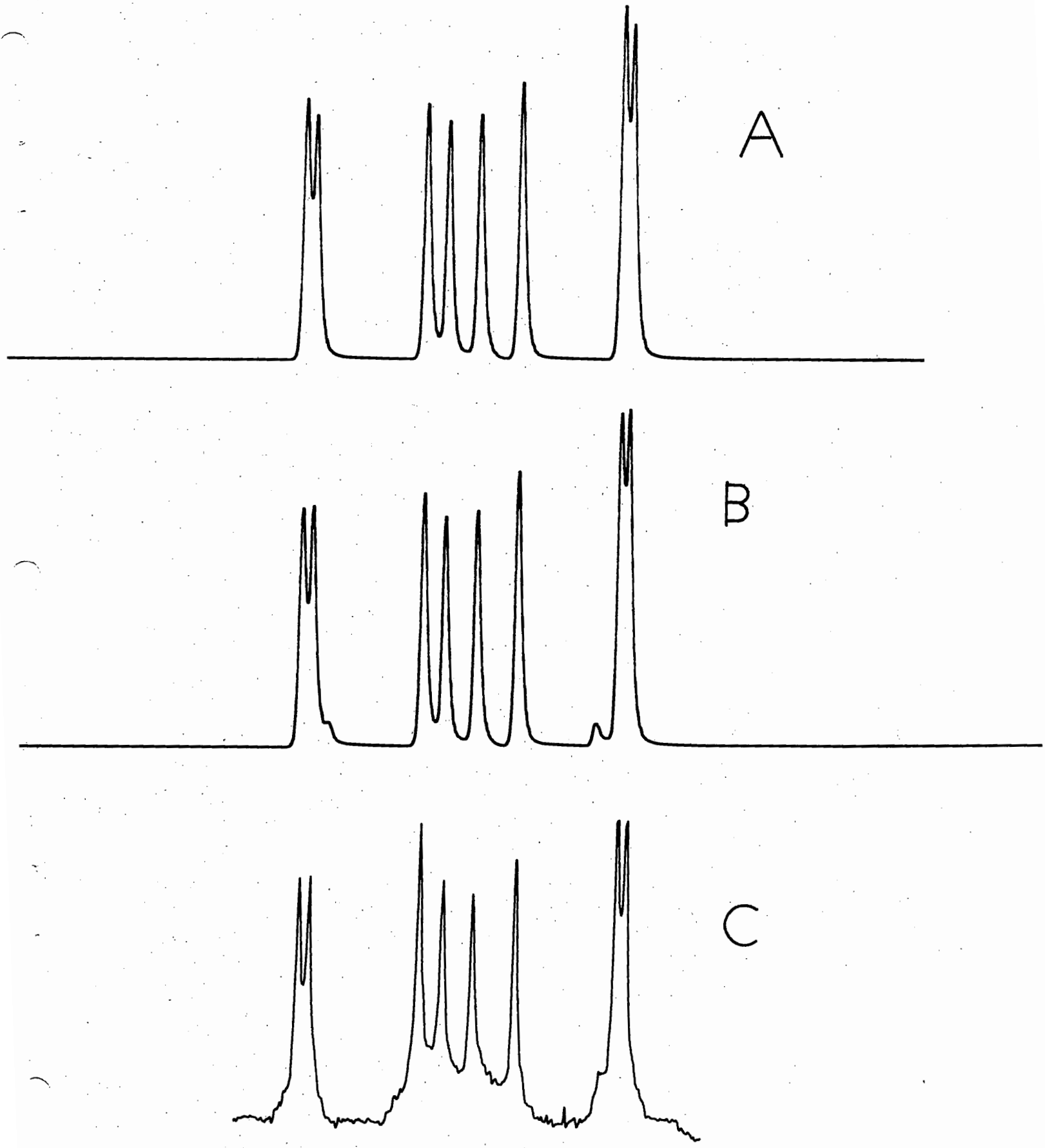
Table I

Calculated Couplings Constants

For 1,2-Dimethyltetrafluorodisilane

	Solution 1	Solution 2
$1/2\,(J_{^{29}SiF} + J_{^{29}SiSiF})$	+194.0	+194.0
J_{FF}	+4.8	-5.9
J_{FSiSiF}	+17.1	+17.1
J'_{FSiSiF}	+9.2	+9.2

Caption for Figure 1: Low field satellite for proton-decoupled $^{29}SiF_2Me^{28}SiF_2Me$. A is a computer-based simulation using the parameters of Solution 2; B is a simulation using the parameters of Solution 1; C is the experimental spectrum.


A
B
C

UNIVERSITY OF BRADFORD

Bradford West Yorkshire BD7 1DP
Telephone Bradford 33466 (STD Code 0274)
Telex 51309 University Brad

School of Studies in Chemistry

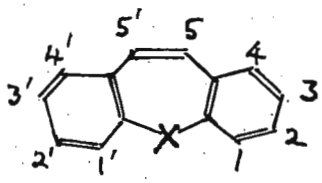
7th September, 1976.

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

Dear Dr.Shapiro,

Solvent shifts in 220 MHz ^{1}H spectra of dibenz [b,f] oxepin

From 60 MHz ^{1}H spectra of dibenz [b,f] oxepin (I) in CS_2 solution, P.M.G.Bavin, K.D.Bartle and D.W.Jones [J.Heterocyclic Chem., 5, 327 (1968)] demonstrated that electrophylic substitution occurs at the ethylene bond (position 5 in our nomenclature, but usually designated 10).



I X = O

II X = CO

100 MHz spectra show, apart from the singlet at 6.6p.p.m. attributed to the central-ring protons, a closely coupled group of protons near 7 p.p.m. and, at slightly lower field, a one-proton multiplet. 220 MHz ^{1}H spectra (Fig.) of I, recorded at a range of concentrations in $CDCl_3$ solution, were almost first-order and readily solved with LAOCOON III, whereas J.A.G.D. found analysis of the spectra in CS_2 solution more difficult owing to overlap of the three-proton multiplet (spread over 6 Hz). Long-range coupling (0.30 Hz) between H(1) and H(5) was detected by decoupling H(5) on a Perkin-Elmer R34 (courtesy of Dr.R.A.Spragg) so that the spin system might be described as $(ABCMX)_2$.

Other coupling constants (in Hz, means of 16 determinations) are $J_{1,2} = 8.08$, $J_{2,3} = 7.39$, $J_{3,4} = 7.60$, $J_{1,3} = 1.20$, $J_{2,4} = 1.70$, $J_{1,4} = 0.33$. Chemical shifts, δ in p.p.m. extrapolated to zero concentration in the two solvents, are shown below:

H	$CDCl_3$	CS_2	$\Delta(CDCl_3 - CS_2)$	Shift ratio
1	7.18	6.98	0.20	1.67
2	7.29	7.17	0.12	1.0
3	7.11	6.99	0.12	1.0
4	7.17	7.01	0.16	1.33
5	6.71	6.55	0.16	1.33

Solvent shifts and analogy with II (J.A.G.Drake and D.W.Jones, unpublished measurements) aided assignment of H(4) and H(1). In view of the (surprisingly) lower field of H(2) than H(1), H(2) in I may be especially susceptible to nucleophyllic attack.

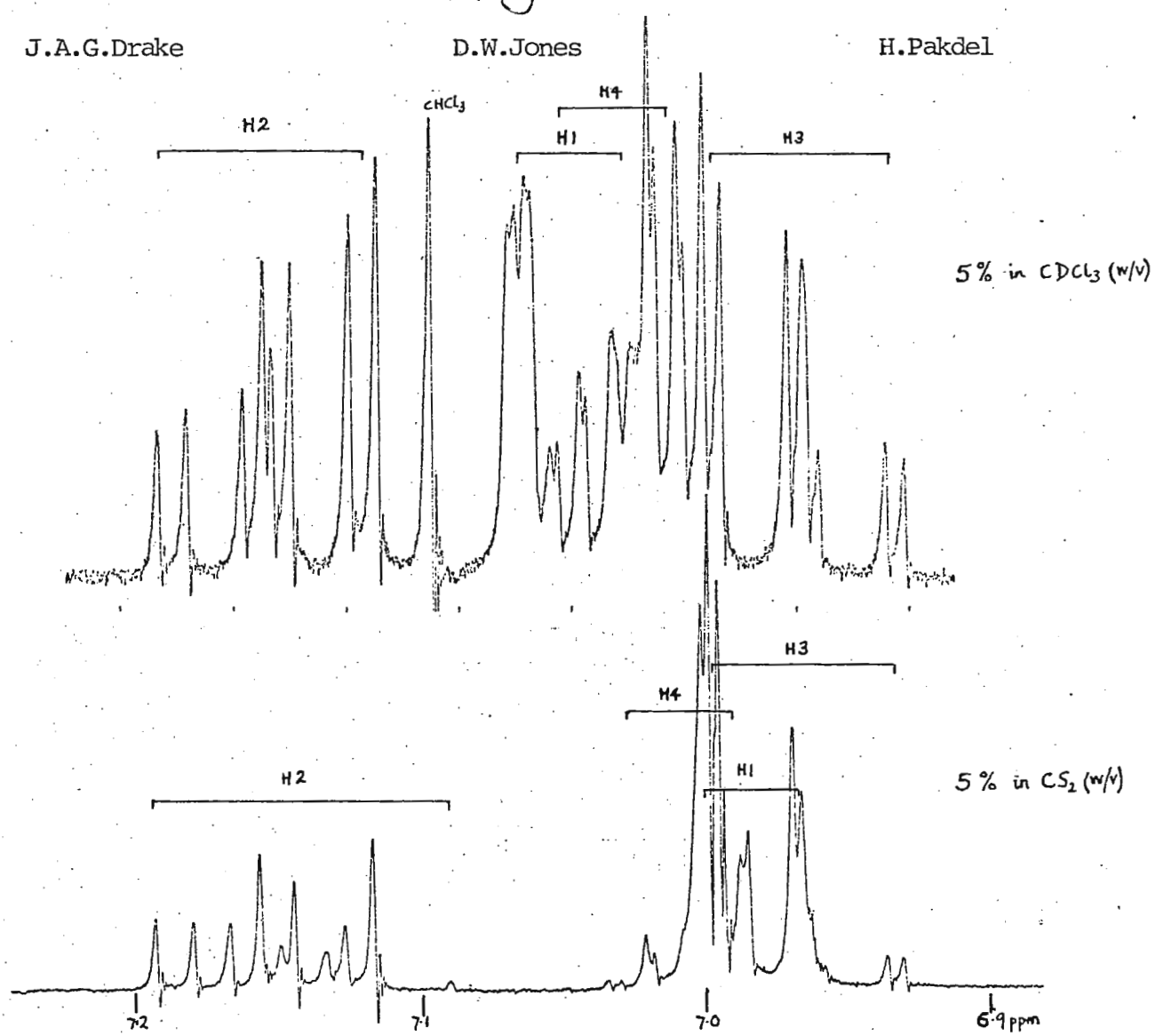
Our recent (unpublished) X-ray crystal-structure analysis of I indicates that, in the solid state, the central ring takes up a boat form with the benzene rings inclined at 46° to one another. UV evidence [T.Toth and L.Klasinć, Z.Naturforschung, 29A, 1371(1974)] favours this shape in solution. The disparate meta couplings involve dihedral angles from the ring plane of about 0° and 24° respectively. Constancy of shifts and line widths for I and II over the range -50 to 50°C suggests that if there is any conformational mobility [known to occur when the central ring is heavily substituted (M.Nogradi, W.D.Ollis and I.O.Sutherland, Chem.Comm.,158 (1970)], it is fast in I. The H(2) multiplet in the readily assigned spectrum of I in $CDCl_3$ is markedly changed when the δ_1 and δ_2 shifts are close, as in CS_2 solution: this appearance may be helpful in aiding recognition of orthosubstitution in other ring systems.

With apologies for the late submission of this contribution.

Yours sincerely,

J.A.G. Drake D.W.Jones H-Pakdel

J.A.G.Drake D.W.Jones H.Pakdel



UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, September 13, 1976.-

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

Title: Consumer Report: Nicolet NMR-812

Dear Dr. Shapiro:

Since about half a year we are the happy onwers of a minicomputer system specially designed for F.T. Spectroscopy and I thought perhaps the T.AU.M.U.N readers would be interested in our experience.

To begin with I must warn that nobody in this lab has had previous experience with a minicomputer.

We learned very soon that it is not so important to know what to do with a computer than to know what not to do. At the beginning the computer used some times to go mad. Then we almost went mad!

Though our F.T. System in not yet operating, due to the already mentioned difficulties with the materials for the F.T. home made probe we simulated a F.I.D. signal and so learned to use the program. It works beautifully.

All people in the lab. are delighted with the Basic Language Interpreter. Though with our machine (without disk!) we are rather limited and 12 K of memory is just the "minimum minimorum", we find the language wounderful. It can be learned in a day and mastered after a few programs and has opened our lab. new "vistas" in the NMR field. Incidentally: The instructions given to store on tape programs written in Basic apply only for owners of a high speed puncher. We found (after hard work) a way to made these tapes and we would be glad to sent the instructions to eventually interested readers.

UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

The Spectra simulation program NMRCAL is also very nice. We have it modified to allow us to simulate spectra of molecules oriented in nematic solvents. We just sent these modification as a contribution to the Nicolet Users Society Library, but interested people can ask us directly for a copy of the overlay tape.

We heartily recommend eventual buyers to accquire a high speed paper tape reader, particularly for systems without disk. We found that we change programs several times a day, and this fast loading feature is very much apreciated.

Instruction manuals: some are very nice and clear, like the NMRCAL and the F.T.-74. The Basic Manual is only fair and so is the Assembler Language one.

Other acessories: the input system NIC-301 is O.K. We are not so happy with the NIC-293 Universal Controller. We would rather have a knobs-controlled than a soft-ware controlled timers system. For one reason: we think it would be more flexible. For another: the Assembler Language is hard to master. The timers are controlled with a special program which must be loaded each time the timers are being adjusted since they"forget" the instructions if they are switched-of overnight. (They are not-needed for routine F.T.S., only for T_1 measurement and other experiments).

Yours, sincerely,

Dr. Valdemar J. Kowalewski

217-21 National Research Council Canada | Conseil national de recherches Canada

Division of Biological Sciences | Division des sciences biologiques

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

File Référence

9 September 1976

Dear Barry:

A Comprehensive Review of Deuterium NMR in Chemistry, Physics and Biology

In collaboration with Dr. H. H. Mantsch and Dr. H. Saitô I have just (finally!) completed the above review. We have tried to include the entire ^2H literature but are still concerned that nothing has been left out and that the review be very up-to-date. Although the manuscript has already been sent to Progress in Nuclear Magnetic Resonance Spectroscopy, we are willing to include any reprints or preprints that we receive by December 1, 1976. Preprints of the review are available on writing to me at the above address, and critical opinions will be gratefully received.

With best personal regards.

Yours sincerely,

Ian

Ian C. P. Smith.

INSTITUT FÜR ORGANISCHE CHEMIE
DER UNIVERSITÄT KÖLN
Prof.Dr.H.Günther

5 KÖLN 41, GREINSTRASSE 4
TELEFON: (0221) 4701
DURCHWAHL: 470-4102

Sept. 13, 1976

Prof.Dr.B.L.Shapiro
Dept. of Chemistry
Texas A+M University
College Station, Texas
USA

Postdoctoral Position Available

A postdoctoral position is available immediatly in my group. The research program involves organic synthesis and nmr work on carbon-13. Persons interested in problems of physical organic chemistry should write me soon.

Sincerely yours,

Harald

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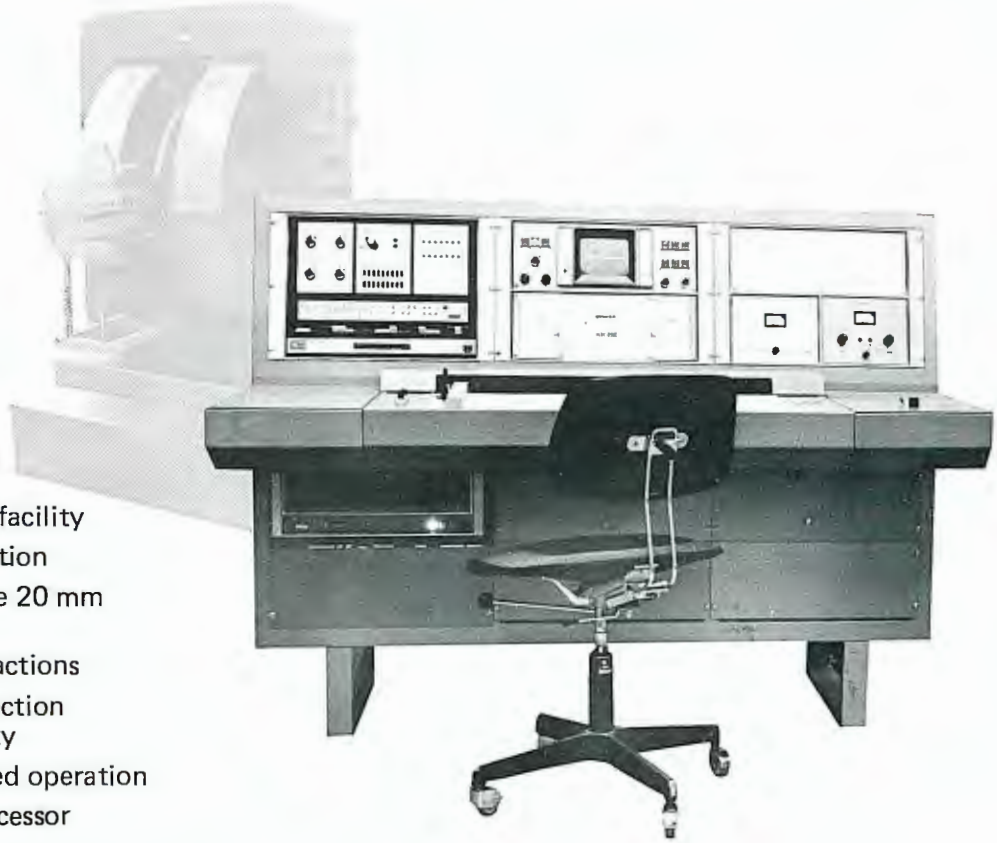

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UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN *Urbana, Illinois 61801*

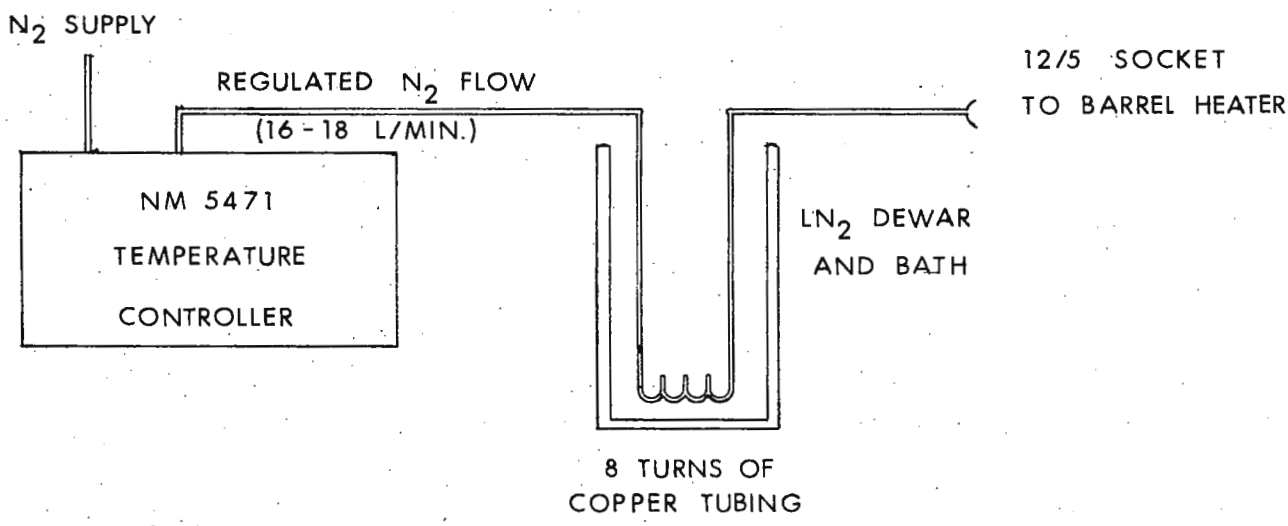
School of Chemical Sciences

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

September 14, 1976

Low Temperature Studies on a JEOL NMR Spectrometer

We have found the 10 ℓ. boil-off dewar to be insufficient for long term (greater than ca. 6 hours) low temperature data accumulation on the JEOL FX-60 NMR Spectrometer. As an alternative to the dewar we are now using an exchange coil immersed in a cooling bath (see Fig 1).



The existing variable temperature controller (NM 5471) is retained for temperature regulation and its flowmeter is used for exchange gas regulation. The regulated gas is then passed through an 8 turn exchange coil immersed in a liquid nitrogen bath. The cooled nitrogen is then passed into the barrel heater (at the back of the magnet) where the line is attached with a ₮ 12/5 socket.

With a flow rate of 16-18 ℓ/min we have made 16 hour runs at -95°C. A dry ice/acetone bath was found to be optimum in the -30°C to room temperature range. Proper adjustment of exchange gas flow was found to be important in alleviating large temperature fluctuations.

Sincerely,

Stephen E. Ulrich

Stephen E. Ulrich

DEPARTMENT OF BIOCHEMISTRY

THE UNIVERSITY OF ALBERTA
EDMONTON, CANADA T6G 2H7

September 14, 1976

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

Dear Barry:

"T_2 Measurements at 270 MHz"

We have recently been measuring some T_2's in high resolution spectra at 270 MHz on our Bruker spectrometer. When Jim Courtney was with Bruker Canada (he is now with Nicolet Canada) we set up the following pulse sequence:

$$[(\pi/2)_x \{\tau-\pi_y-2\tau-\pi_y-2\tau-\pi_{-y}-2\tau-\pi_{-y}-\tau\}_N]-T$$

and Fourier transformed the second half of the last echo. The enclosed figure shows T_1 and T_2 measured for 7 mM L-Ala-L-Tyr. Grayson Snyder helped me with some of these measurements. For the T_2 measurement, the spectrum at each delay value represents 200 accumulations. One thing to note in these spectra is that the apparent T_1's are different for the ortho and meta tyrosine doublets but the T_2's are equal as expected in the fast pulsing limit (here τ=.001).

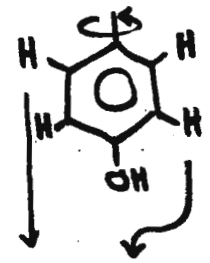
Yours sincerely

Brian

Brian D. Sykes
Associate Professor of Biochemistry.

BDS/jr
Enclosure.

ALA-TYR T_1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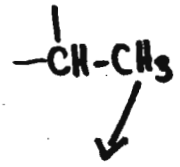
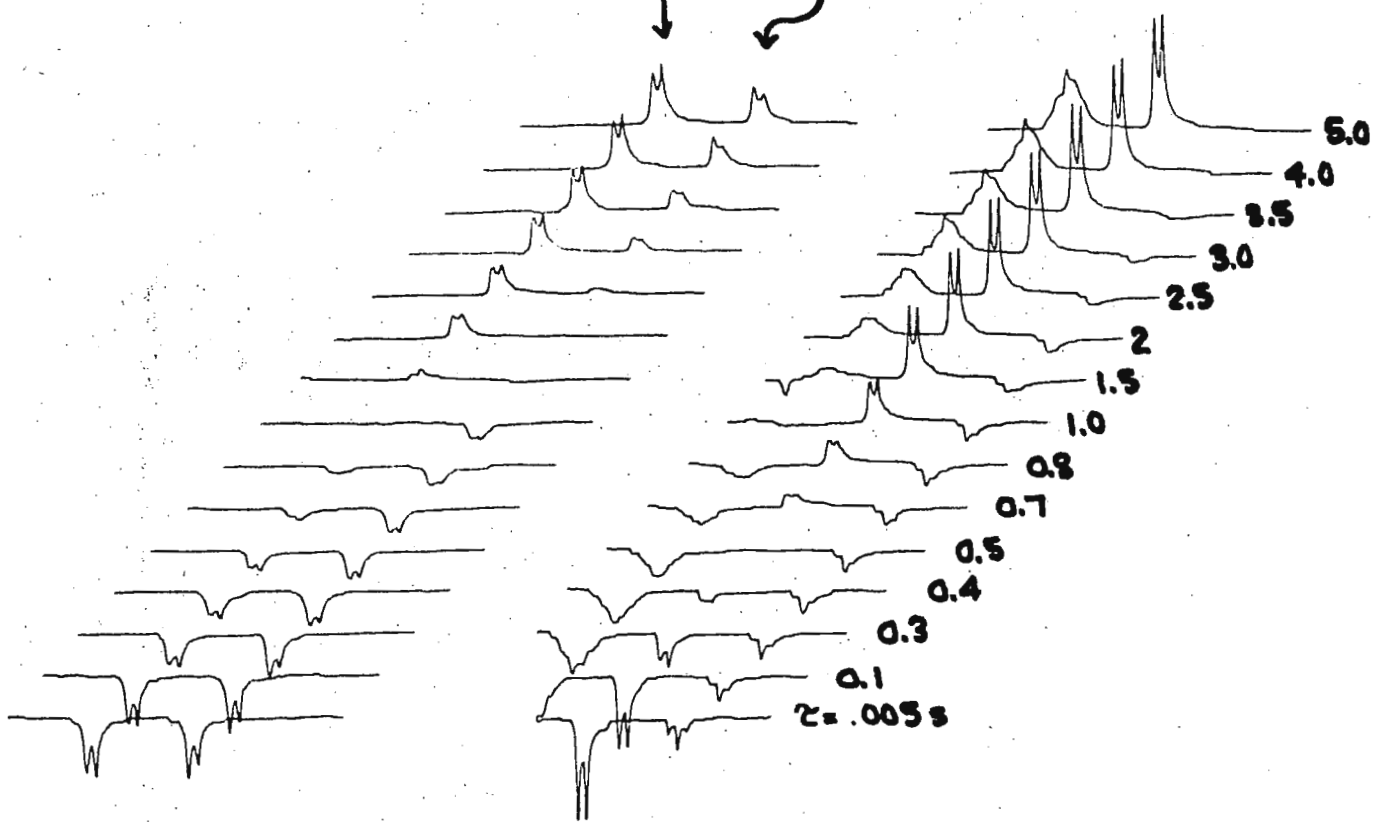

CH-CH3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3.0
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2
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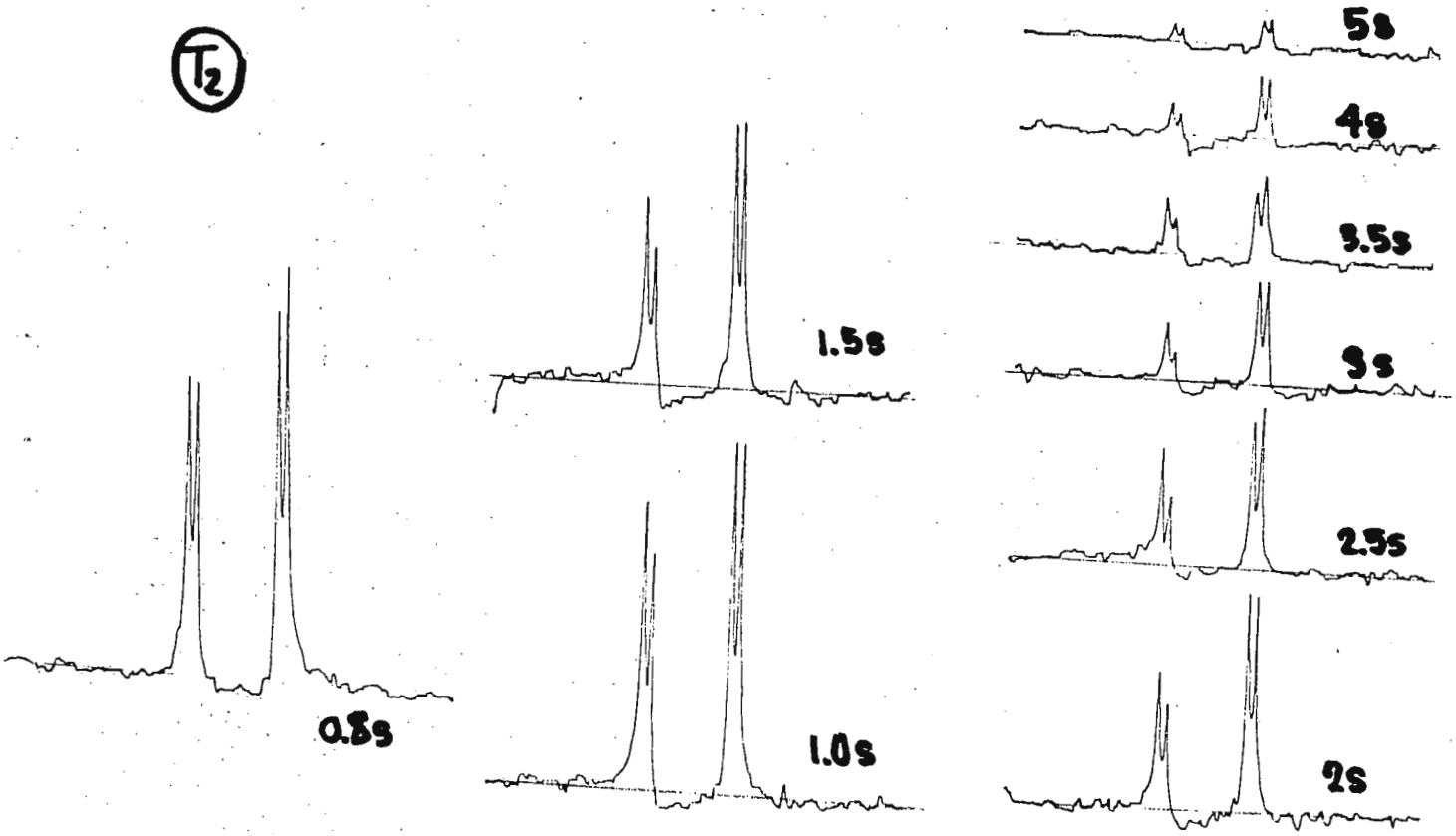
0.7
0.5
0.4
0.3
0.1
τ = .005 s

T_2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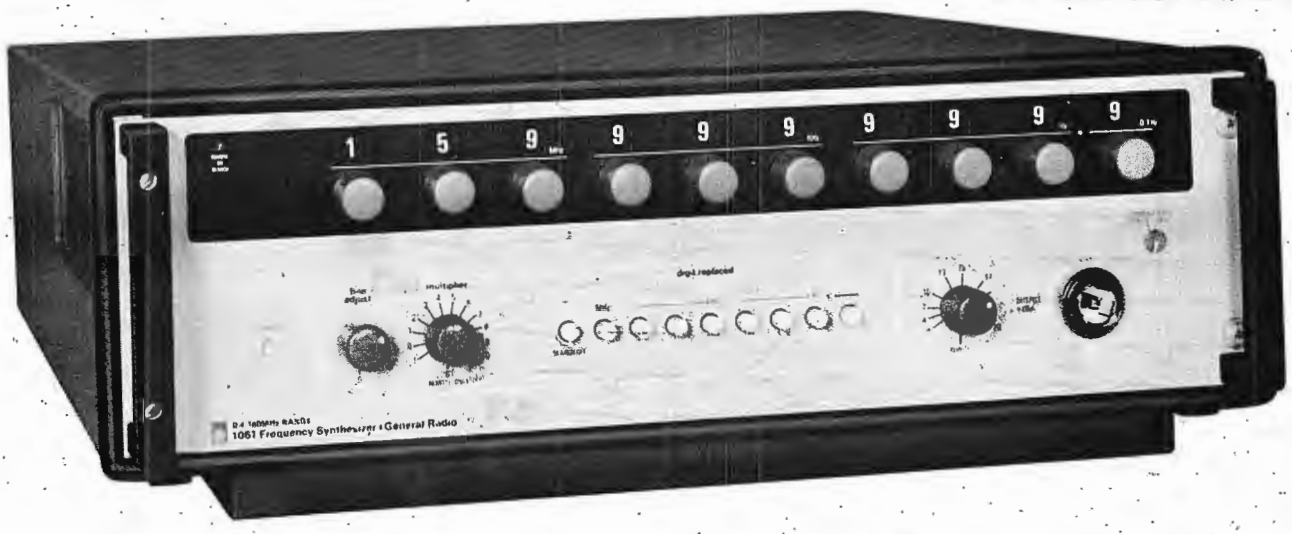

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DEPARTMENT OF CHEMISTRY
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September 10, 1976

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

Title: A Multinuclear 18mm Probe, ^{113}Cd NMR of Metalloproteins, and Availability of a Postdoctoral Position

Dear Barry:

I would like to report some recent results from the nmr laboratory in South Carolina. Mr. Andy Byrd has completed final adjustments on a multinuclear 18mm nmr probe for our XL-100. The design uses the cross-coil configuration and "snap-in" inserts. The probe is capable of operating over the frequency range of 10 to 100 MHz. Some signal to noise comparisons between the 18mm probe and a standard Varian 12mm system are made in Figure 1 for ^{19}F and ^{31}P. The gain in S/N is quite impressive, further the approximate sample volume needed for each sample was between 4 and 5 ml. A detailed account of the probe construction and other modification to our XL-100 will be sent to the Journal of Magnetic Resonance. Preprints will be available.

One of the projects currently in progress at South Carolina is the application of multinuclear magnetic resonance techniques to metals of environmental significance, e.g. ^{113}Cd, ^{207}Pb, ^{119}Sn, etc. An example of some of the biological applications utilizing the 18mm probe in ^{113}Cd NMR, done by Mr. David Bailey, is shown in Figure 2. This is the ^{113}Cd nmr spectrum of the protein Concanavilin A. Under the conditions employed to achieve this spectrum, two octahedral binding sites are occupied by ^{113}Cd on the protein. These binding sites are easily visualized in the spectrum.

Professor Odom and myself are currently seeking a postdoctoral fellow to participate in this exciting area of research involving metal nuclide magnetic resonance. The salary for the position will be commensurate with the applicant's experience and ability.

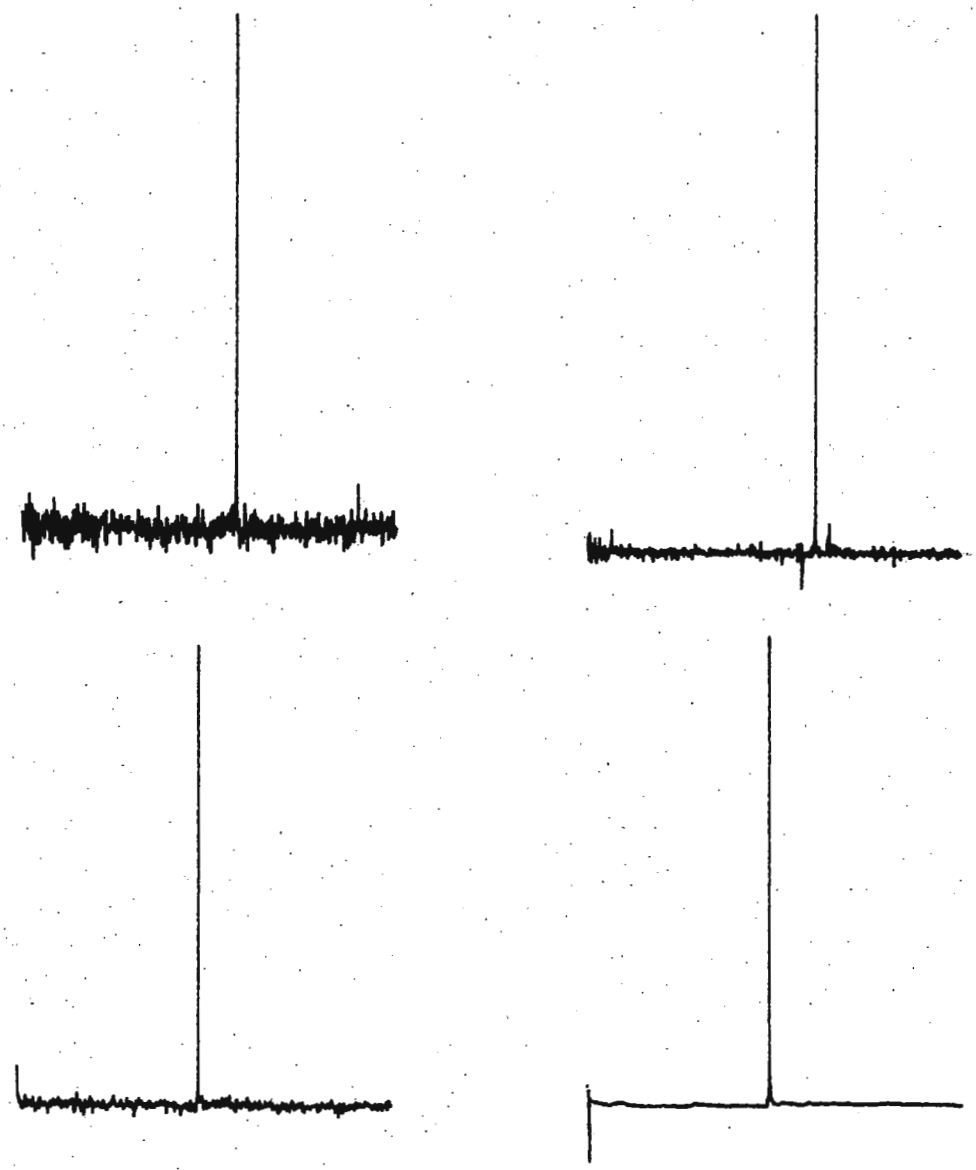
Warmest regards,

Paul

Paul D. Ellis
Associate Professor

PDE/pk

Figure 1. ^{19}F nmr spectra of trifluoroacetic acid (20 mM in ^{19}F) recorded in (A) a 12 mm tube and (B) in an 18 mm tube using a 2000 Hz sweep width and ^{31}P nmr spectra of 25 mM aqueous potassium phosphate recorded in (C) a 12 mm tube and (D) in an 18 mm tube using a 2500 Hz sweep width. All spectra were recorded following a single 90° pulse.



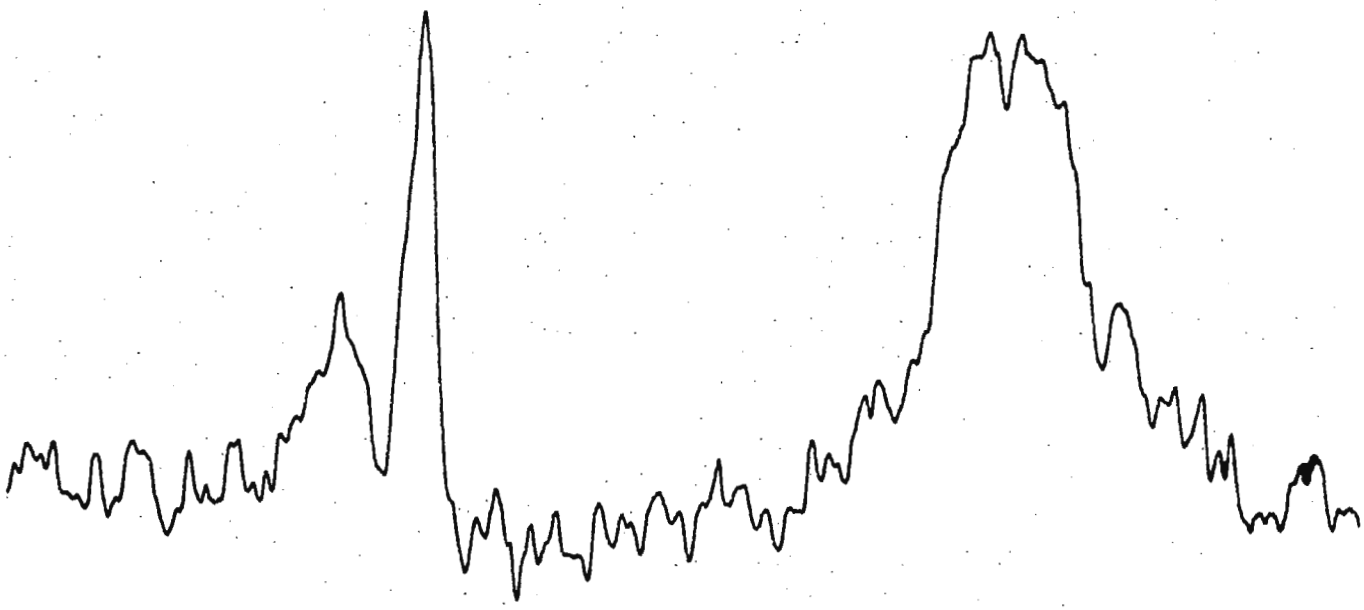


Figure 2. the ^{113}Cd nmr spectrum of Concanavilin A recorded at a protein concentration of 5.6 mM after approximately 10 hrs of accumulation in an 18 mm tube.

Diamond Shamrock

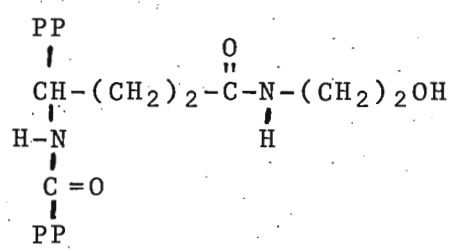
September 20, 1976

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

Detailed Interaction of Aqueous Salts with Random Coil Polypeptides

Dear Professor Shapiro:

I would like to initiate our subscription to the TAMU Newsletter by describing some ^{13}C NMR studies of the interaction of salts with the random coil polypeptide polyhydroxyethylglutamine (PHEG) (I) being carried out in collaboration with L. Mandelkern of Florida State University and W. L. Mattice of Louisiana State University.



(I)

Certain classes of salts disrupt the ordered structures of proteins and polypeptides, but little is known concerning the detailed interactions involved. Circular dichroism (CD) has been used with some success in this regard, but little information was forthcoming at the molecular level.

In the table are the ^{13}C chemical shift changes of the amide carbonyl carbons in PHEG, relative to no added salt, for $CaCl_2$ and LiCl. Data for the conformationally rigid model cyclo(L-alanine)$_2$ is also given. For $CaCl_2$, rather large, though gradual, changes are seen. This is in contrast to the CD results, where an abrupt change is seen between 4 and 6M $CaCl_2$. It is of interest that the Ca^{+2} ion binds more strongly to the backbone peptide moiety than to that of the side chain, a fact that may be of significance in protein denaturation by concentrated solutions of

divalent cations. The observation of a substantial shift change in cy(Ala)$_2$ suggests that a good portion of the changes in PHEG can be attributed to disturbance of the electronic distribution of the electronically labile amide moieties. Conformational changes at the backbone can not be ruled out, however.

For LiCl, an entirely different behavior is seen. Here, the backbone amide is not affected. The side-chain carbonyl resonance shifts opposite to that of $CaCl_2$, a fact that's surprising in view of the similarities exhibited by Ca^{+2} and Li^+ in other types of experiments. One might speculate that, while the Ca^{+2} cation acts by binding directly to the polymer, Li^+ acts by affecting the water structure in the vicinity of the polypeptide.

Sincerely,

Richard A. Komoroski

Richard A. Komoroski

Table I

^{13}C Shift Changes for the Carbonyl Carbons of PHEG and Cyclo(L-ala)$_2$ with Added Salt

[$CaCl_2$]	$\Delta C°_{sc}$(PHEG)	$\Delta C°_{bb}$(PHEG)	$\Delta C°$(cy[Ala]$_2$)
0.09	-0.01	0.00	-
0.18	0.03	0.07	0.03
0.43	0.06	0.18	-
0.85	0.11	0.27	0.19
2.25	0.34	0.61	0.54
4.7	0.60	1.39	0.99
6.6	0.64	1.76	-
[LiCl]			
0.2	0.00	0.02	-0.03
1	-0.08	0.00	-0.08
2	-0.16	0.00	-0.11
5	-0.38	0.02	-0.19
10	-0.73	0.19	-0.38

Measured with respect to external dioxane. Estimated accuracy ±0.05 ppm. Given as δ(in D_2O) - δ(in salt).

Carr Laboratory, Department of Chemistry
MOUNT HOLYOKE COLLEGE
South Hadley, Massachusetts 01075
Telephone 413 538-2214

20 September 1976

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

Dear Barry,

"High Speed" Optical Paper Tape Reader

We would like to bring to the attention of Newsletter readers an inexpensive alternative to the fast paper tape reader, an alternative that is borrowed from the ever-growing market of microcomputer products. It is the OP-80A optical paper tape reader available from Oliver Audio Engineering, 1143 North Poinsettia Drive, Los Angeles, CA 90046.

This unit reads punched paper tape as it is pulled through by hand. Illumination for the optical sensor array is provided by a low-wattage incandescent lamp, e.g. a Tensor lamp. A lamp kit which mounts directly on the unit is available as an option. The latter is strongly recommended if high tape speeds are desired since the reader is small (3 x 4-1/2 x 1 inches), lightweight, and, if not firmly fixed, can easily be displaced from the light source while pulling on the tape.

The reader can be connected across a UART to load programs through a TTY port, or by an 8-bit parallel interface as in our own system. The interface which we developed is shown in the figure. It is specific for our Digilab NMR-3 FT system but you will note that it is quite basic including a network (Z1 and Z2) for decoding the device selection word and the remaining logic devices providing the necessary buffering. Signals associated with the reader are the lines and designations given to the right side of the figure while those associated with the Nova computer are at the left and bottom. The terminals S1 and S2 refer to light emitting diodes contained on the unit which we use to monitor operation.

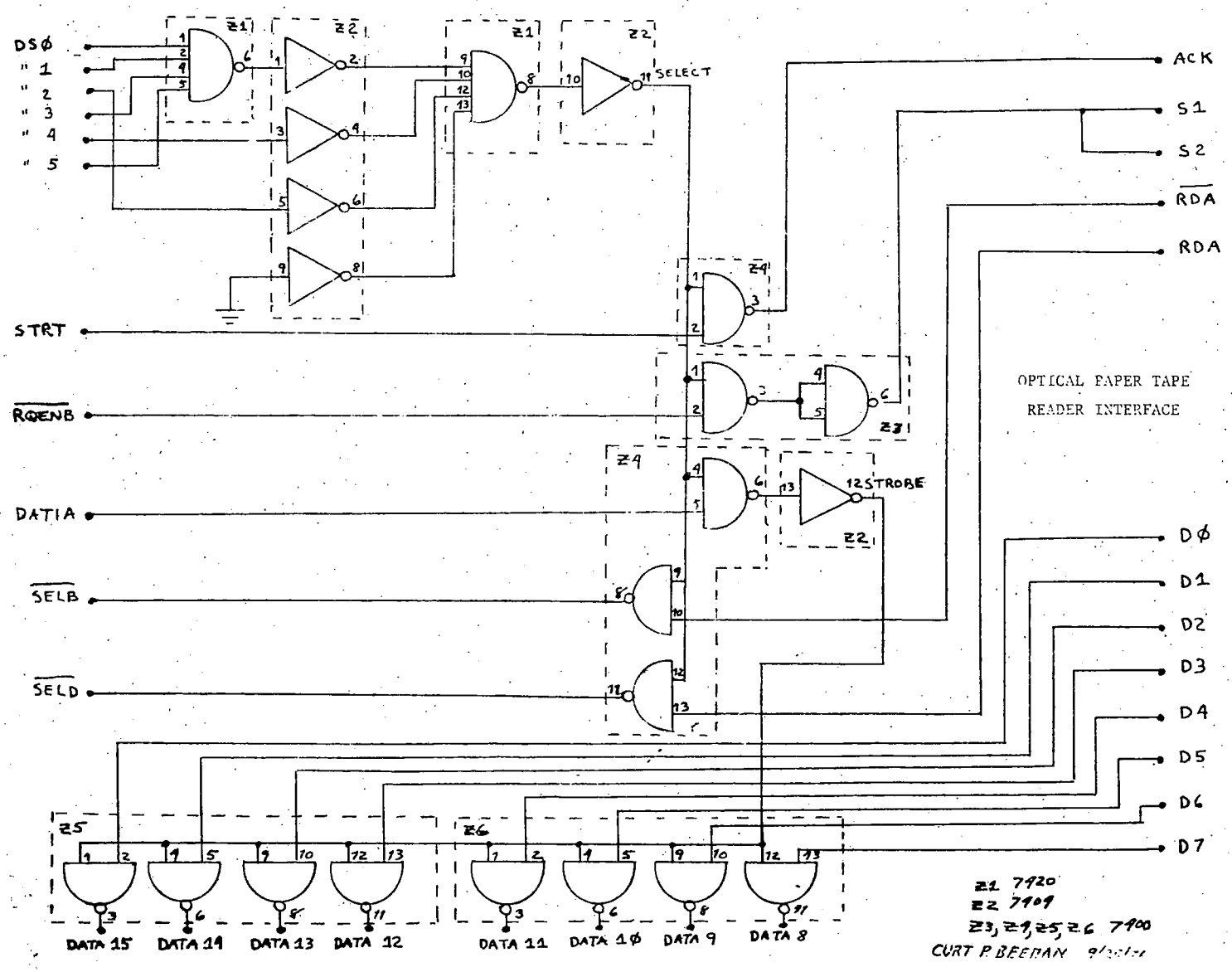
We have not really put it to the test, but specifications indicate the reader is capable of speeds up to 5000 characters per second and it is said to be able to load 12K extended BASIC in 30 seconds. In any event, the tape speeds which we have achieved by this manual mode of transport is a great improvement over the slow teletype reader. However, the best feature, in these times of cost effective consciousness, is the price: $74.50 for a kit, $95.00 assembled.

Anyone desiring additional information concerning our experience with this "high speed" tape reader is welcome to contact us.

Sincerely yours,

Curt P. Beeman
Postdoctoral Fellow

Kenneth L. Williamson
Professor of Chemistry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Z2 7409
Z3, Z4, Z5, Z6 7400
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UNIVERSITÄT DES SAARLANDES
Fachbereich 14 - Organische Chemie
Professor Dr. H. Dürr

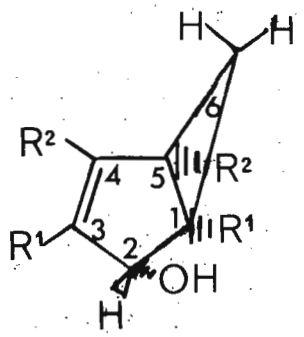
66 Saarbrücken, den 20.9.1976
Telefon: (0681) 302.3409

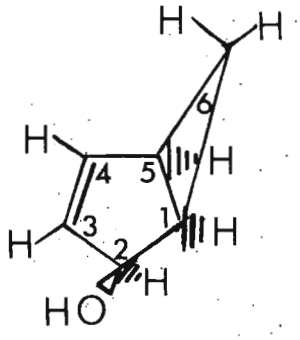
Herrn
Professor Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station,
Texas 77843
U.S.A.

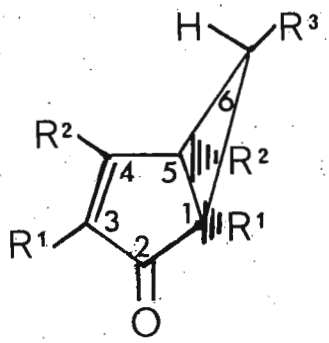
Dear Professor Shapiro

^{13}C-NMR-Studien an Bicyclen

An den Bicyclohexenolen 1 - 4 und den Bicyclohexenonen 5 - 8 sollten mit Hilfe der ^{13}C-Verschiebungen die Ladungsübertragung am Cyclopropanteil von Bicyclen studiert werden.







1 $R^1=R^2=H$
2 $R^1=Et$, $R^2=Ph$
3 $R^1=R^2=Ph$

4

5 $R^1=R^2=R^3=H$
6 $R^1=Et$, $R^2=Ph$, $R^3=Me$
7 $R^1=R^2=Ph$, $R^3=H$
8 $R^1=Ph$, $R^2=\alpha$-Pyr, $R^3=H$

Dazu wurden folgende chemischen Verschiebungen δ_{TMS} an einem Bruker HX 90-Spektrometer gemessen.

Tab.1: Chemische Verschiebungen δ[in ppm] der Kohlenstoff-Signale in 1, 2, 3 und 4

C-Atom	1	2	3	4
C4	139,6	142,2	140,4	137,7
C3	130,3	134,7	130,9	130,9
C2	77,0	78,3	78,0	78,1
C5	25,7	35,3	36,7*	24,0
C1	22,5	31,2	36,4*	18,1
C6	21,4	12,9	13,8	16,4

*) Zuordnung nicht gesichert

Die Zuordnung erfolgte auf Grund von relativen Intensitäten, der Aufspaltung in frequenzabhängigen Off-Resonance-Spektren und Inkrementberechnungen. Beim Bicyclo[3.1.0]hex-3-en-2-ol (1 bzw. 4) sehen wir eine Inversion der chemischen Verschiebungen der Kohlenstoffe 1 und 5 analog zu den chemischen Verschiebungen der Kohlenstoffe 3 und 4 an der Doppelbindung. Der induktive Abzug von Teilladungen durch die OH-Gruppe führt zu einer Tieffeldverschiebung des Signals für den Kohlenstoff 6, die bei den substituierten Verbindungen 2 und 3 nicht so ausgeprägt erscheint. Bei den Bicyclo[3.1.0]hex-3-en-2-onen 5 - 8 finden wir größere Tieffeldverschiebungen.

Tab. 2: Chemische Verschiebungen δ[in ppm] der Kohlenstoff-Signale in 5 - 8

C-Atom	5	6	7	8
C2	193,2	205,8	202,8	209,8
C4	162,9	163,3	169,4	166,8
C3	128,0	135,3	131,8	133,5
C5	40,0	49,3	45,0	47,0
C6	35,2	46,2	40,2	41,0
C1	22,8	51,6	46,5	48,0

Am unsubstituierten Bicyclo[3.1.0]hex-3-en-on 5 weisen die zur Carbonylgruppe β-ständigen Kohlenstoffe 4 und 5 bzw. 6 eine größere Tieffeldverschiebung auf als die beiden α-ständigen Kohlenstoffe 3 und 1. Dies kann durch Änderung der Elektronendichte erklärt werden. Die Kohlenstoffe 2,3 und 4 sind durch ein π-Elektronensystem miteinander verbunden.

Dadurch kann das durch Elektronenzug des Sauerstoffs hervorgerufene Ladungsdefizit am Kohlenstoff 2 auf die Kohlenstoffe 3 und 4 übertragen werden. Am Cyclopropansystem muß eine ähnliche Ladungsverschiebung angenommen werden. Durch konjugative Wechselwirkung wird jeweils am zur Carbonylgruppe α-ständigen Kohlenstoff ein kleineres Ladungsdefizit als am β-Kohlenstoff erzeugt, wodurch die Signale der α-Kohlenstoffe nicht so stark nach tieferem Feld verschoben werden wie die der β-Kohlenstoffe. Bei dem von Mamatyuk et al.[1] gemessenen Hexamethyl-bicyclo[3.1.0]-hexenyl-kation sind dieselben Effekte in noch stärkerem Umfang vorhanden. Die aus den ^{13}C-NMR-Daten abgeleiteten Elektronendichten ließen sich durch eine EHT-Rechnung belegen.

Tab. 3: Berechnete Elektronendichten von 5

C-Atom	Elektronendichte σ
C1	4,306
C2	2,710
C3	4,421
C4	3,917
C5	4,081
C6	4,139

Sie belegt die höheren Elektronendichten an den α-Kohlenstoffen 3 und 1 im Vergleich zu den β-Kohlenstoffen 4 und 5 bzw. 6. Die chemischen Verschiebungen $\delta_{^{13}C}$ der Kohlenstoffe des Cyclopropansystems ließen sich mit der EHT-Elektronendichte σ korrelieren und ergaben die Beziehung:

$$\delta_{^{13}C} = -76{,}25\ \sigma + 351{,}06$$

Mit freundlichen Grüßen

Professor Dr. H. Dürr Dipl.-Chemiker K.H. Albert

1) V.I. Mamatyuk, A.I. Rezvukhin, I.S. Isaev, V.I. Buraev und V.A. Koptyk, Zh. Org. Khim. 10, 662 (1974).

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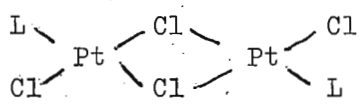
Hr/Mw

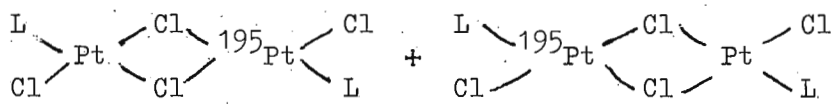
Dear Professor Shapiro,

Title: Measurement of ^{195}Pt NMR parameters in $Pt_2Cl_4(Pn\text{-}Bu_3)_2$

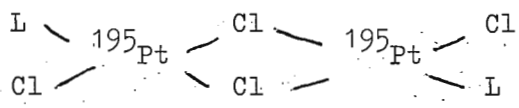
Owing to the natural abundance of the ^{195}Pt isotope of 33.8%, ^{195}Pt - ^{195}Pt coupling is present in $Pt_2Cl_4(Pn\text{-}Bu_3)_2$ which must therefore be considered as the following isotopic mixture:

I 

43.8% relative abundance

II 

44.8%

III 

11.4%

The trans configuration of this material has been confirmed from X-ray crystallography. [1]

Component I contains no ^{195}Pt and therefore gives no signal. Components II and III give rise to different spectra since in III there is 195Pt - ^{195}Pt coupling. The observed, proton-noise decoupled spectrum is shown in fig. 1d and may be compared with the simulated spectrum in fig 1c. The simulated total spectrum is a composite of the simulated spectra for the components II and III after applying the appropriate factors for the isotope distributions and neglecting the relatively small shift difference between Pt - 195 Pt and 195Pt - 195 Pt.

Koninklijke/Shell-Laboratorium, Amsterdam

d.d.

The parameters used to obtain the simulated spectra are as follows, these are compared with values obtained from ^{31}P NMR.[2)]

	^{1}J (^{195}Pt–^{31}P)	^{3}J (^{195}Pt–^{31}P)	^{2}J (^{195}Pt–^{195}Pt)	^{4}J (^{31}P–^{31}P)
^{195}Pt NMR	3820 Hz	- 23.0	195	2.7
^{31}P NMR	3822	- 23.5	199	2.8

The ^{195}Pt chemical shift was 3461 ppm upfield to H_2PtCl_6.

Yours sincerely,

(J.P.C.M. van Dongen, C. Masters and A.D.H. Clague)

References:

1) M. Black, R.H.B. Mais and P.G. Owston, Acta Cryst., 1969, 1325, 1760

2) A.A. Kiffen, C. Masters and J.P. Visser, J.C.S. Dalton 1975, 1311

Enclosure: 1.

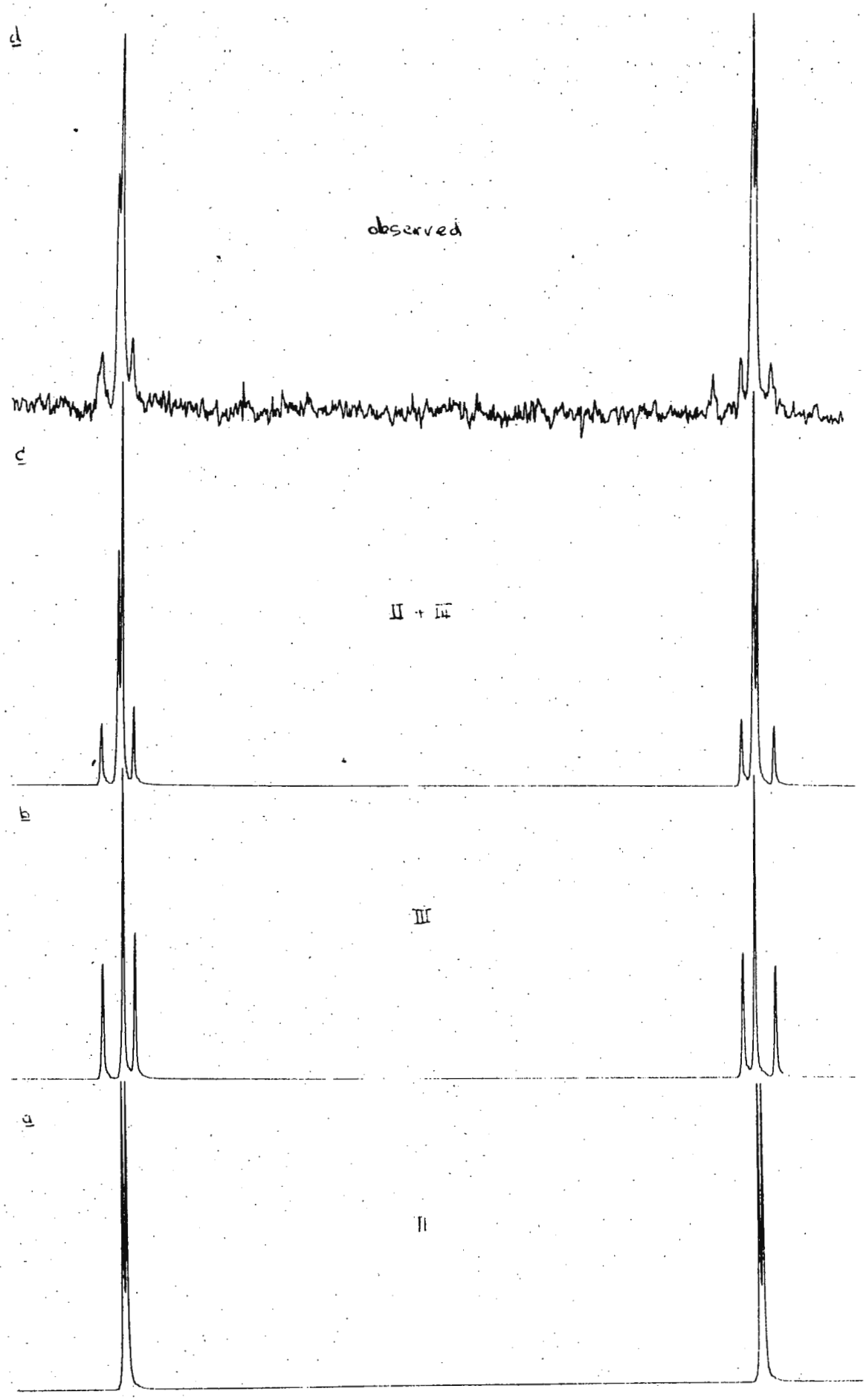


Fig 1

GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN
SUB-FACULTEIT - SCHEIKUNDE

Wassenaarseweg 76
Postbus 75

Telefoon 48333
toestel:

Afdeling: Bio-organic chemistry

Onderwerp:

LEIDEN, 21 september 1976

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

Dear Professor Shapiro:

Modification of the JEOL - DP-1 pulse programmer,

To increase the resolution of the digital setting of the delay time.

Elimination of the residual HDO-peak in ^{1}H-FT-NMR by the so-called WEFT-pulssequence is essential in the study of bio-organic molecules (1,2) especially when some resonances are hidden by this signal.
As we started using this method we soon discovered that the two digit selection of the interval time of the DP-1 pulsprogrammer of our JEOL PS-100 system seriously limited the complete elimination of the water peak when the interval time τ was longer than one second.
Krugh and Schaefer (2) have described a pulse adding circuit to overcome (among other things) this limitation, a circuit on which a delay time up to 2.3 second can be set with a ten-turn potentiometer.

However, we liked the easy referencing, easy setting of the thumbwheel switches provided on the DP-1 pulsprogrammer, so we tackled this problem from another point of view.
The solution we came up with is shown on the accompanying circuit diagram. The IC-4 (SN 7400) is removed from the print PCB-2 of the pulsprogrammer and replaced by the additional circuit shown.
The additional thumbwheel switch can be purchased from the local JEOL-office and replaces the "fixed zero", which is normally the last digit of the delay time setting.

Yours sincerely,

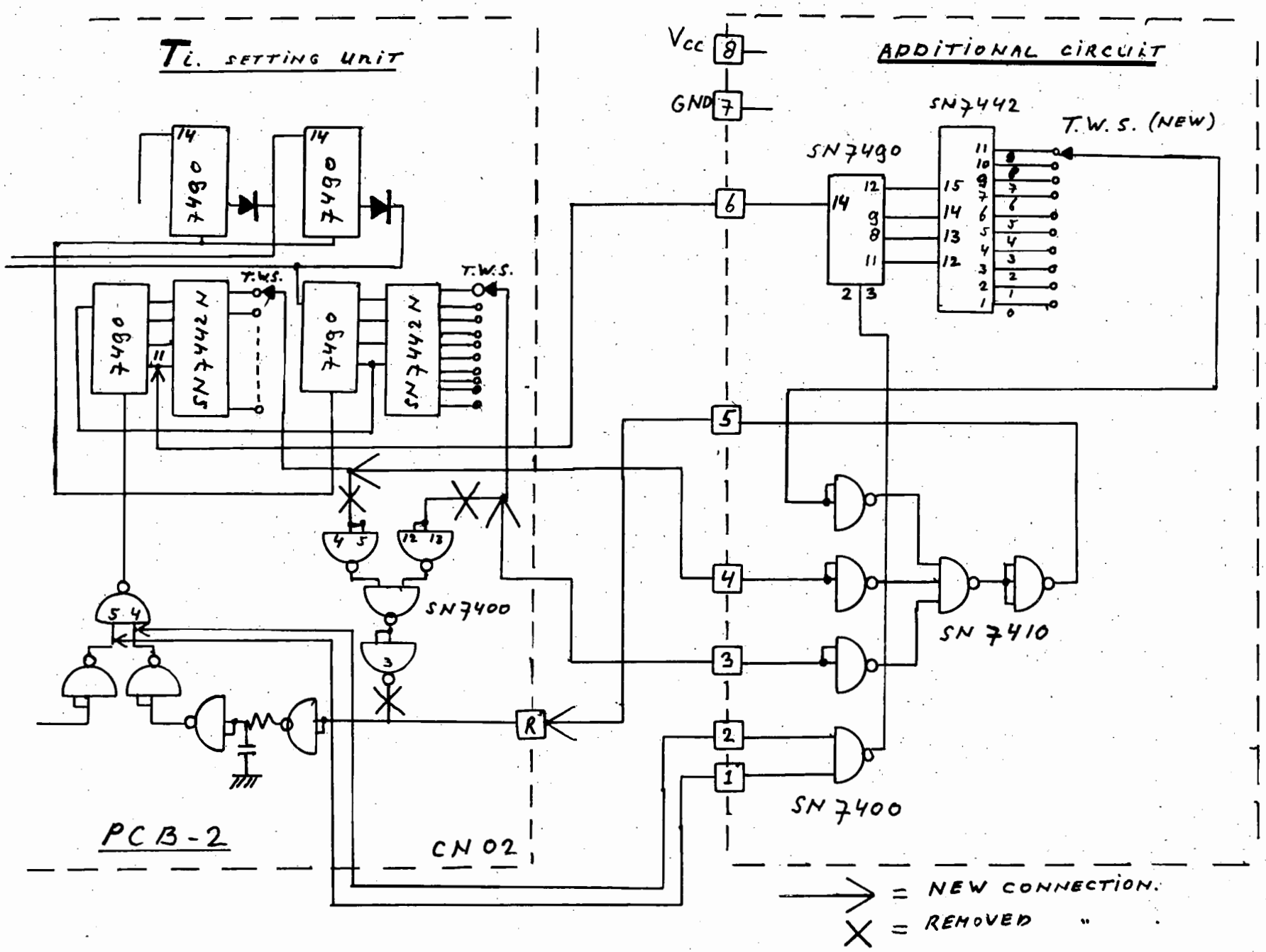
K. Takahashi

C. Erkelens

C.A.G. Haasnoot

J. Lugtenburg

References:
1) F.W. Benz, J.Feeney and G.C.K. Roberts-J.Magn.Res. 8, 114 (1972)
2) T.R. Krugh and W.C. Schaefer-J.Magn.Res. 19, 99 (1975)


Ti. SETTING UNIT
ADDITIONAL CIRCUIT
Vcc
GND
SN7442
T.W.S. (NEW)
SN7490
T.W.S.
T.W.S.
SN7400
SN 7410
SN 7400
PCB-2
CN 02
= NEW CONNECTION.
= REMOVED "

RIJKSUNIVERSITEIT GENT

LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, September 22, 1976
KRIJGSLAAN 271 - S 4 Tel. 22 57 15
(België-Europa)

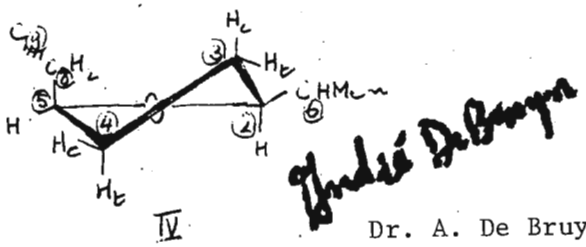
Conformation and remarkable high coupling values of the 2,5-cis-disubstituted tetrahydrofurane ring in NONACTIN-potassium complex.

Dear Barry,

We looked to the ^{1}H-NMR spectra of NONACTIN (1) and some of its cation-complexes, and the preliminary results (confirmed by SIMEQ 16/II simulations) disclose that in the KSCN-complex the tetrahydrofurane possesses a unique conformation, e.g. the $^3_4$T-form (or south-form, IV) with the most branched substituent C_2 in pseudo-equatorial position. Only for this S-form we may have very small values of $^3J(3t,4c) \approx {}^3J(4c,5) \approx 1$ Hz and such large values for $^3J(3c,4t) \sim 12.0$ Hz, and also expected is $^3J(2,3c) > {}^3J(2,3t)$. This conformation is not too far removed from the ^{3}E form observed in the solid state for the free antibiotic, but is at variance with the $_5$E form found for the solid K^+-complex (2). Noticable are the very large values of $^3J(2,3c)$ [and $^3J(3c,4t)$], somewhat unexpectedly large for a five membered ring where the maximal puckering would be 40-45° (around C_3-C_4).

It is however interesting to note that the preferred form is identical to the one encountered in a large number of furanoses found in nature (2).

The data, confirmed by double irradiation, are gathered in the table. A previous study at 220 MHz (3) enabled only the extraction of a limited number of informations (e.g. $^3J(2,6)$, $\Sigma^3J(5,8)$ and $\Sigma^3J(8,9)$). As found earlier, the present data confirm the backbone conformation of the tetrolide, which is "tennis-ball" shaped, the monovalent cation being held in the middle by the 4 carbonyl oxygens and 4 tetrahydrofurane ether oxygens as the ligands with a cubic arrangement around the central cavity.



IV

Yours truly,

Dr. A. De Bruyn. Prof. M. Anteunis.

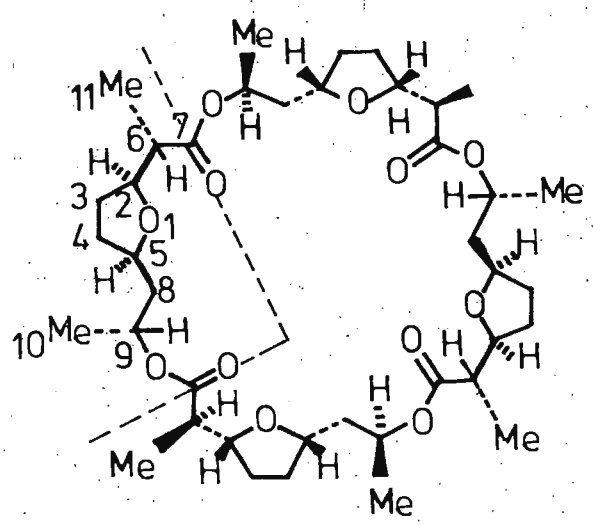
(1) M. Dobler, J.D. Dunitz and B.T. Kilbourn; Helv.Chim.Acta 52, 2573 (1969); M. Dobler; id. 55, 1371 (1972); Y. Haka, T. Sakamaki and Nawata; Chem. Letters (Japan) 1225 (1972); cf. for other nactins: Y. Nawata and K. Ando; Acta Cryst. B27, 1680 (1971).

(2) C. Altona and Sundaralingham; J.Am.Chem.Soc. 95, 2333 (1973), and C. Altona; private communication.

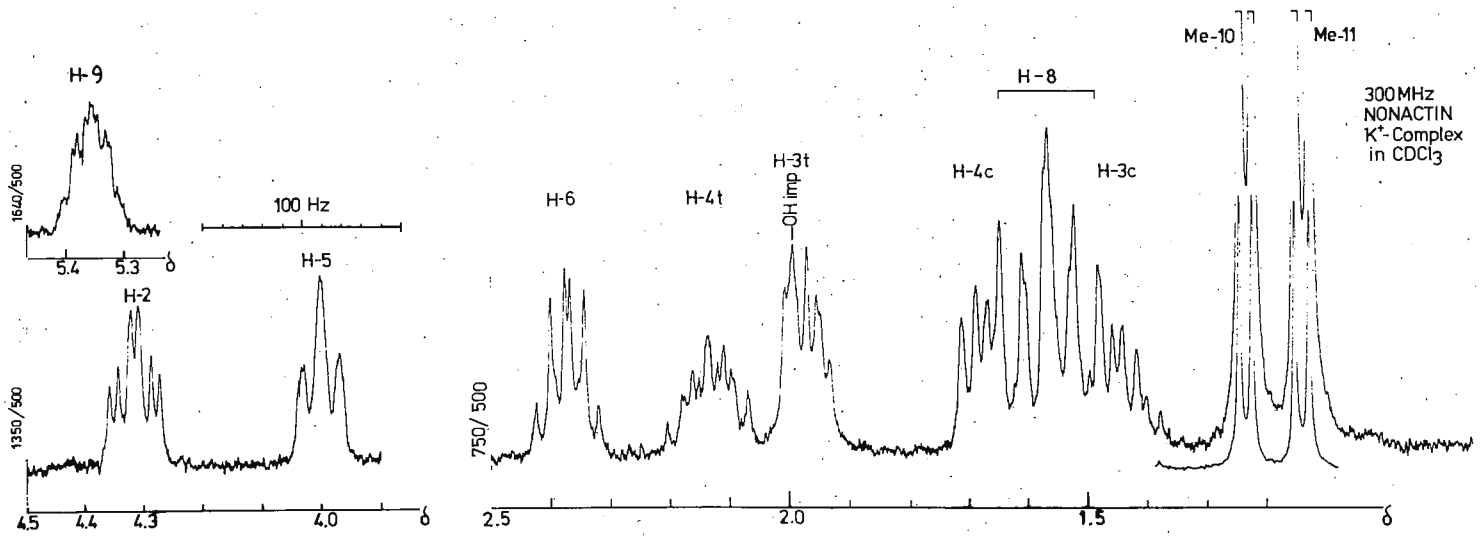
(3) J.H. Prestegard and S.I. Chan; J.Am.Chem.Soc. 92, 4440 (1970); cf. ibid., Biochemistry 8, 3921 (1969).

	2	3t	3c	4t	4c	5	6	8A	8B	9	10	11
2	4.31											
3t	5.0	1.97										
3c	12.0	-12.5	1.43									
4t		7.0	12.0	2.13								
4c		∿1.0	7.0	-12.2	1.68							
5				8.5	∿1.0	4.00						
6	9.9						2.37					
8A						11.5*		∿1.59				
8B						{& 2.4		-12.0	∿1.54			
9								11.5 &	2.4*	5.35		
10										6.4	1.23	
11							7.2					1.13

* (may be reversed)



1



DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF ALBERTA
EDMONTON, CANADA
T6G 2G2

September 27, 1976

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

Title: Homemade ^{13}C micro insert for HFX-90's

Dear Barry:

I realize that this contribution to the Newsletter is a bit early*, but I felt that some of your readers who own HFX-90's (or similar systems) might be interested in a micro insert for ^{13}C that we built here in Alberta. HFX-90 owners know that changing from nucleus to nucleus requires switching glass dewared inserts in the probe body. We had a broken 10 mm $^{13}C/^{2}D$ lock insert in the lab and decided to try to build a micro insert with the remaining pieces after seeing many 5 mg cholesterol ^{13}C spectra.

The epoxy holding the dewar to the Teflon spacers was loosened by soaking the insert overnight in toluene. Our machine shop made Teflon spacers to accommodate the new insert. The insert was built by close winding about 50-60 turns of 34 gauge insulated copper wire on a 1.8 mm form and carefully inserting this coil into a 4 mm (O.D.; 2.2 mm I.D.) pyrex tube. The top lead of the coil is passed through a hole cut in the side of the tube and the coil was held in place with Aron Alpha (a quick setting adhesive). The coil had an inductance of 1.4 μH and a self resonate frequency of 81 MHz; these values closely match those of the original 10 mm coil.

With this configuration we obtained the ^{13}C spectrum of 5 mg of cholesterol shown in Fig. 1 in a 1.7 mm (O.D.) melting point capillary. The lock level from neat acetone-d_6 is about a factor of two lower on the micro insert vs. the 10 mm tube/10 mm insert. Spinning was accomplished via a windmill mechanism. Further details will be sent to those who are interested.

Sincerely,

Tom Nakashima

Tom Nakashima

TN/ls

*
There is no such thing as an early Newsletter contribution, although there are such things as late Newsletter contributions. Sometimes even too late Newsletter contributions. Our policy of one contribution per 9-ish months is a minimum number, and implies no maximum number or minimum interval.

B. L. Shapiro

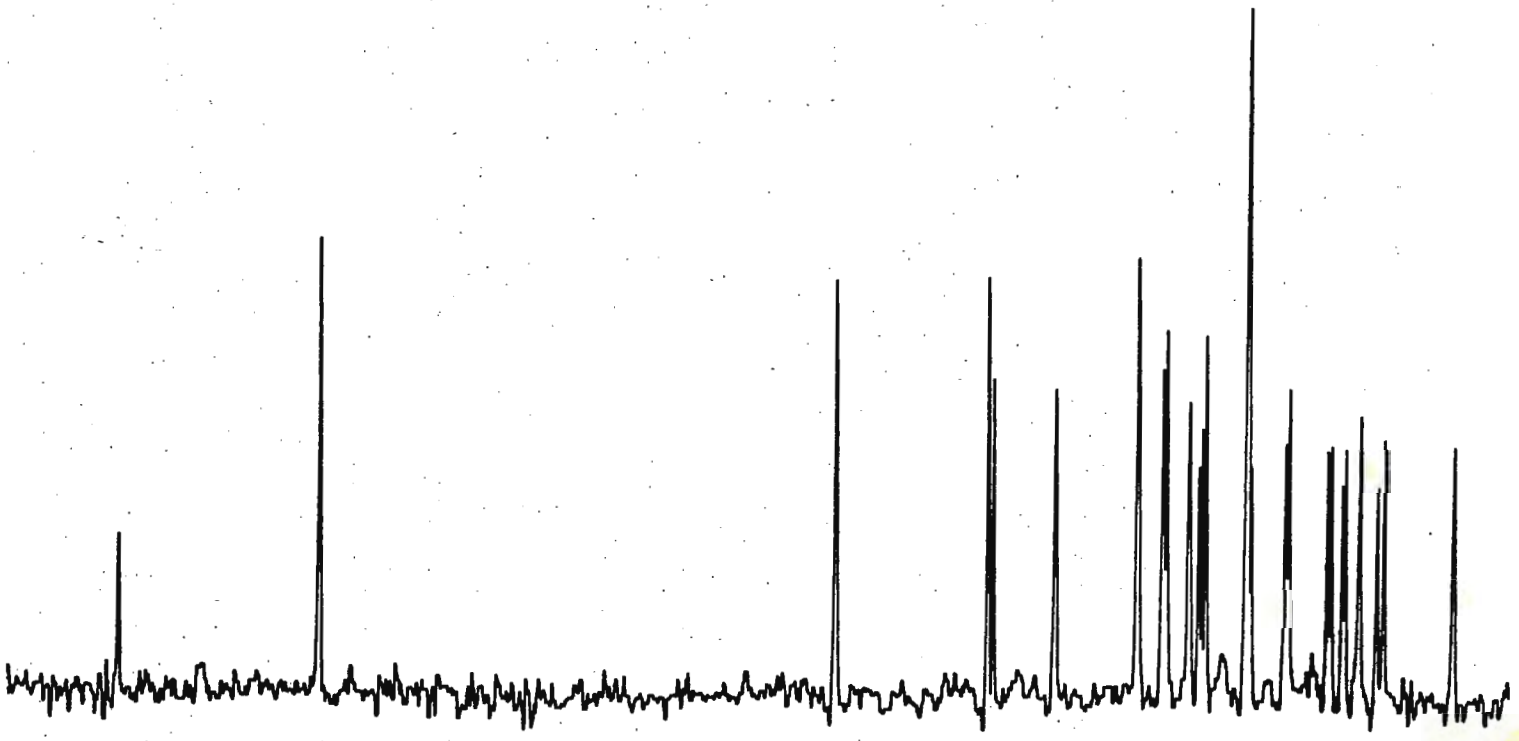


Fig. 1

^{13}C spectrum of 5 mg (~15 μl $CDCl_3$) cholesterol. 3088 pulses

[1250 pulses (1000 sec. accum. time, 0.8 sec/pulse) × 2 (Quad) × $\left(\frac{25.15}{22.63}\right)^2$ = 3088]

8K data pts (zero filled to 16K)

LB of 0.5 Hz

8 μs pulse width (12 μs = 90°)

Spectrum plotted with 0.1 × 1.96 filter on Bruker console

GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN
SUB-FACULTEIT - SCHEIKUNDE

Wassenaarseweg 76
Postbus 75

Telefoon 48333
toestel:

Afdeling: Theor. Org. Chem.

Onderwerp:
Dr. J.A. den Hollander

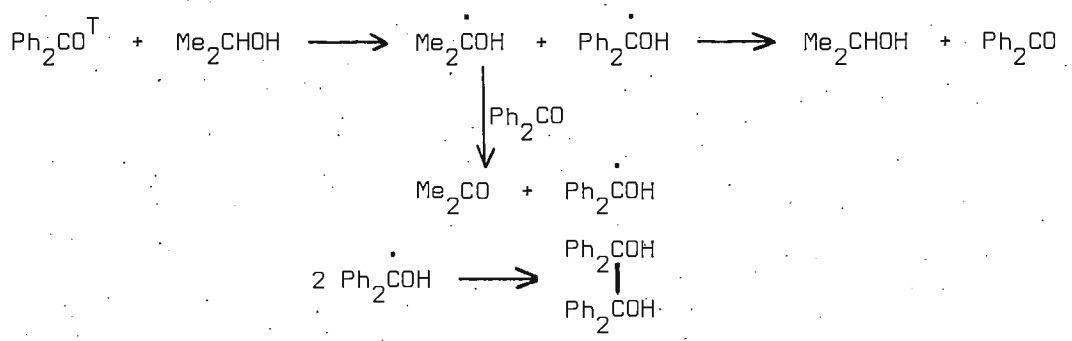
LEIDEN, 29 September 1976

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

Title: Rate Constants from CIDNP Enhancement factors

Dear Professor Shapiro:

During UV irradiation of a solution of benzophenone and isopropanol (0.1 M) in hexadeuterobenzene CIDNP is observed for the parent compounds benzophenone (enhanced absorption) and isopropanol (CH_3 enhanced absorption and OH and CH emission) and for the products acetone (emission) and benzopinacol (emission for the aromatic region and OH). The polarizations observed for isopropanol and acetone are interpreted straightforwardly by the well known hydrogen abstraction of triplet benzophenone from isopropanol (Scheme)



SCHEME

The polarizations observed for isopropanol and benzophenone demonstrate that the dimethylketyl and the diphenylketyl radicals can regenerate the parent compounds, a reaction step not found before.

CIDNP is a useful tool to obtain information about the hydrogen transfer reaction of the dimethylketyl radical to benzophenone. The enhancement factor observed for acetone is dependent on the lifetime of the dimethylketyl/diphenylketyl radical pair, which is limited by this hydrogen transfer reaction. The

dimethylketyl radical disappears with the pseudo first order rate k determined by the benzophenone concentration $[B]$ and the second order rate constant k_t of the transfer reaction

$$k = k_t \, [B]$$

For a given nuclear state $|n\rangle$ the recombination probability for a triplet radical pair is given by[1]

$$P_{Tn} = \frac{1}{6} \lambda \, m \sqrt{2\pi} \left(\sqrt{\sqrt{k^2 + 4a_n^2} + k} - \sqrt{2k} \right)$$

a_n is the singlet triplet mixing coefficient, $m \simeq 10^{-6} \, s^{\frac{1}{2}}$ and λ the probability of recombination during a singlet collision of the radical pair. The probability of formation of the escape product acetone is now given by $D_n = 1 - P_n$

We measured the enhancement factor for acetone during the irradiation as a function of the benzophenone concentration. This is most easily done by measuring the NMR intensity for acetone during (I) and after (I_0) a total irradiation time t'. The enhancement factor is then given by[2]

$$V = \frac{I \, t'}{I_0 T_1}$$

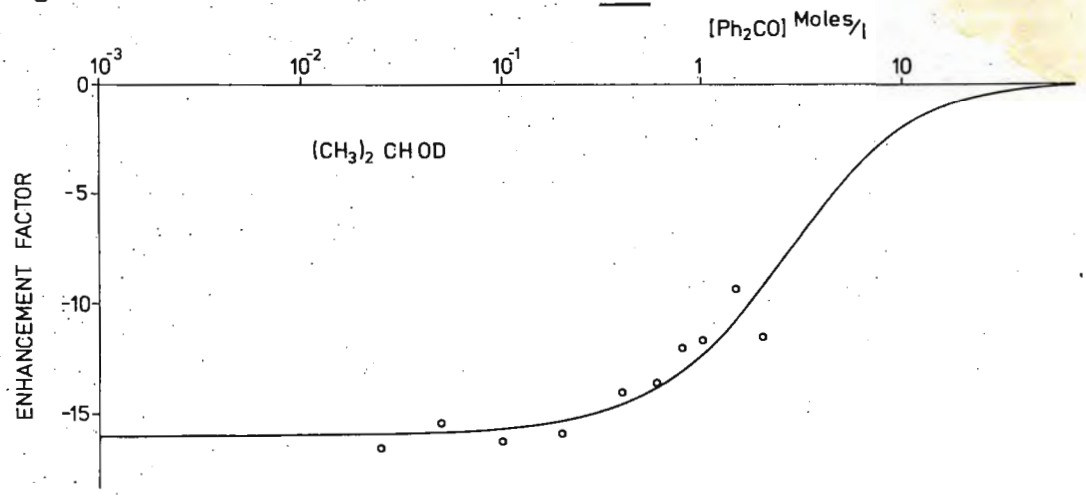
in which T_1 is the spin lattice relaxation time for acetone during the irradiation. Intensities during irradiation were corrected for product formation

The theoretical curve for the enhancement factor as given by the formulae was fitted to the experimental points by a least squares procedure (Figure), yielding values for the rate constant k_t and the scaling factor λm. Using isopropanol-OH we found for the hydrogentransfer reaction a rate constant of $2.8 \, (\pm 0.4) \times 10^8 \, M^{-1} sec^{-1}$, for isopropanol-OD $1.5 \, (\pm 0.3) \times 10^8$ (deuterium transfer reaction).

Yours Sincerely,

(Dr. J.A. den Hollander)

1. J.A. den Hollander, Chem. Phys., 10, 167 (1975)
2. M. Lehnig, and H. Fischer, Z. Naturforsch., 25a, 1963 (1970)



BAYLOR COLLEGE OF MEDICINE
TEXAS MEDICAL CENTER
HOUSTON, TEXAS 77025

September 30, 1976

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

Title: Temperature Effects on Dextran ^{13}C NMR

Dear Professor Shapiro:

During a structural study of dextrans, it was noticed that few spectroscopists have considered the effect of temperature on carbohydrate ^{13}C spectra. In some instances, the temperature of the samples was not reported. High resolution spectra of large carbohydrates may be facilitated by heating. This ameliorates problems with solubility and viscosity giving good spectra in a short time. There is a temperature dependence (in addition to that caused by change in bulk susceptibility) of the chemical shift that is influenced by structure. It is confusing when researchers report monomer spectra at ambient temperature for comparison with polymer spectra at high temperature.

27° 90°

The spectra reproduced here are of B-1355-S, a highly purified, branched dextran. Clearly, the high temperature spectrum shows more resolution, the improvement in resolution being greatest for the more branched polymers. Also note the change in relative intensities. A differential shift of more than one p.p.m. is observed and carbon-6 (∿60 p.p.m.) demonstrates the greatest shift, about twice the average.

Sincerely,

Roger

Roger D. Knapp, Ph.D.
Instructor in Experimental Medicine

RDK/dm

NATO ADVANCED STUDY INSTITUTE

ON

"CHEMICALLY INDUCED MAGNETIC POLARIZATION"

A NATO Advanced Study Institute on this subject will be held at "SOGESTA", Urbino, Italy, April 17-30, 1977. The scientific programme includes lectures by

F.J. Adrian, P.W. Atkins, G.L. Closs, R.W. Fessenden, H. Fischer, J.H. Freed, R. Kaptein, R.G. Lawler, K.A. McLauchlan, L.T. Muus, and J. Boiden Pedersen.

The School is open to Research Scientists and Graduate Students interested in the field.

For application blank and further information please contact

Professor L.T. Muus
Chemistry Institute
140 Langelandsgade
DK-8000 Aarhus C, Denmark.

Deadline for applications is January 20, 1977.

- - - -

217-55

SANDOZ, Inc.

PHARMACEUTICAL
RESEARCH & DEVELOPMENT

EAST HANOVER, N. J. 07936

TELEPHONES
201 - 386 - 1000
212 - 349 - 1212
TWX: 710 - 986 - 8208
TELEX: 13 - 8352

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

August 18, 1976

Sir:

Nuclear Magnetic Resonance Spectrometer Probe Protection

The high RF power fed into nmr probe transmitter coils, typically for proton broad band decoupling in e.g. ^{13}C observe operation, necessitates cooling of the probe. Interruption of this cooling may cause heat damage to the probe, and examples are known to nmr users.

A scheme was devised which would prevent such damage. It was implemented on an XL-100 (Varian) spectrometer, but is also applicable to other spectrometers. Simply, it switches over high pwer decoupling to low power decoupling whenever the cooling gas line pressure, upstream of the probe, falls below an adjustable threshold or exceeds another adjustable limit.

Our implementation utilizes a double pressure switch of the same type[1] which is used inside the temperature controller module of the XL. The latter was not shared for the two purposes for fear of signal interferences. The unit was conveniently mounted on the back of the console, at the decoupler module, and short connections were made into the upper portion of the decoupler, details of which appear on the attached diagram.

The protection device has been successfully tested and is in constant use. It will protect the probe in the following situations: unintentional turning on of high power decoupling (will not go on), accidental disconnection (e.g. "slipping off") of cooling gas line upstream or downstream of pressure switch (pressure drop), pinching of gas line upstream (drop) or downstream (increase) of switch, obstruction of the exit passage, and of course, reduced cooling gas supply.

The fact that changing to low power rather than to no decoupling occurs by the switchover, helps to salvage some of the results of experiments -- a valuable asset in long overnight or weekend runs.

Cordially,

S. Barcza

J. H. Eckhardt

SB/JHE:rck
attach.

References:

1. Varian part no. 71-619-900 "Barksdale Switch" Model D2S-A3-Q25.

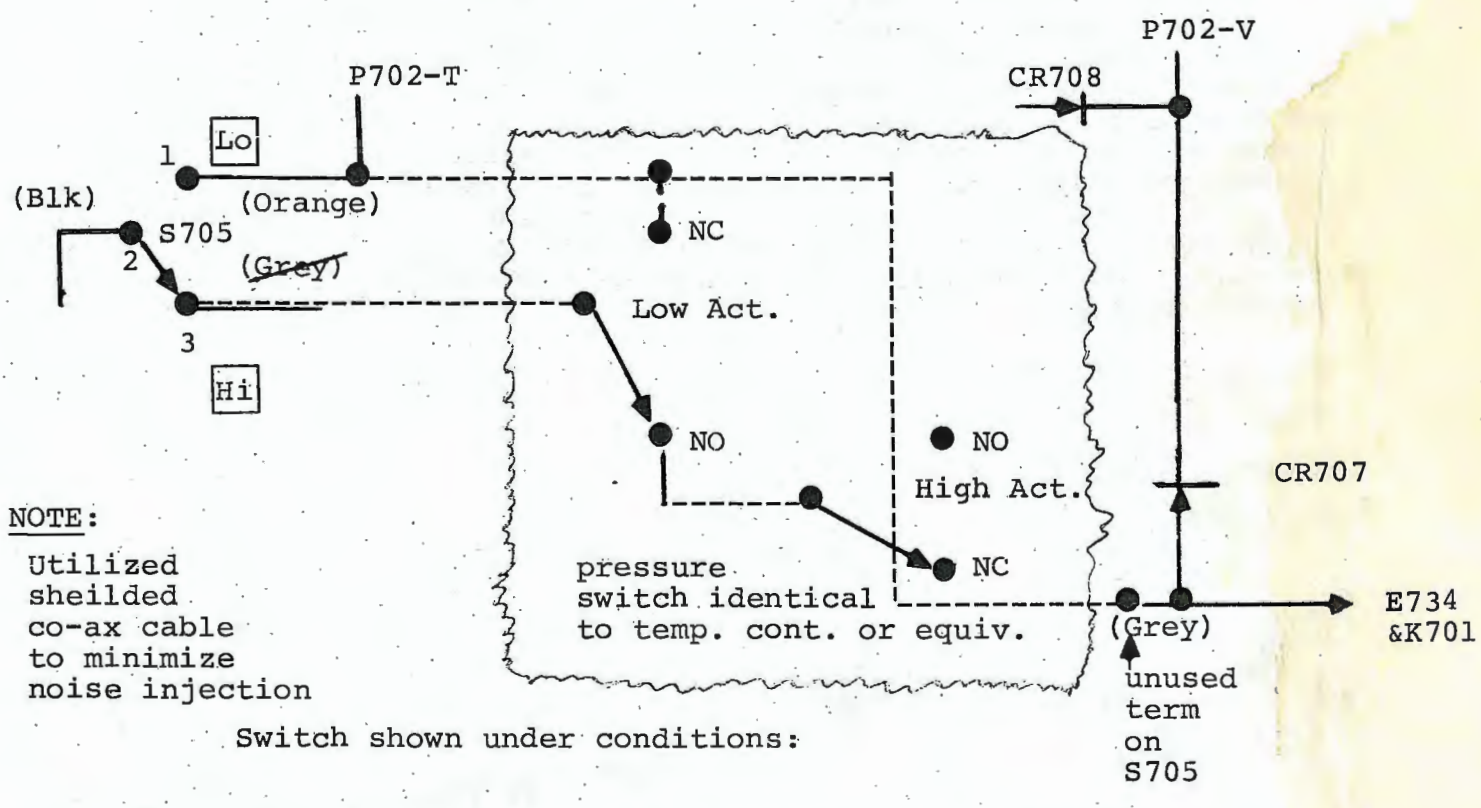
2. Utilizing Varian Schematic No. 87-126-859 Rev. F970 Sheet No. 1.

Acknowledgement:

The authors wish to thank Mr. Charles S. Peters for helpful technical advice, Mr. James A. Crawford for approving the warranty-compatibility of the modification, and Mrs. Alicia D. Kahle for independent testings.

CIRCUIT MODIFICATION[2]

Low Level - High Level Gas Pressure Protection



NOTE:

Utilized sheilded co-ax cable to minimize noise injection

Switch shown under conditions:

Low pressure $< N_2$ Pressure $<$ High Pressure

217-57

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

September 21, 1976

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

Dear Barry:

A UBIQUITOUS IMPURITY IN OUR ^{14}N nmr SPECTRA

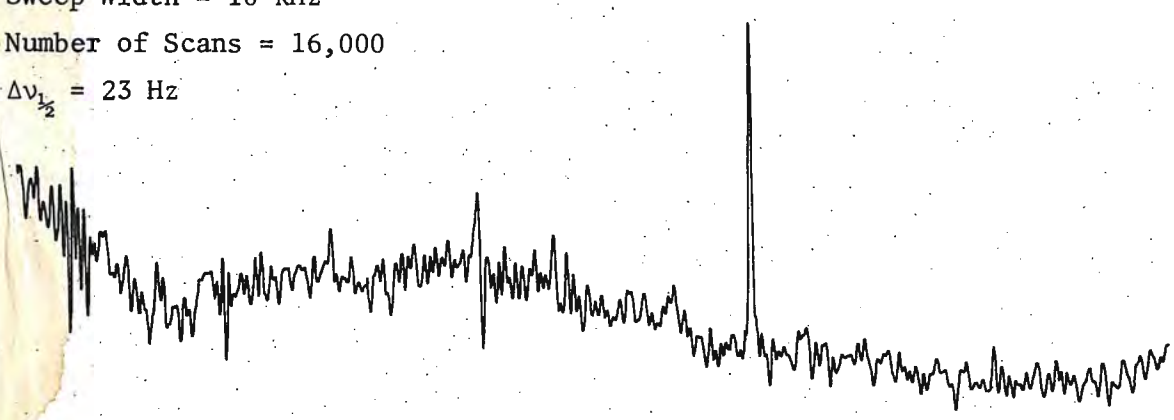
We were recently disturbed to find some of our ^{14}N nmr samples contaminated with a rather ubiquitous impurity. As part of a study on the motion of linear molecules in hydrocarbon solvents, we made up solutions of dicyanoacetylene in n-hexane. As these samples were made more dilute and more signal averaging was required, a narrow shoulder appeared on the nitrile ^{14}N peak. Since this sample was not degassed and was handled so much, it seemed possible that the dicyanoacetylene (not the most stable molecule) had decomposed. A fresh dilute sample was prepared and the resulting spectra found to still contain this impurity; furthermore, even pure n-hexane gave a sharp line at this frequency! There seemed to be only one (to us surprising) explanation, and bubbling argon thru this n-hexane sample confirmed that it was dissolved atmospheric nitrogen that was the culprit. Shown below is a room temperature spectrum of n-hexane saturated with N_2 gas.

Spectrometer Frequency = 4.340 MHz

Sweep Width = 10 KHz

Number of Scans = 16,000

$\Delta\nu_{1/2}$ = 23 Hz



Professor B. L. Shapiro
September 21, 1976

Incidentally, it appears that the reorientation of these small linear molecules does not fit conventional descriptions of molecular motion in terms of a white distribution of spectral densities.

Our pulse spectrometer has undergone some improvements lately. With the ADC in our Nicolet 293 box, some addition to the Nicolet NTCFT software, and a very inexpensive temperature sensing system we now get a printed listing of sample temperatures during the course of an experiment. A software controlled temperature regulation system, based on our ancient Varian V-4340 Heater Control, has been successfully bench tested and will be installed shortly. Anyone interested in the details of NTCFT and NIC 293 modification is welcome to write us.

Best Regards,

Nikolaus Gitte Bob

Nikolaus M. Szeverenyi Regitze R. Vold Robert R. Vold

mb

<u>Position available</u>: Organic NMR

Supervision of NMR service lab within medicinal chemistry, spectral (esp. ^{13}C) interpretation, problem-solving, instrument operation (T-60, EM-360, XL-100FT). Interfacing with requestors, co-workers, subordinates. Excellent command of organic chemistry as well as NMR experience required. Skill with gadgets desirable. Physical and mathematical-computer inclination helpful.

Send resumé to S. Barcza, 403/3, Sandoz, Inc., Rt. 10, East Hanover, NJ, 07936

217-59

THE INSTITUTE FOR CANCER RESEARCH
7701 BURHOLME AVENUE
FOX CHASE · PHILADELPHIA, PENNSYLVANIA 19111
215 FIDELITY 2-1000 · CABLE ADDRESS: CANSEARCH

October 1, 1976

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

Dear Barry:

NOTICE OF POSITION AVAILABLE

A long term position, that of Research Associate or Senior Research Associate in the field of magnetic resonance instrumentation exists in our research group. The requirements are a B.S. degree in electrical engineering or its equivalent, and experience with pulsed NMR instrumentation and associated computers. The work involves the development, modification, maintenance, and repair of pulsed NMR and EPR instruments for biophysical research, and to attend and participate in meetings in these fields.

Advanced degrees, as well as an interest in biochemistry, biophysics or chemical physics are desirable but not essential. Candidates should send their curriculum vitae to us at the above address.

The Institute for Cancer Research is an equal employment opportunity/affirmative action employer.

Sincerely yours,

Al Mildvan

Albert S. Mildvan

Raj K. Gupta

Raj K. Gupta

ASM/RKG/sm

New 18-mm Probe for the XL-100

^{13}C Spectra 10 Times Faster

Now Varian XL-100 users can run natural abundance ^{13}C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose — clearly this new probe could extend the application of ^{13}C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs ^{13}C spectra of samples of limited solubility or limited molarity; or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10 — with results second to none.

Not only is the absolute **sensitivity** of the V-4418 Probe outstanding, it also offers excellent **sensitivity per milliliter** of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

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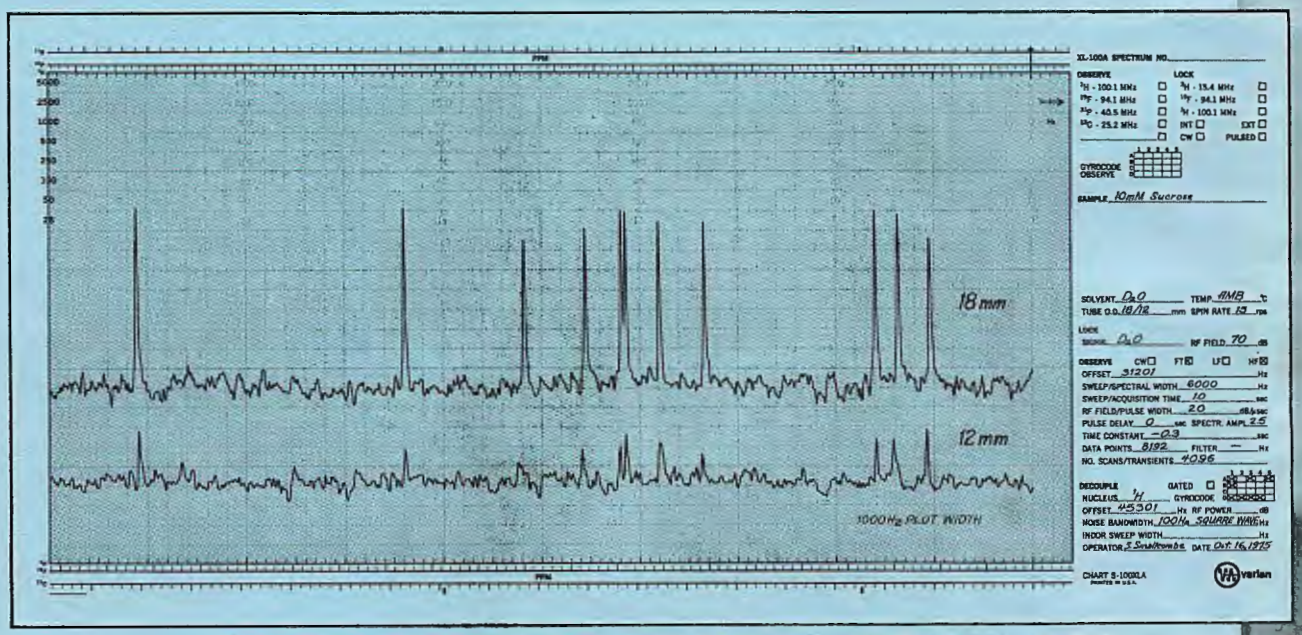

Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D_2O, one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.

Sample tube shown actual size.

For further information contact your local Varian representative or write to: Varian Instruments, 611 Hansen Way, Box D-070, Palo Alto, CA 94303.

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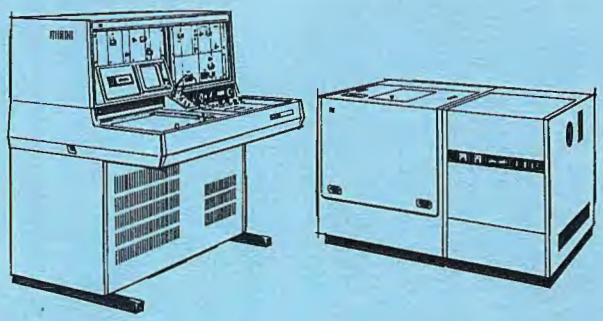

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