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Newsletter

No. 211

April, 1976

V. Bystrov New Data on Solution Conformation of Valinomycin.	1	C. Gust V-4311 R.F. Unit Used for F.T.; XL-100 Recorder Problem.	22
S. A. Knight and W. Wheatley Block-Averaging with a Fabritek (Nicolet) 1074 Instrument Computer	3	R. M. Dowben Varian DP-60 Spectrometer Available	23
S. Combrisson and B. P. Roques Influence of the Chain Length on the Differ- ences $\Delta\delta^E$ Between Cis and Trans α and δ ^{13}C of L-Proline Dipeptides.	4	J.P. Albrand, A. Cogne and J.B. Robert ^{31}P NMR Spectrum of Hexaphenylcyclohexaphosphine Oriented in a Nematic Liquid Crystal	24
A. S. Boyd Referencing and Plot Registration on the XL-100	7	Ir. A. F. Mehlkopf and G. Reckweg A Complete IRFT Sequence Averaging Method for T_1 -Measurements	26
W. B. Smith Postdoctoral Position Available	8	J. A. Deegan Opportunity Within the Bruker Organization in Japan	27
R. M. Oesterling and A. S. Mildvan High Energy COP-Out (and CCOP-Out)	10	R. E. Santini and J. B. Grutzner Let the Nuclei Speak, A Free-Standing 0.01- 110 MHz. Transceiver	28
L. Guidoni, P.L. Indovina, R.D. Guardia and E. Tettamanti Effects of Molecular Weight on Sol-Gel Transition in Water-Agarose Systems.	11	J. S. Cohen Observation of Individual Carboxyl Carbon Atom Resonances in a Protein with High Field CMR.	30
P. Diehl and J. Vogt Dipole-Dipole Splittings of $^{13}\text{CH}_4$ in Anisotropic Solvents.	13	J. N. Shoolery Carbon-13 NMR for the Micro-Chemist	32
K. Pachler and P. L. Wessels Assignment of Directly Bonded C-H Couplings in a Methylene Group with SPI.	15		
C. D. Hall and P. M. Schalke ^1H and ^{19}F NMR Data of Hydroxylamine Adducts of Cytosines.	18		
E. Kauffmann and J. M. Lehn Cation Exchange Rates in Cryptate Complexes by Temperature Dependent ^{13}C -NMR Spectros- copy	20		

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DEADLINE DATES: No. 212: 3 May 1976
 No. 213: 31 May 1976

(Due to vacation scheduling, it will
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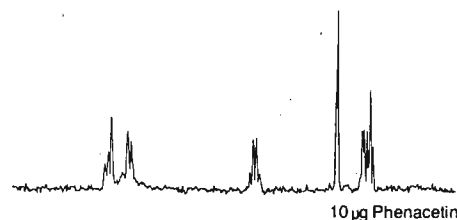
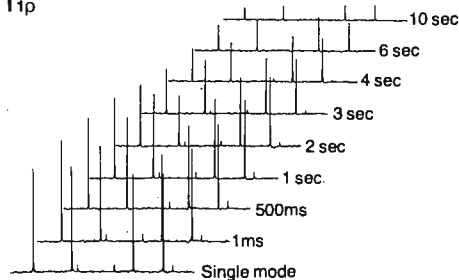
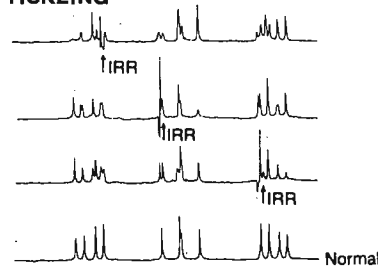
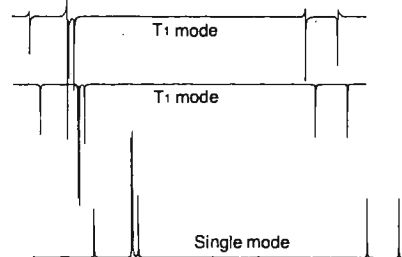
Dr. Bernard L. Shapiro
 Department of Chemistry
 Texas A&M University
 College Station, TX 77843 U.S.A.

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 211

Albrand, J. P.	24	Knight, S. A.	3
Boyd, A. S.	7	Lehn, J. M.	20
Bystrov, V.	1	Mehlkopf, Ir. A. F.	26
Cogne, A.	24	Mildvan, A. S.	10
Cohen, J. S.	30	Oesterling, R. M.	10
Combrisson, S.	4	Pachler, K.	15
Deegan, J. A.	27	Reckweg, G.	26
Diehl, P.	13	Robert, J. B.	24
Dowben, R. M.	23	Roques, B. P.	4
Grutzner, J. B.	28	Santini, R. E.	28
Guardia, R. D.	11	Schalke, P. M.	18
Guidoni, L.	11	Shoolery, J. N.	32
Gust, C.	22	Smith, W. B.	8
Hall, C. D.	18	Tettamanti, E.	11
Indovina, P. L.	11	Vogt, J.	13
Kauffmann, E.	20	Wessels, P. L.	15
		Wheatley, W.	3

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Dr. V. Bystrov
USSR Academy of Sciences
Shemyakin Institute
of Bioorganic Chemistry

Ul. Vavilova 32
Moscow 117312 USSR

March 3, 1976

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

Title: New Data on Solution
Conformation of Valinomycin

Dear Barry:

The empirically evaluated dependence of the vicinal $^{13}\text{C}'-\text{NC}^{\alpha}-^1\text{H}$ coupling on the $\text{N}-\text{C}^{\alpha}$ bond rotation⁽¹⁾ can be used for refining of the torsional ϕ angles determined by the proton $^1\text{H}-\text{NC}^{\alpha}-^1\text{H}$ coupling and, as a result, the conformational states of peptide molecule can be defined more unambiguously.

The comparison of these couplings (Figure) measured in the ^{13}C and proton NMR spectra of the cyclodepsipeptide ionophore - valinomycin in nonpolar (cyclohexane- d_6) and in medium polarity solvents (3:1 CCl_4 - $\text{DMSO}-\text{d}_6$) shows that the ϕ angles for both conformational forms are in the region from -80° to -120° for L-residues and, correspondingly, 80° - 120° for D-residues. Thus the previously described conformations (see a review⁽²⁾), which have the ϕ angles in the from 40° to 60° (L-residue) and from -40° to -60° (D-residues) have to be reconsidered.

According to the new data the valinomycin in nonpolar solvents has a "bracelet" conformation with the amide carbonyls involved in intramolecular H-bonding and the ester carbonyls oriented almost in parallel to the symmetry axis of the molecule. This structure is quite prepared to accommodate the potassium cation thereby forming a stable complex. Contrary to the unsymmetrical X-ray conformation of free valinomycin⁽³⁾ the solution conformation is

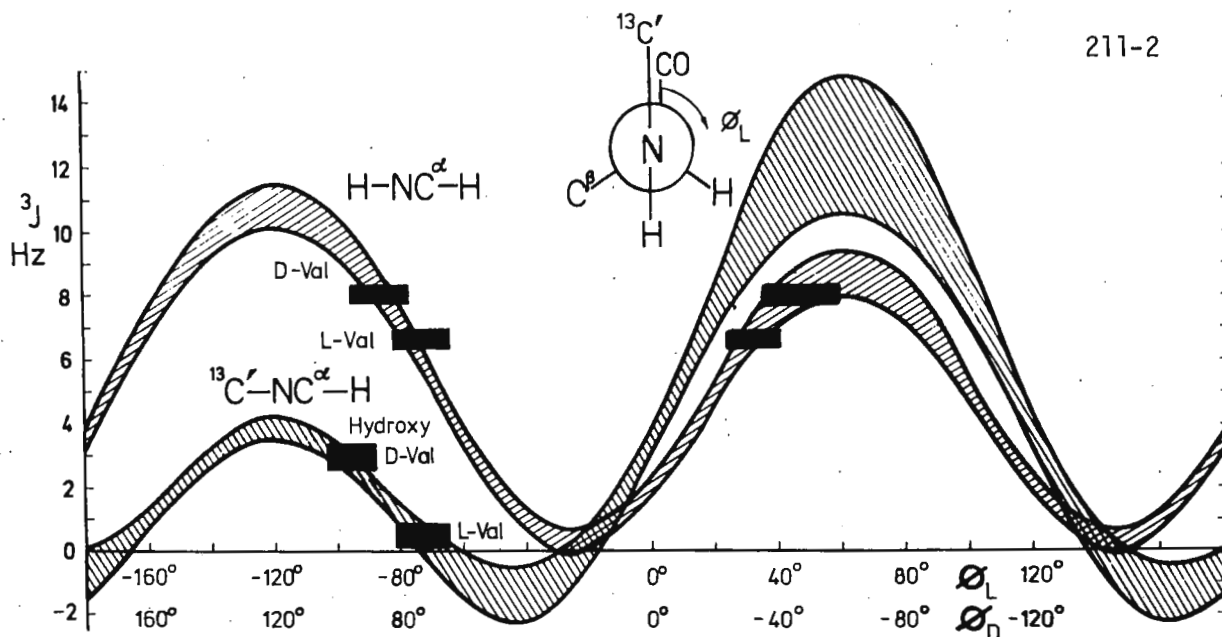


Figure. Angular ϕ -dependencies of the $^1\text{H}-\text{NC}^\alpha-^1\text{H}$ and $^{13}\text{C}'-\text{NC}^\alpha-^1\text{H}$ couplings. The experimental data are presented for valinomycin in $\text{c}-\text{C}_6\text{H}_{12}$ solution.

symmetrical. However, if the X-ray structure is slightly bent along the arrows as shown on Fig. 1a in Ref. (3) to form the 10-membered intramolecular H-bonded rings (β -turns) instead of 13-membered rings, there will be actually much less difference between the X-ray and the solution conformation than had formerly supposed and had been the source of some surprise on the part of those working in this area.

For the potassium-valinomycin complex the ϕ angles determined by coupling constants are in complete agreement with those of the X-ray structure.

The side chain X_1 torsional angles for valinomycin and its complex in various solvents have been also determined unambiguously by combined as of the $^1\text{H}-\text{C}^\alpha-\text{C}^\beta-^1\text{H}$ and $^1\text{H}-\text{C}^\beta-\text{C}^\alpha-^{13}\text{C}'(=\text{O})$ coupling constants.

Sincerely yours,

Vladimir

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BLOCK-AVERAGING WITH A FABRITEK (NICOLET) 1074 INSTRUMENT COMPUTER

The problem of obtaining an adequate signal to noise (S/N) ratio for very small peaks in carbon-13 spectra that contain a large peak using a computer of limited word length is well known. Selective saturation techniques cannot be used if quantitative information is required concerning the relative peak heights of the large and small bands. Such a situation is common in many polymer analyses. Block averaging does offer a solution to this problem but with the 1074 some data manipulation problems exist. Given a typical polyethylene sample with a 1250 Hz 'window' (4K data points, 400 μ sec per point) it can be seen that nearly all the spectral (FID) information is contained in the first half of the memory, the second half containing essentially only noise. Thus if only the first half of the memory is used to accumulate the FID (same digitisation rate) the second half can be used as a 'dump' store. Once the first half of the memory is full, accumulation is stopped and a reductive transfer made from the first to the second half of the memory. Care is taken not to distort the relative band intensities by a 'too large' reductive transfer ratio. The first memory block is then cleared and a new set of accumulations started. The cycle is repeated until the second memory block is filled by rescaled FID's or some known S/N ratio is achieved. After the final data transfer the first memory block is cleared and the contents of the second memory block are transferred to the first half and the second memory block cleared of all data. This gives a final FID of the 'correct' appearance over 4K data points (the final 2K points are of course all zeros). Transformation of this final FID in the normal manner yields a spectrum with an enhanced S/N ratio. On the 1074 all the data manipulations have to be done manually by pressing the appropriate buttons in the correct sequence (seven operations in all). However it is possible to operate the 1074 push buttons by solenoid plungers and we have constructed a simple system to do this. A timer (NS 555) provides a trigger voltage, the repeat time of which is set for a little longer than the time required for one block of accumulation. The timer output triggers off a series of subsidiary timers. The output voltage pulse (\sim 2 seconds duration) from each timer is fed to a 2N1613 transistor the output of which goes to a power transistor (2N3055) which has the solenoid coil in its emitter circuit. The solenoids are mounted on an aluminium panel which can be attached to the front of the 1074. The system has worked remarkably well for nearly a year and many overnight 'block averaged' accumulations have been made yielding spectra of excellent quality. We were interested to see (TAMU 199-8, Canet, Gordon-Gisset, Marchal) that given a larger contemporary computer system it is possible to do these data manipulations by programming.

S.A. Knight

S.A. Knight

W. Wheatley

W. Wheatley

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PARIS, le March 4, 1976

Prof. B.L. SHAPIRO
Dept. of Chemistry
Texas A and M University
College Station/Texas 77843

Influence of the chain length on the differences $\Delta\delta_C^t$ between cis and trans α and δ ^{13}C of L-Proline dipeptides.

Dear Professor SHAPIRO,

The rotation around the amide bond ($\omega 0^\circ \rightarrow 180^\circ$) of several N-acyl-Prolines leads to very large differences $\Delta\delta_C^t$ in the chemical shifts of the carbon rings between cis and trans rotamers (1). However, the values of $\Delta\delta_C^t$ are much lower on the carbons α and δ in the case of X-Pro dipeptides as reported by several authors (1)(2)(3). At our knowledge, no explanation of this phenomenon has been given.

It seems that steric effect of the substituent X can be excluded since $\Delta\delta_C^t$ on α and δ are of the same order in acetyl Pro ($X = \text{CH}_3$) and p. chlorobenzoyl Pro ($X = \text{pClC}_6\text{H}_5$).

We have recently shown a change of the ring conformations between cis and trans acetyl L.OH-Pro isomers (4). However, this effect can't be retained as a major cause of the above discrepancy because the conformational changes might affect particularly the β and γ carbons for which the $\Delta\delta_C^t$ are constant in all the studied dipeptides. TABLE I.

On the other hand, the ionisation state of the carboxylic group has no effect on $\Delta\delta_C^t$ ($\Delta\delta_C^t$ in Ac L-Pro $\alpha = 1.76$, $\delta = -1.68$, in Ac L-Pro ethyl ester $\alpha = 1.64$, $\delta = -1.75$). Moreover, the $\Delta\delta_C^t$ on α and δ are not greatly modified during the titration of Gly-Pro or Ala-Pro.

On the contrary, the variation in the $\Delta\delta_C^t$ on α and δ can be due to the electric field effects of either or both the carbonyl group of COOH (5) and the heteroatom in the X group chain. We have explored this hypothesis by synthesis and ^{13}C analysis of the spectra of $\text{NH}_2-(\text{CH}_2)_n$ Co-Pro ($n = 1, 2, 4$). All these compounds shows the usual cis - trans isomerism, but the difference $\Delta\delta_C^t$ on α and δ decreases from Ac L-Pro to Gly-Pro ($n = 1$) and reincreases for Ala L-Pro ($n = 2$) and 5-Amino valeryl-L-Pro ($n = 4$). Figure. At the same time, $\Delta\delta_C^t$ for β and γ remain constant.

Consequently, it seems that the field effect of the heterotam plays a major role in the differences $\Delta\delta_C$ on the carbons α and δ in cis and trans rotamers of Proline peptides(6)(7). This result can be of some interest in the structural analysis of peptide containing Prolines.

Sincerely yours,

S. Combrisson

B.P. Roques

S. COMBRISSE

B.P. ROQUES

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- 6) S. Combrisson, B.P. Roques - Tetrahedron (in press).
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FIGURE I

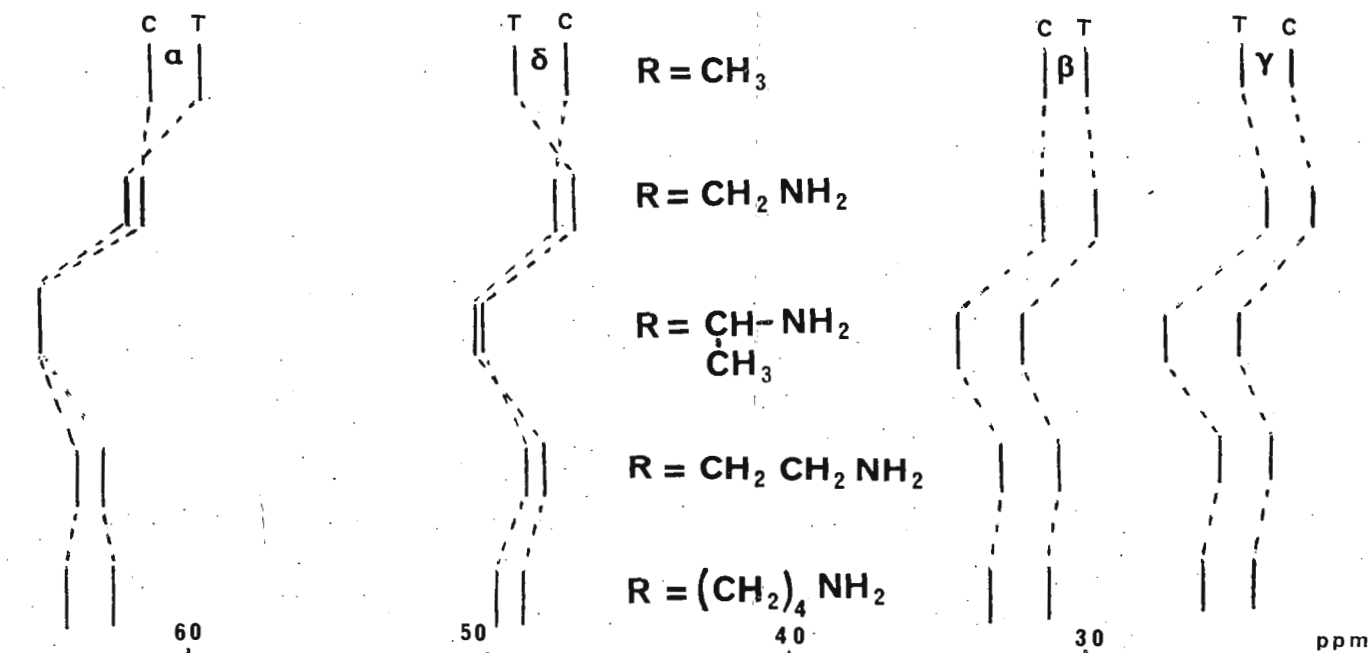
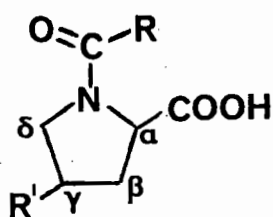
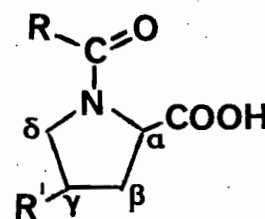


TABLE I

Chemical shifts and $\Delta\delta_c^t$ for cis and trans rotamers of N-Acyl Prolines.in D₂O pD ~ 5.

CIS



TRANS

R	R'	δ_α	$\Delta\delta_{\alpha c}^t$	δ_β	$\Delta\delta_{\beta c}^t$	δ_γ	$\Delta\delta_{\gamma c}^t$	δ_δ	$\Delta\delta_{\delta c}^t$
CH ₃	H	c 61.5 t 59.7	1.8	31.6 30.1	1.5	23.2 25.0	-1.8	47.5 49.2	-1.7
-pC ₆ H ₅ Cl [*]	H	c 61.3 t 59.3	2.0	31.5 29.4	2.1	22.7 25.4	-2.7	46.7 50.0	-3.3
-CH(NH ₂)CH ₃	H	c 65.0 t 65.0	0.0	34.4 32.3	2.1	25.1 27.6	-2.5	50.4 50.3	+0.1
-CH ₂ -NH ₂	H	c 61.6 t 62.0	-0.4	31.6 29.7	1.9	22.4 24.1	-1.7	47.3 46.7	+0.6
-CH ₂ -CH ₂ NH ₂	H	c 63.7 t 62.9	0.8	32.7 31.0	1.7	23.8 25.5	-1.7	48.2 48.8	-0.6
-(CH ₂) ₄ -NH ₂	H	c 64.1 t 62.6	1.5	32.2 30.6	1.6	23.6 25.2	-1.6	48.7 49.6	-0.9

^{*} Sol in CDCl₃.

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DEPARTMENT OF CHEMISTRY
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5 March 1976

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

Dear Professor Shapiro

Referencing and Plot Registration on the XL-100

The standard Varian XL-100 spectrometer programme, 994100-D (and -E), appears to have been written primarily for operation with carbon and proton nuclei, since it contains the assumption that the normal position for the reference is on the zero line of the chart, at the right hand side of the paper. The programme automatically plots the spectrum with the reference, set with OS, on zero, and also will only accept entries for OS that are less than SW, the spectral width.

For nuclei with the reference in the middle of a wide chemical shift range this automatic plot registration and the restriction on the maximum size of entry is something of a nuisance. Many times when observing phosphorus (our most important nucleus) or fluorine spectra a long way from the reference, we have had to resort to some lengthy arithmetic to get the true chemical shifts.

To overcome this problem a patch has been written for the programme which makes a number of improvements. To accommodate part of it, the chart paper positioning routine, command OK, has had to be overwritten. Firstly, values for plot registration and chemical shift calculation are now entered separately and do not interact. Secondly, all references to the word 'offset' are removed from the programme. As used by Varian this word has three different meanings, (a) reference for calculating chemical shifts, (b) chemical shift in hertz, as listed by LS, (c) spectrometer frequency setting. The last meaning is the only one not involved in the programme, so that remains. Finally, a change implemented in the 'E'-revision programme but not (as far as I know) generally communicated provides a negative sign for negative p.p.m. values.

Operation of the modified programme is quite straightforward. The command OS has been replaced by two commands, RL, reference line and CZ, chart zero. The value and sign to be entered for RL is given by the expression:

$$RL = (\text{spectrometer offset for reference line}) - (\text{spectrometer offset for chart zero})$$

The maximum entry allowed is 32767. (Due to the XL-100 frequency phase-locking system, once the spectrometer offset setting for a reference line (e.g. H_3PO_4 , CFCl_3) has been found with a given lock, it never need be determined again¹.) If a peak in the spectrum is to be used as the reference this may be set from the scope routine as before, but the command has been changed to CTRL+R and the peak is no longer plotted on zero.

The value to be entered for CZ is the position in the plot that is to be placed on the zero line of the chart. For those spectra in which it would be pointless to try

to plot the reference line on zero, e.g. most phosphorus and fluorine spectra, and most narrow spectral width spectra, the entry is 0.0. For those in which the reference is usually on zero, e.g. most carbon and proton spectra, the entry is the same as that made for RL. The entry must be less than SW.

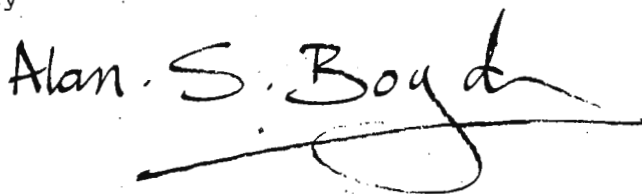
For both these new commands the entry 0 (zero) means no plot registration or reference line calculation will be done, whereas 0.0 (zero point zero) or just .0 enters that value as such and uses it.

An important consideration is whether the spectrum is displayed with the pulse at the low frequency (right hand) end or at the high frequency (left hand) end. In the second case the spectrometer offset for chart zero is not the same as the setting on the dials but is dependent on SW. The offset for chart zero must therefore be calculated before entering a value for RL. Also, the internal value for CZ is different depending on the display and thus part of the modification is a prompt to reset CZ after changing the orientation with LH.

We have found this modification to be very useful and easily used, and hope others will find it so too.

Finally, something completely different, I would be glad to hear from anyone who has had experience of, or interest in modifying the XL-100 for dual phase-detector operation ('quad detection').

Yours sincerely



Alan S Boyd

1

R K Harris, B J Kimber, J.Mag.Res., 17, 174 (1975).

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Professor W. B. Smith
Department of Chemistry
Texas Christian University
Fort Worth, TX 76129

Programme Changes

The changes given below are for the 'D'-revision programme. Some of the addresses will be different for the 'E'-revision.

<u>Location</u>	<u>New Contents</u>	<u>Location</u>	<u>New Contents</u>
3151	3101	7634	140452
		5	50453
4141	12022	6	10245
		7	20246
4423	5000	40	5034
		1	70307
6220	10236	2	1000
6221	5000	3	10563
6224	50245	4	120303
6225	60246	5	144301
6233	5000	6	151324
6234	5000	7	120332
6235	5000	50	142722
		1	147650
6301	10307	2	144332
6643	10307	3	124675
		7654	0
7616	2000		
7	10130	10741	7616
20	70313	10753	7621
1	2000	10754	1503
2	10447	10756	44622
3	7644		
4	2000	11216	120322
5	6150	11217	142706
6	4560	11220	120314
7	1040	11221	147250
30	10563		
1	170456	11332	120323
2	60446	11333	144311
3	5021	11334	143324

A fully annotated version of the above changes is available on request.

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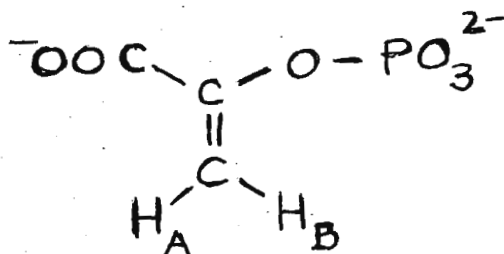
March 8, 1976

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

Dear Barry:

High Energy COP-out (and CCOP-out)

Phosphoenolpyruvate (PEP) a substrate of pyruvate kinase is, energetically, the most potent phosphorylating agent in biochemistry. As part of our studies of the mechanism of pyruvate kinase, we have synthesized PEP enriched with ^{13}C in positions 1 and 2. This has permitted us to determine the absolute values of the following coupling constants using ^{13}C , ^{31}P , and ^1H NMR



$$J_{\text{COP}} = 8.6 \text{ Hz}$$

$$J_{\text{CCOP}} = 7.5 \text{ Hz}$$

$$J_{\text{H}_A\text{CC}} \sim 0.3 \text{ Hz}$$

$$J_{\text{H}_B\text{CC}} = 4.9 \text{ Hz}$$

and to confirm H----C₁ and H----P coupling constants in the literature (Cohn et al., J.A.C.S. 92, 4095 (1970)).

The newly determined J_{COP} and J_{CCOP} values of PEP of /8.6/ and /7.5/ Hz respectively, are similar to those of EtOP(0)Cl_2 (-8.9, +8.8) and $(\text{EtO})_2\text{P(0)Cl}$ (-7.1, +7.5), which are good phosphorylating agents, but differ from those of $(\text{EtO})_2\text{P(0)H}$ (-4.5, +6.1) which is not, suggesting that there may be something to the concept of the "high energy phosphate bond" after all.

X-ray data on this molecule (Watson and Kennard, Acta Cryst, B29, 2538 (1973)) reveal a slightly long P-OC bond (1.63 Å) corresponding to ~18% double bond character, and a slightly large P-O-C angle (121.2°), suggesting an sp^2 oxygen.

Sincerely yours,

Marc Oesterling
 R. Marc Oesterling

Al Mildvan
 Albert S. Mildvan

Rome, March 15th, 1976

ISTITUTO SUPERIORE DI SANITA'
R O M A

Viale Regina Elena, 299
Tel 4990
Telegr: ISTISAN-ROMA

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

"Effects of molecular weight on sol-gel transition in water-agarose systems".

Dear Professor Shapiro,

numerous nuclear magnetic resonance studies have been undertaken to investigate the role of water and macromolecules in the agarose-water systems in order to understand the microscopic molecular mechanism of the sol-gel transition.

The sudden broadening (and therefore shorter T_2 value) observed for water PMR signal at the sol-gel transition for decreasing temperature has been generally interpreted in terms of two different models: i) the exchange model (1) justifies the shorter spin-spin relaxation time assuming that the structure of the water layer adjacent to the surface of the macromolecule is modified by the presence of the surface itself. If a rapid molecular exchange occurs between this layer and bulk water, average relaxation times are obtained; ii) the collective model (2) points out a cooperative onset of a different dynamical and geometrical structure of water in the presence of the macromolecules. In contrast to the model i) the collective model tries to explain the existence of a thermal hysteresis in the sol-gel transition.

In order to investigate the geometrical and dynamical structure of the system water-macromolecule we measured the water relaxation times T_1 and T_2 with pulsed PMR and chemical shifts and linewidths with high resolution PMR, as functions of different agarose molecular weights. Different molecular weights were obtained heating 2% agarose-water samples for different times.

Both the transition temperature and the line width are markedly correlated with the different molecular weight of the macromolecule as shown in the accompanying figure obtained for decreasing temperature. The same behaviour was found for increasing temperature, showing that the hysteresis is controlled by molecular weight.

On the contrary, the temperature dependence of T_1 for different times of heating is very similar to the pure water behaviour, due to the insensitivity of this relaxation time to slow molecular motions. Finally we observed the same

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temperature dependence for the chemical shift of the water signal, between 0 and 100°C, for either pure water, or degraded or undegraded agarose-water samples. So that the average charge density experienced by the water protons is practically unaffected by the dynamical and structural aspects of sol-gel transitions.

Yours sincerely,

Laura Guidoni

(Laura Guidoni)

Pietro Luigi Indovina

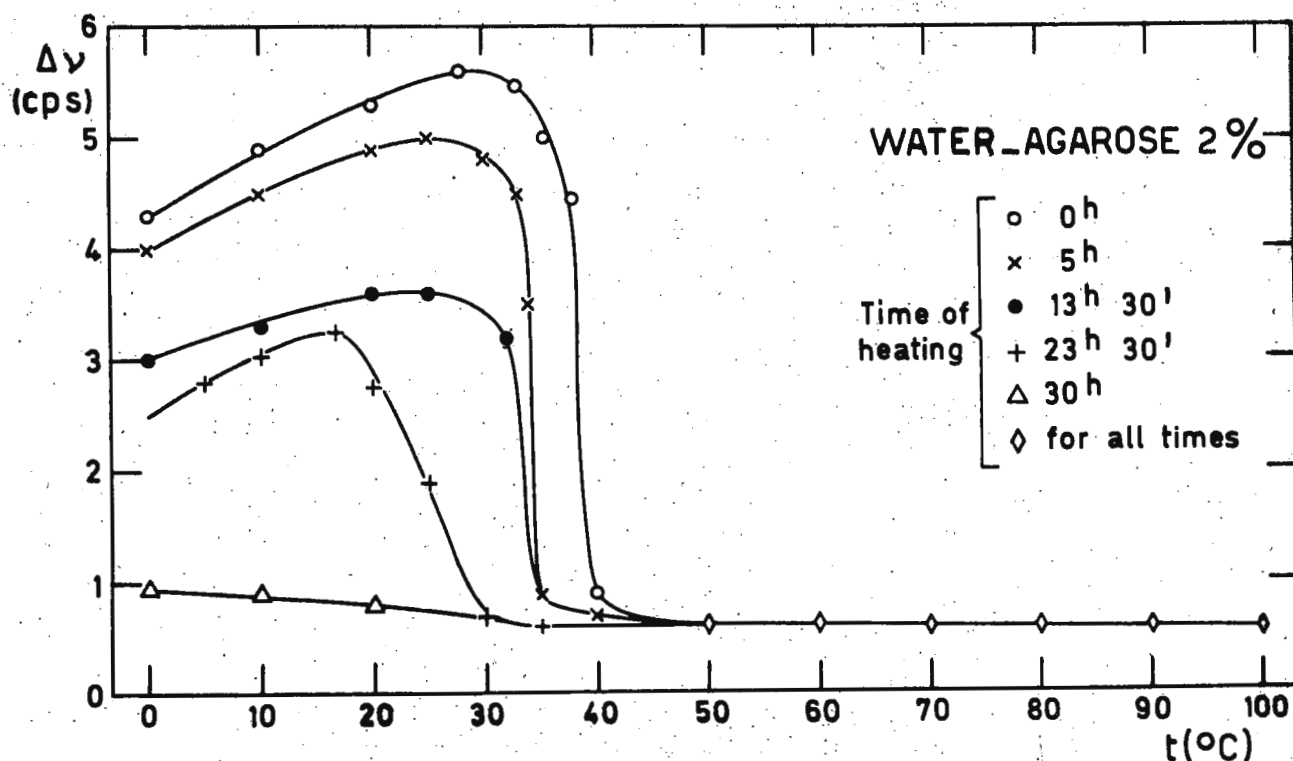
(Pietro Luigi Indovina)

Roberto Della Guardia

(Roberto Della Guardia)

Enzo Tettamanti

(Enzo Tettamanti)

(1) T. F. Child, N. G. Pryce - Biopolymers, 11, 409 (1972)W. Derbyshire, I. D. Duff - Far. Disc. Chem. Soc., 57, 243 (1974)(2) M. S. Micciancio Giammarinaro, S. Micciancio, M. B. Palma Vittorelli, M. U. Palma, M. L. Marino - Ann. N. Y. Acad. Sci., 240, 134 (1973)

EXPERIMENTELLE KERNPHYSIK

Klingelbergstrasse 82, Telefon 061 - 44 22 80

Prof. Dr. P. Diehl
Dr. I. Vogt

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

Dipole-dipole splittings of $^{13}\text{CH}_4$ in anisotropic solvents.

Dear Barry,

The fact that the molecule CD_4 displays quadrupole splitting if dissolved in an anisotropic liquid crystal solvent was observed in 1972¹⁾. But only recently reasonable theories have been suggested for this phenomenon ²⁾³⁾. Both assume distortion of the tetrahedral molecule depending upon the angle between the CH-bonds and the liquid crystal optic axis. The first model²⁾ averages over the sphere, whereas the second³⁾ interchanges the bonds, i.e. averages over 4 positions. This model seems to account quite well for the observed effects in NH_4^+ , ND_4^+ and BF_4 .³⁾

To our surprise we now found that it fails for $^{13}\text{CH}_4$. For this molecule the "continuum theory" ²⁾ predicts per angular degree of deformation 26 Hz for D_{HH} , - 28 Hz for D_{CH} and 618 Hz for the quadrupole splitting; the "4-position-theory" ³⁾ gives (again per degree of deformation) 65 Hz for D_{HH} , - 288 Hz for D_{CH} and 3146 Hz for the quadrupole splitting. The observed quadrupole splitting¹⁾ is 20 Hz and we just observed $D_{\text{CH}} = + 10$ Hz together with $|D_{\text{HH}}| \leq 1$ Hz. So, obviously, neither the sign, nor the relative magnitude are in agreement with the discussed models. We have, at present, no explanation for this discrepancy.

Sincerely yours

Peter

J. Vogt

P. Diehl

J. Vogt

References:

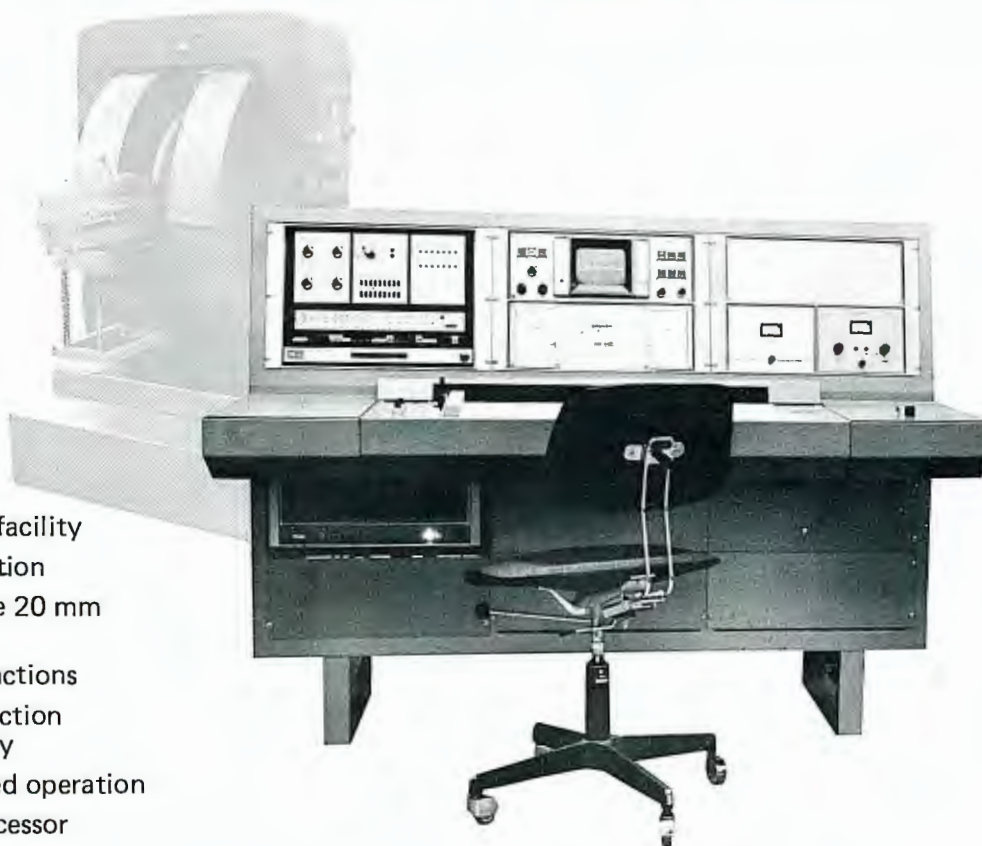
- 1.) R. Ader and A. Loewenstein, Mol. Phys. 24, 455 (1972).
- 2.) J. Builthuis et al, J. Magn. Resonance 14, 13 (1974).
- 3.) D. Bailey et al, " " 18, 344 (1975).

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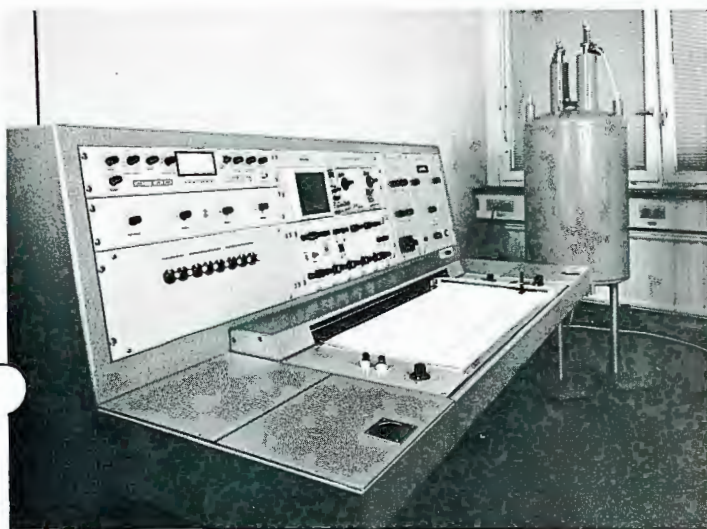
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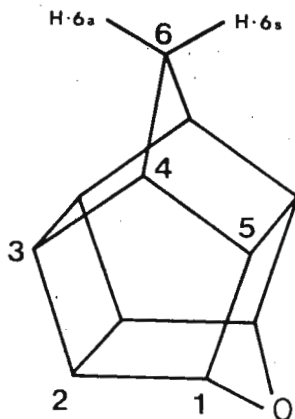
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION
Texas 77843
USA

25. MAR. 1976

Dear Prof. Shapiro

ASSIGNMENT OF DIRECTLY BONDED C-H COUPLINGS IN A METHYLENE GROUP WITH SPI

The application of heteronuclear $^{13}\text{C}-\{^1\text{H}\}$ selective population inversion (SPI) (1) in the assignment of ^{13}C resonances and the sign determination of long-range carbon- 13 -proton coupling constants has been reported before (2). In an NMR study of 3,6-epoxy-pentacyclo[6.2.1.0^{2,7}.0^{4,10}.0^{5,9}]undecane (I) it has been found that the directly bonded C-H couplings of the bridge methylene-group are very similar. SPI proved to be a very elegant method to assign these couplings.



I

The methylene bridge protons of (I) gave rise to an AB-system centred around $\delta=1.74$. LIS experiment led to the assignment of the high-field proton to H-6a. The directly bonded C-H couplings within the methylene group are 131.6 Hz and 130.5 Hz and the central peak of the methylene triplet in the carbon- 13 spectrum is in fact a closely spaced doublet (Figure 1a). The following experiments led to the assignment of the smaller C-H coupling to $^1J(\text{C6-H6a})$: Figure 2a shows the expected proton spectrum of the C-6-isotopomer of the title compound together with an arbitrary line numbering, corresponding spin states and SPI experiments performed. Inverting line 8 (SPI experiment [1]) will affect the carbon- 13 transitions with the spins of H-6a in the β -state, increasing the progressively and decreasing the

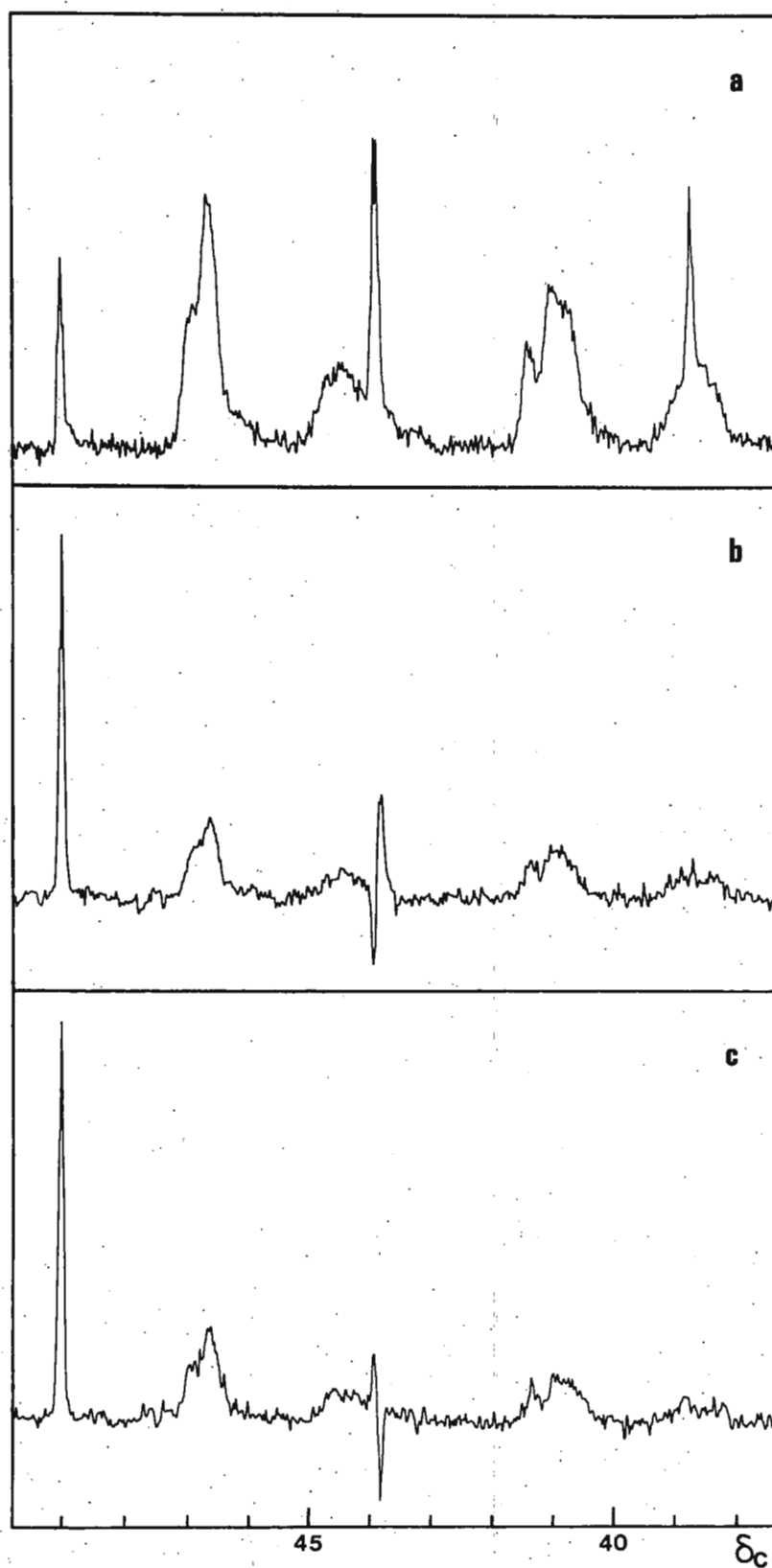


FIGURE 1: (a) High-field region of the proton-coupled ^{13}C FT-NMR spectrum of (I).
(b) Result of SPI experiment [1].
(c) Result of experiment [2].

regressively connected transitions as indicated in Figure 2b. The experimental result is shown in Figure 1b. The experiment proves two points: (1) The smaller $^1J(\text{CH})$ coupling is between C-6 and H-6a. (2) The relative signs of $^1J(\text{CH})$ and $^2J(\text{HH})$ are of opposite sign (as expected and assumed in the construction of figure 2). Inverting line 6 in the proton spectrum served as a cross-check on the results (Figures 1c and 2b, SPI [2]).

The power of the inverting pulse ($\gamma H_2 = 5 \text{ Hz}$) was so high as to influence the neighbouring proton lines 7 and 5 in the SPI experiments [1] and [2], respectively. This led to a slight increase of lines 11 and 10, respectively, and a decrease of line 12 which, as a consequence, is too small to be observed.

Yours sincerely

K. Pachler

K. Pachler
SENIOR CHIEF RESEARCH OFFICER
CHEMICAL PHYSICS GROUP

P.L. Wessels

P.L. Wessels
SENIOR RESEARCH OFFICER

1. K.G.R. Pachler and P.L. Wessels, J. Magn. Resonance, **12**, 337 (1973).
2. A.A. Chalmers, K.G.R. Pachler and P.L. Wessels, Org. Magn. Resonance, **6**, 445 (1974).

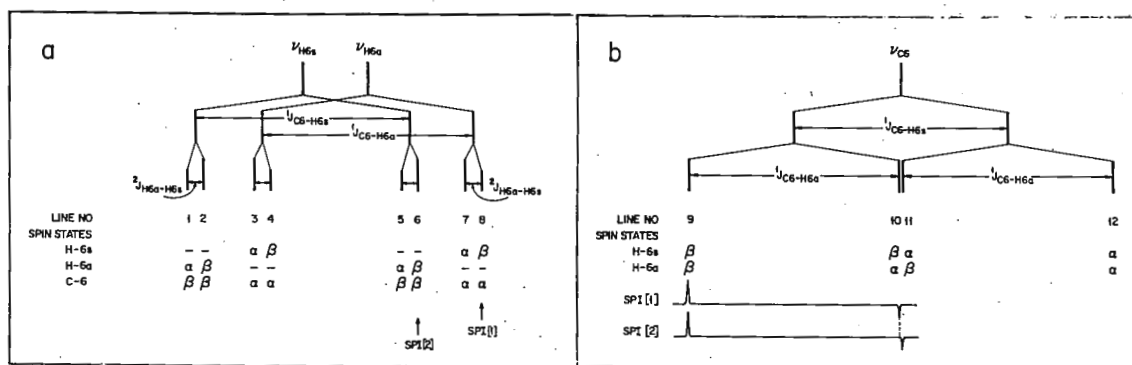


FIGURE 2: Theoretical ABX spectrum of the methylene bridge nuclei of (I).
 (a). AB (^1H) part with SPI experiments indicated.
 (b). X (^{13}C) part with expected SPI results.



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DEPARTMENT OF CHEMISTRY

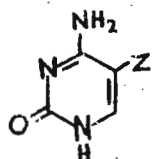
18th March, 1976.

Dear Professor Shapiro,

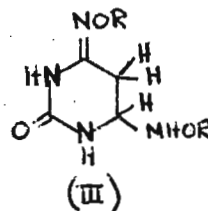
^1H AND ^{19}F NMR DATA OF HYDROXYLAMINE ADDUCTS OF CYTOSINES

Your blue note, - a lament in Dixieland or so we understand, has *galvanised* us into reporting some results on the ^1H and ^{19}F nmr spectra of hydroxylamine adducts of cytosines.

The reaction of cytosine (I, Z=H) and some derivatives with hydroxylamines (II) at pH 5 - 6 gives (III) as a major product^{1,2}.



pH 6



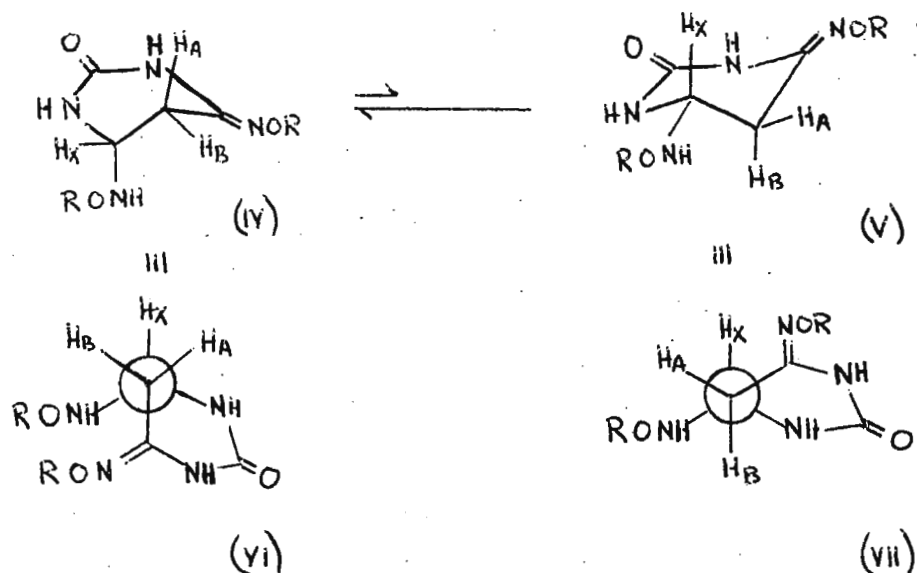
(I); Z=H or F (II); R=H, alkyl or aralkyl.

With Z=H and R=alkyl or aralkyl, the CH_2 group at C-5 is part of an ABX system, analysis of which gives the values of J_{AB} , J_{AX} and J_{BX} shown in Table 1.

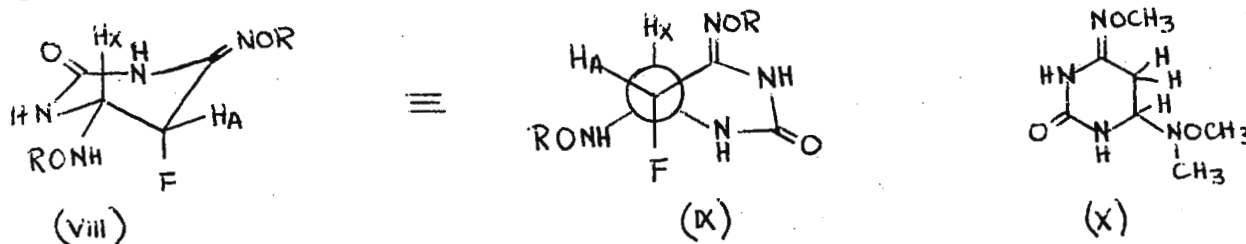
TABLE 1
ANALYSIS OF THE ABX ^1H NMR SPECTRA OF COMPOUNDS (III)

R	J_{AB}/Hz	J_{AX}/Hz	J_{BX}/Hz	$(\nu\text{A}-\nu\text{B})/\text{Hz}$
Bu ⁿ	-15.5	4.4	4.2	15.0
Bu ⁱ	-15.4	5.2	4.2	16.6
Bu ^s	-15.5	5.1	4.4	17.3
Bu ^t	-14.8	4.7	4.4	18.4
PhCH ₂	-16.9	5.8	3.3	13.0

Two conformers (IV) and (V) - also shown as their Newman projections (VI) and (VII) respectively, are possible. The data in Table 1 reveal that in chloroform as solvent, (IV) is the predominant conformer. This follows since J_{AX} and J_{BX} are almost equal which implies torsion angles of *ca.* 60° between H_A or H_B and H_X ³. At first sight this is surprising since the bulky alkoxyamino group in position 6 would not be expected to occupy an axial position. It probably arises, however, through intramolecular hydrogen bonding between the H of RONH in position 6 and the oxygen of the 4-alkoxyimino group plus hydrogen bonding between N(1)-H and the oxygen of the 6-alkoxyamino group.



With $Z=F$, only one diastereomer is detectable by ^{19}F nmr (δ ($CFCl_3$) = 100.1, doublet of doublets) and both the 1H and ^{19}F spectra reveal $J_{H_X-F} = 18$ Hz, $J_{H_A-F} = 49$ Hz and $J_{H_X-H_A} = 2.6$ Hz. This provides the first proof of a stereospecific, *trans* addition to C(5) - C(6) and furthermore it reveals that in this case, (VIII) \equiv (IX), is the predominant conformer. Presumably this is due to intramolecular hydrogen bonding between N(1)-H and the oxygen of RONH (position 6) coupled with hydrogen bonding between RONH and the adjacent fluorine at position 5.



Variable temperature 1H nmr reveal little change over a temperature range from -60 to $+60^\circ C$. This suggests that conformers (IV) for $Z=H$ and (VIII) for $Z=F$, are unique in each case. Substantial support for this suggestion is provided by the observation that compound (X) shows a doublet at δ 2.72 for the AB protons and a triplet at δ 4.1 for the X proton with $J_{A(B)-X} = 4.0$ Hz. Decoupling AB or X protons causes collapse of the triplet or doublet to singlets. One concludes that replacement of the NH proton at C(6) by NCH_3 removes the intramolecular hydrogen bonding to $NOCH_3$ at C(4) which in turn allows a rapid conformational interchange between structures equivalent to (IV) and (V). Since H_A and H_B become equivalent, the intrinsic non-equivalence term must be very small.

Yours sincerely,

Dennis Hall
C. D. HALL

P. M. Schalke
P. M. SCHALKE

REFERENCES

1. D. M. Brown et al., *Prog. Nuc. Acid Res. and Mol. Biol.*, **7**, 1967, p 349.
2. N. K. Kochetkov, et al., *ibid.*, **9**, Academic Press, New York, 1969, p.403.
3. P. M. Schalke and C. D. Hall, *J. Chem. Soc., Perkin I*, 2417, 1975.

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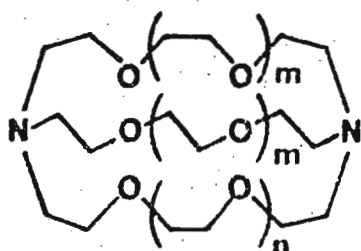
Professeur J.-M. LEHN

STRASBOURG, le 20 Mars 1976

Professor Bernard L. SHAPIRO
Texas A & M University
College of Science
COLLEGE STATION, TEXAS 77843
U.S.A.

Dear Barry,

We have been studying cation exchange rates in cryptate complexes by temperature dependent ^{13}C -NMR spectroscopy. The following coalescence temperatures T_c and free energies of activation ΔG_c^\ddagger have been obtained (in water):



Cryptate	T_c	ΔG_c^\ddagger (kcal/mole)
$[\text{Na}^+ \subset 2.1.1]$	$+35^\circ$	15.1
$[\text{Li}^+ \subset 2.2.1]$	-2°	13.0
$[\text{Na}^+ \subset 2.2.1]$	$+72^\circ$	16.75
$[\text{Na}^+ \subset 2.2.2]$	$+26^\circ$	14.75
$[\text{K}^+ \subset 2.2.2]$	$+46^\circ$	16.35
$[\text{Rb}^+ \subset 2.2.2]$	$+13$	14.5

$\underline{m} = 0; \underline{n} = 1$ [2.1.1]

$\underline{m} = 1; \underline{n} = 0$ [2.2.1]

$\underline{m} = \underline{n} = 1$ [2.2.2]

Studies of other complexes and of exchange rates in other solvents are in progress. The figure shows an example of the spectra obtained.

Sorry for the delay in answering!

Yours sincerely,

E. KAUFFMANN

E. Kauffmann

J.-M. LEHN

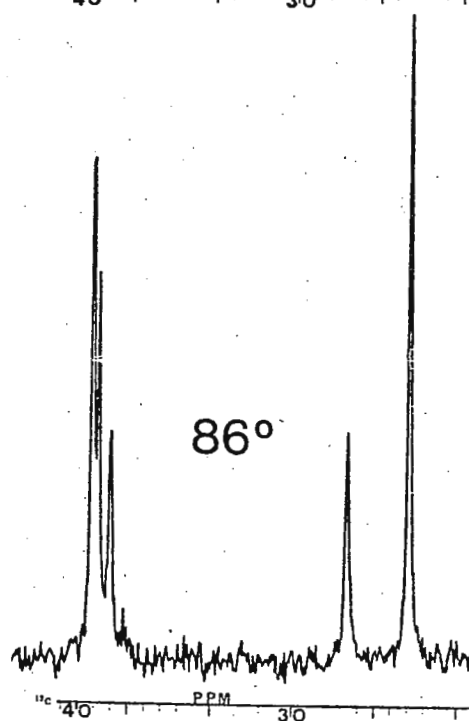
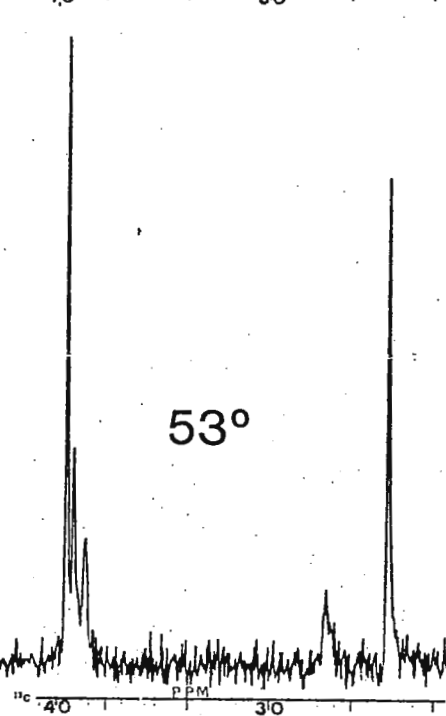
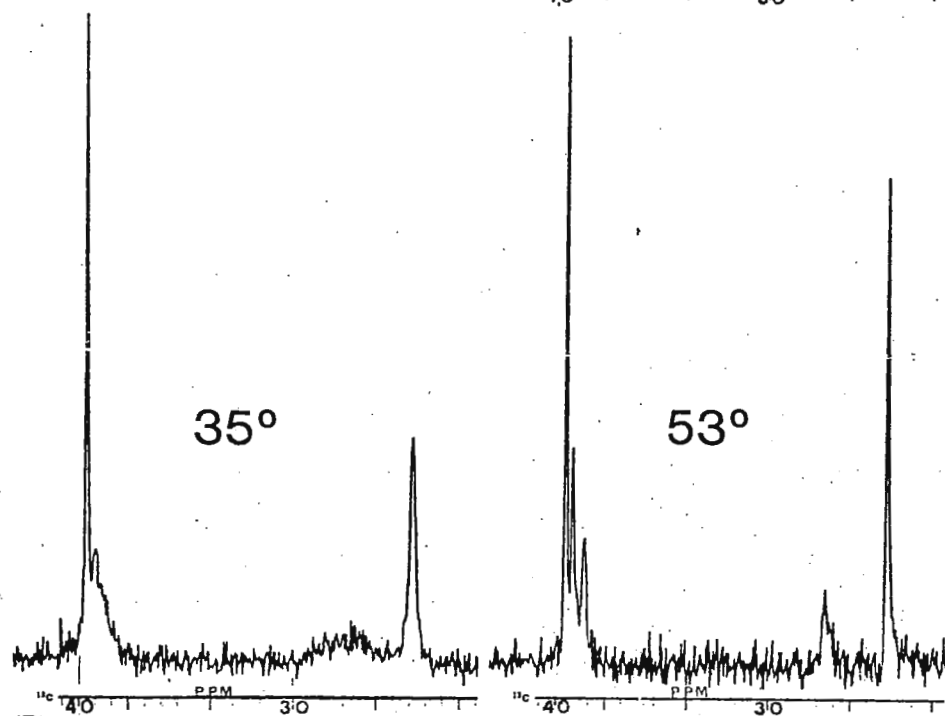
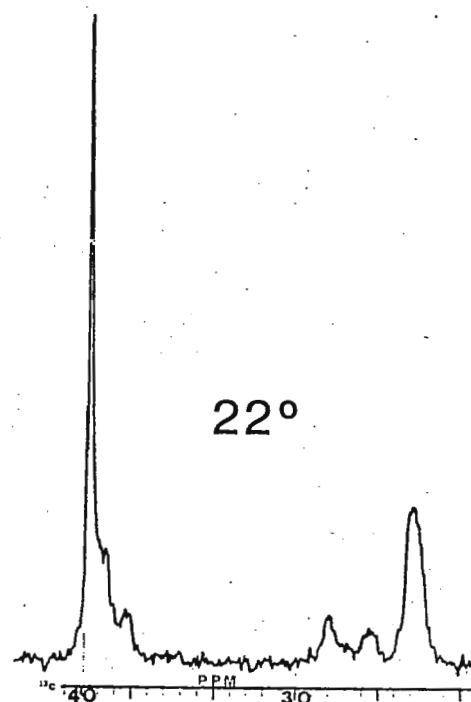
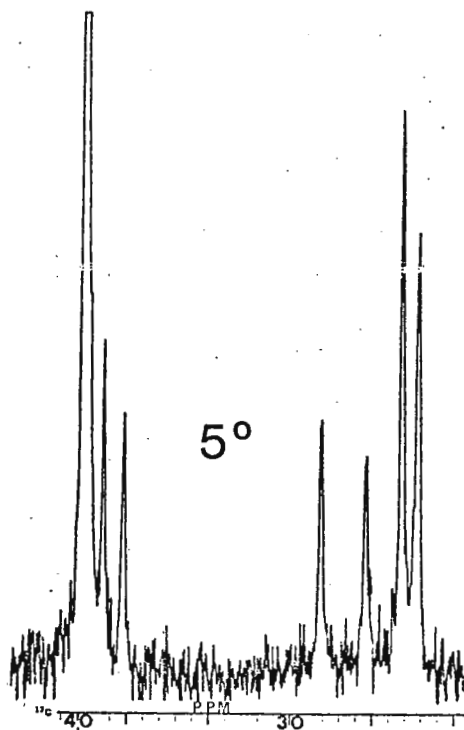
J.-M. Lehn

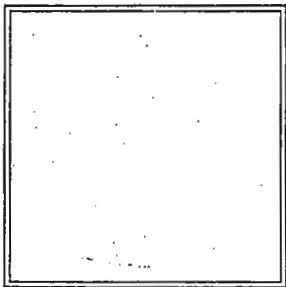
$^{13}\text{C}\{\text{H}\}$ **211 + NaCl**

2 / 1

SOLV.: D₂O

ref.: +OH





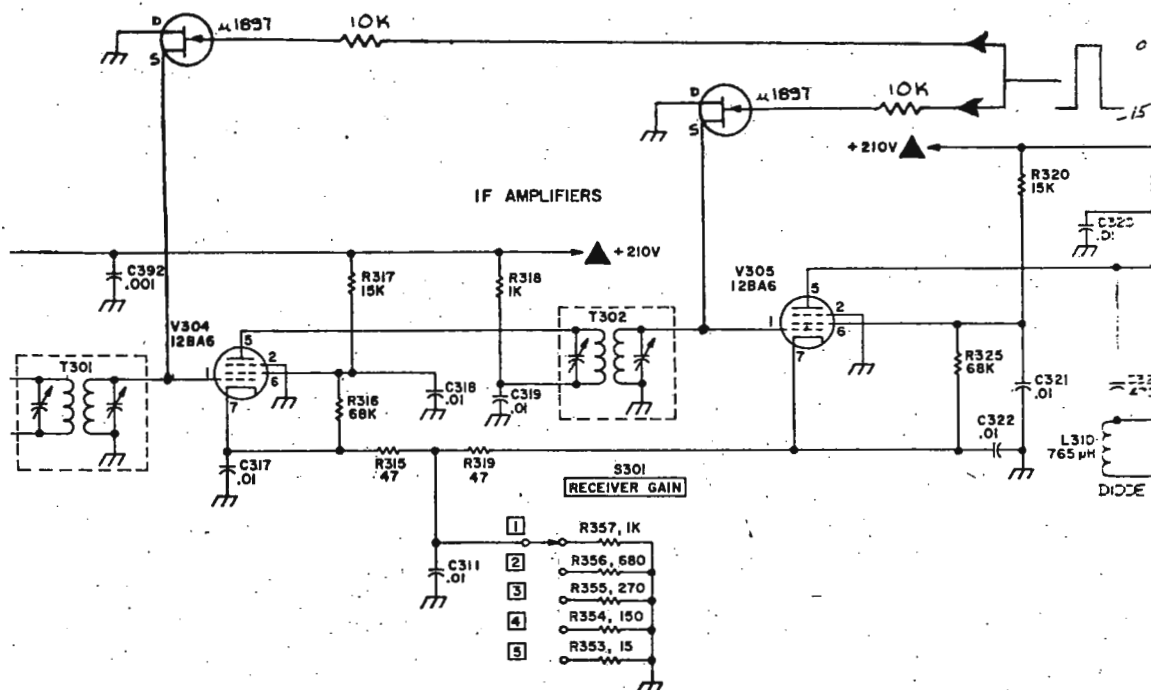
March 22, 1976

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

Dear Barry:

Title: V-4311 R.F. Unit used for F.T.

Our HA-60 F.T. system (Newsletter 200) had baseline roll when we attempted to run over 500 passes on a dilute C^{13} sample. Most of the problem was eliminated by installing a solid state gate in the grid circuit of both I.F. stages as follows:



Professor Shapiro
March 23, 1976

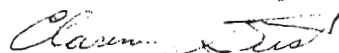
The gate pulse is applied 10 μ sec before until 40 μ sec after the R.F. pulse is delivered.

XL-100 Recorder Problem

This problem had been in our XL-100 for over three years and appeared as an intermittent, about an hour every three months. One of the symptoms was that one could not continue to operate the F.T. program once the spectrum was plotted on paper. This happened because the computer was not informed that the plot had been completed. As usual we searched for problems in the computer program and digital circuitry.

The problem was that the ground side of the right and left recorder limit switch was about 2-3 volts instead of ground as it should have been. This was due to a defective ground strap on the recorder itself. One can quickly check for this by measuring the voltage at each limit switch (about 4-5V) and watch it drop to zero as the recorder is swept to its limit.

Sincerely,



Clarence Gust

Dear Barry:

We have a Varian DP-60 spectrometer available for sale. The magnet and power supply is suitable for the Allerhand probe. As you know, a conversion kit can be obtained from Nicolet Technology Corp., Mountain View, California.

Would you please mention this item in the NMR Newsletter.

With warm regards,

Yours sincerely,



Robert M. Dowben, Professor
University of Texas Health Sciences Center
Department of Biophysics
5323 Harry Hines Blvd.
Dallas, TX 75235

RMD/if

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Dr SHAPIRO
Department of Chemistry
Texas A. & M. University
College Station, Texas
U.S.A.

RÉFÉRENCE A RAPPELER :

g/ COP-76-104/ab

VOTRE RÉP

GRENOBLE LE 22 Mars 1976

VOTRE LETTRE DU

Dear Dr Shapiro,

³¹P NMR Spectrum of hexaphenylcyclohexaphosphine oriented in a nematic liquid crystal.

We present here some results obtained from the [¹H]³¹P n m r spectral analysis of hexaphenylcyclohexaphosphine (PC₆H₅)₆ oriented in a nematic liquid crystal.

The spectral analysis (Figure) (D_{3d} symmetry) gives the following values :

$$\begin{array}{lll} J_{12} = -107 \text{ Hz} & J_{13} = 32 \text{ Hz} & J_{14} = -25 \text{ Hz} \\ D_{12} = -39 \text{ Hz} & D_{13} = -76 \text{ Hz} & D_{14} = -31.5 \text{ Hz} \end{array}$$

Assuming a negligible contribution of the ¹J(PP) anisotropy, the puckering angle α of the six-membered ring can be calculated. The α value ($96.5^\circ < \alpha < 97^\circ$) is in good agreement with the X-ray structural data. Such an agreement confirms the validity of the assumption that the coupling anisotropy is negligible.

The ¹J(PP) absolute value in (PC₆H₅)₆ where the phosphorus lone pairs adopt an almost trans disposition, is small as compared with the ¹J(PP) coupling measured in other polyphosphine molecules. Such a behaviour is in agreement with a recent calculation in our group on ¹J(PP) in different conformations of P₂H₄ (1) and which can be expressed in a Fourier expansion $^1J(PP) = -124.43 - 122.86 \cos \phi + 10.87 \cos 2\phi - 1.61 \cos 3\phi$ where ϕ denotes the phosphorus phosphorus lone pair angle.

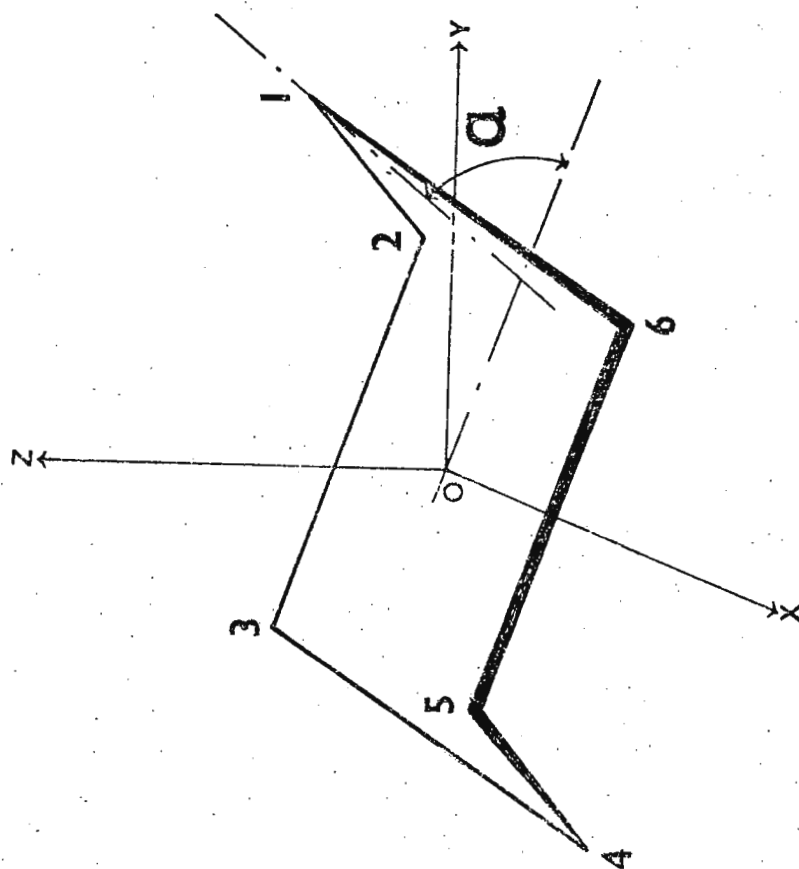
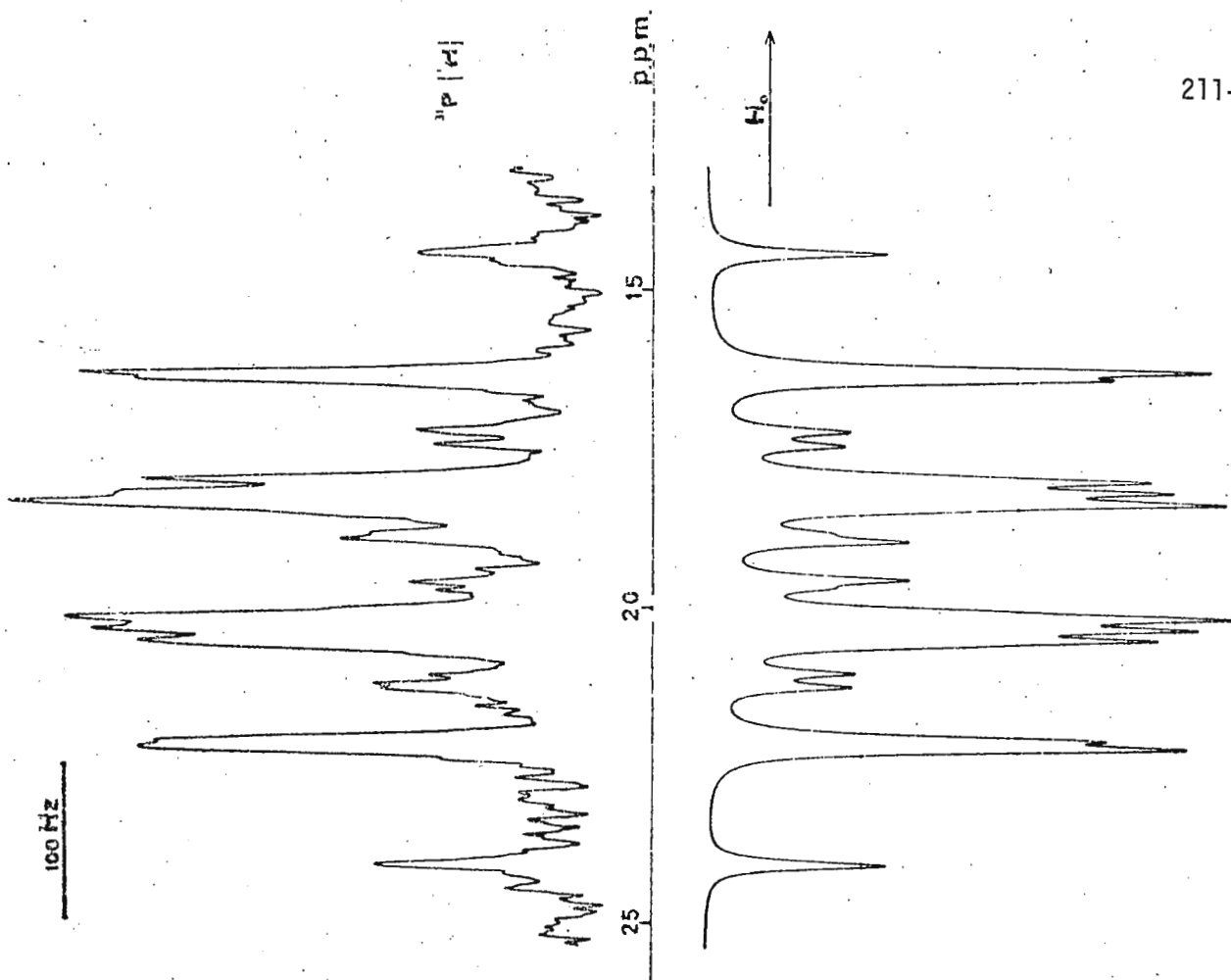
Sincerely yours,

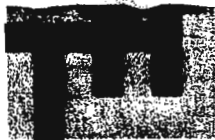
J.P. ALBRAND

A. COGNE

J.B. ROBERT

(1) J.P. ALBRAND, H. FAUCHER, D. GAGNAIRE and J.B. ROBERT, Chem. Phys. Lett., in the press





Technische Hogeschool Delft

Laboratorium voor Technische Natuurkunde

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

Uw kenmerk

Uw brief van

Ons kenmerk

Delft, Nederland, Lorentzweg 1, tel. 01730-33222

25th March 1976

toestel: 5394

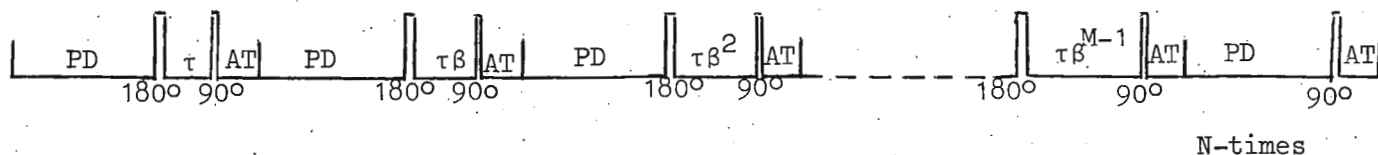
Onderwerp

Dear Professor Shapiro,

A complete IRFT sequence averaging method for T_1 -measurements.

A 70 kOe multipurpose HR-NMR spectrometer system is being developed in our laboratory. The spectrometer part of that system is under an indirect computer control. During a certain time, which we call a stretch, the spectrometer is under the control of a computer programmable timing generator. The spectrometer timing and settings and the way of time averaging can be changed in each stretch (1).

Within this system the following sequence for performing a T_1 -measurement is possible.



$$((PD-180^\circ-\tau|\beta^{(0,1,2,\dots,M-1)}|-90^\circ-AT)_M-PD-90^\circ-AT)_N$$

where

PD = Pulse delay

AT = Acquisition time

β = Ratio of two successive 180° - 90° distances.

Using a **fast** disc as mass storage the different decays in the sequence are time averaged and stored on that disc without any loss of time.

It is felt that with this sequence the influence on the measured T_1 's, due to changes in spectrometer parameters (e.g. field drift and sample temperature), is less than in the case where long and short 180°-90° pulse distances are alternated, but the complete time averaging of one particular pulse distance is done before the next pulse distance is adjusted (2). The reason is that with our sequence the influence for the different 180°-90° pulse distances is almost equal. The combination of the idea of Levy and Peat and the complete sequence will give the best result.

- (1) A.F. Mehlkopf, T.A. Tiggelman, J.H.N. Creyghton and D. Korbee
Paper presented at the second European Experimental NMR Conference, Enschede, The Netherlands, November 1975
(A summary is available on request)
- (2) G.C. Levy and I.R. Peat, J. Magn. Resonance, 18, 500 (1975)

Please credit this contribution to prof. J. Smidt's subscription.

Yours sincerely,

A.F. Mehlkopf
Ir. A.F. Mehlkopf

G. Reckweg
G. Reckweg

OPPORTUNITY WITHIN THE BRUKER ORGANISATION IN JAPAN

The Bruker Group of Companies have now established a Sister Company in Tokyo, Japan. To expand our team we would welcome one or two new members who are familiar with the application of NMR spectroscopy to chemical and physical problems.

The main object would be to assist our many customers in Japan to get the best possible performance out of their Bruker instrumentation and to liaise with our head-office in processing sales enquiries.

At least some basic knowledge of Japanese is required and it may well be particularly interesting for Japanese Nationals. Our office is located in Tokyo City.

Anyone who would like to know more about this should write to me at the address on the bottom of this letter.

Yours sincerely,

BRUKER JAPAN COMPANY LIMITED

J.A. Deegan
J.A. Deegan
21-22, 1-Chome
Higashiyama, Meguroku,
Tokyo, Japan

Dear Barry:

LET THE NUCLEI SPEAK, A FREE-STANDING 0.01-110 MHz TRANSCEIVER.

We have recently constructed a system which can be used to resonate and detect any frequency in the nuclear range of our XL-100 (10 KHz-110 MHz) operating in FT mode. Sensitivity is a little better than the standard XL receiver, and we can set spectral windows from 10 Hz to 300 KHz with optimum filtering. Frequency selection simply requires the twist of a knob (spectrum analyzer), the set of a dial (synthesizer), and the flick of a switch (close feedback loops). The frequency lock is stable to better than 0.01 Hz for 24 hours.

The system is based on a frequency synthesizer (HP 8660-A) and spectrum analyzer (HP containing 8552 R.F. section, 8553 I.F. module and 8443 tracking generator). The basic circuitry necessary to link the units and to provide phase coherence throughout the system (and the XL) is shown in the figures. It should be noted that the second IF stage operates at the sum of the input and first local oscillator frequencies to limit spurious response. Matching of the transmitter frequency to the receiver centerband is achieved by appropriate mixing. The beat frequency between the receiver and synthesizer is sensed and zeroed in a feedback loop.

As a practical example, the ^{27}Al spectrum of a 0.05 M LiAlH_4 solution is shown. The recently corrected¹ Al-H coupling constant is confirmed. We have encountered two limitations to obtaining routine multinuclei nmr on the system. We do not have a broad-band probe and are restricted to nuclei which resonate close to the old favorites. We have had only minor success with proton nmr - the HP detector is so sensitive that proton solvent peaks lead to destruction. Work is in progress to remove these limitations. The work is described in a J. Mag. Res. communication in press; full details are available from the undersigned.

1. S. Hermanek, O. Kriz, J. Plesik and T. Hanslik, Chem. Ind. (Lond.), 42, (1975).

R. E. Santini

J. B. Grutzner *John B. Grutzner*

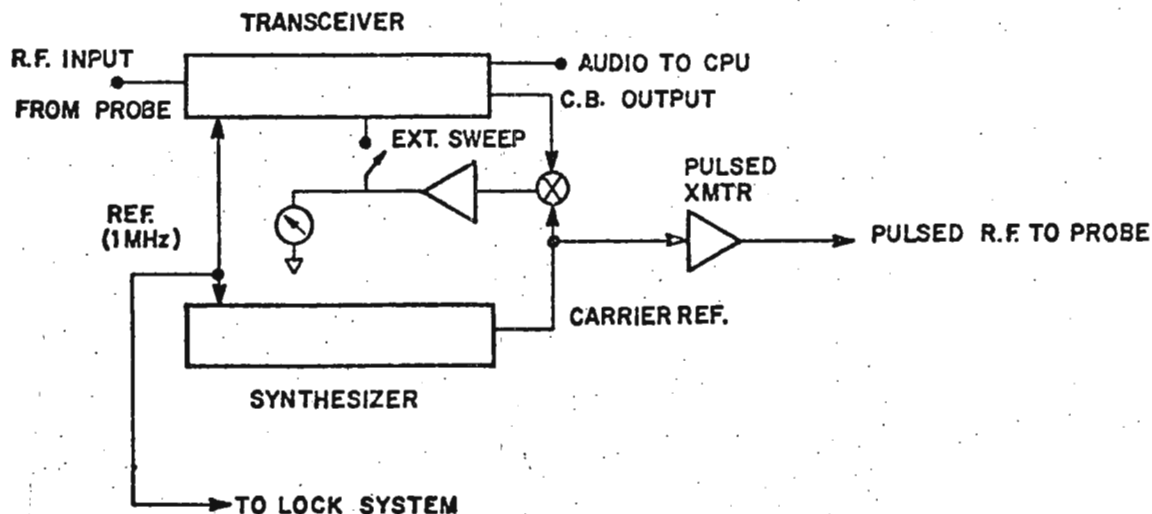


Figure 2 - Carrier frequency phaselock system - block diagram

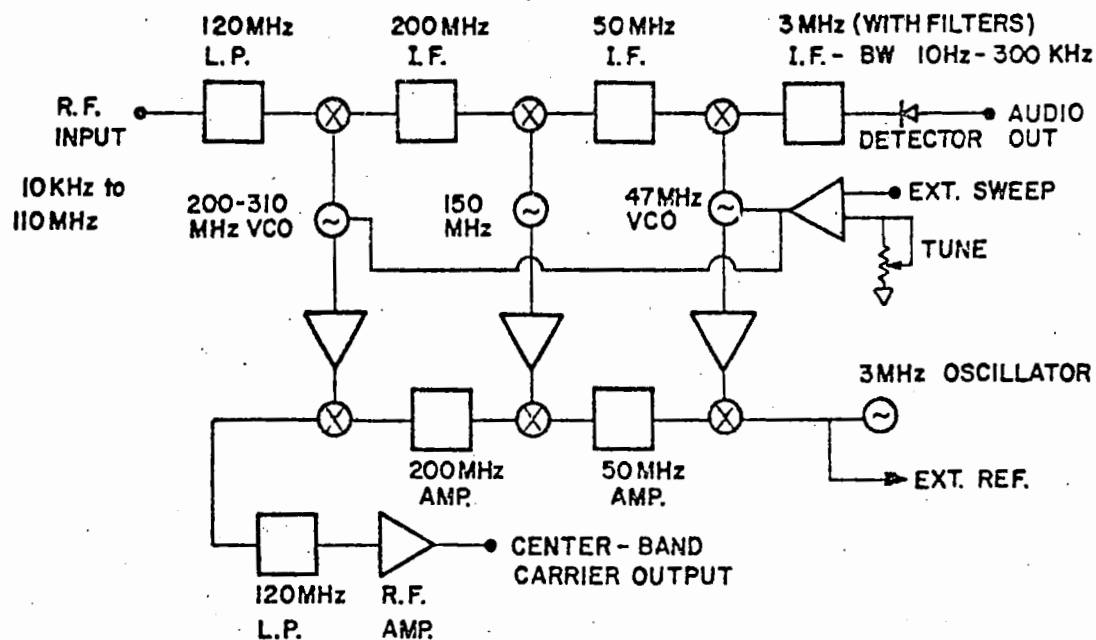


Figure 1 - Transceiver block diagram

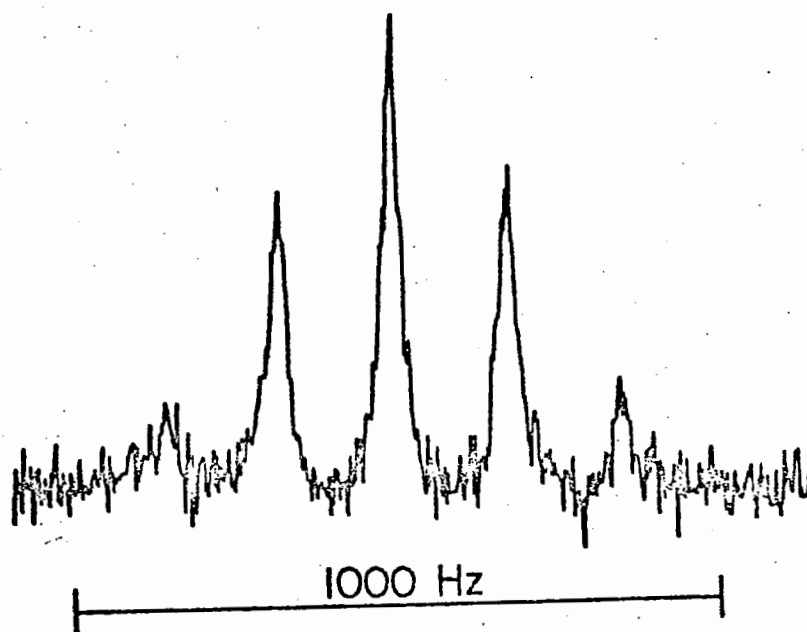


Figure 3 - The ^{27}Al spectrum of LiAlH_4 (0.05M) in THF in a 10mm tube. Spectrum obtained from 16394 pulses with 5KHz bandwidth, 4K data points, and no weighting of FID. Lock was external deuterioacetone.



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
PUBLIC HEALTH SERVICE
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20014

March 30, 1976

Building 2, Room B2-08

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

Title: Observation of individual carboxyl carbon atom
resonances in a protein with high field CMR.

Dear Barry:

In writing this note I was tempted to title it "aesthetics of NMR," since most people react as if having an aesthetic experience upon seeing our beautiful spectra.

The figure shows the carboxyl-carbonyl region of ^{13}C NMR spectra of hen egg white lysozyme (MW 14,600, 10 m M) at 40° , obtained using a Bruker WH-270 spectrometer at 68 MHz. We have recently replaced the Raytheon computer used in this work with a Nicolet 1080 with 36K memory.

Discussion of the carboxyl group titration curves and the question of the efficacy of high fields for such studies of proteins will be found in our forthcoming paper (H. Shindo and J. S. Cohen, Proc. Nat. Acad. Sci., in press). It should be noted that two carboxyl groups are in the active site of hen egg white lysozyme. We are not sure if we have observed their resonances and are currently carrying out inhibitor binding studies.

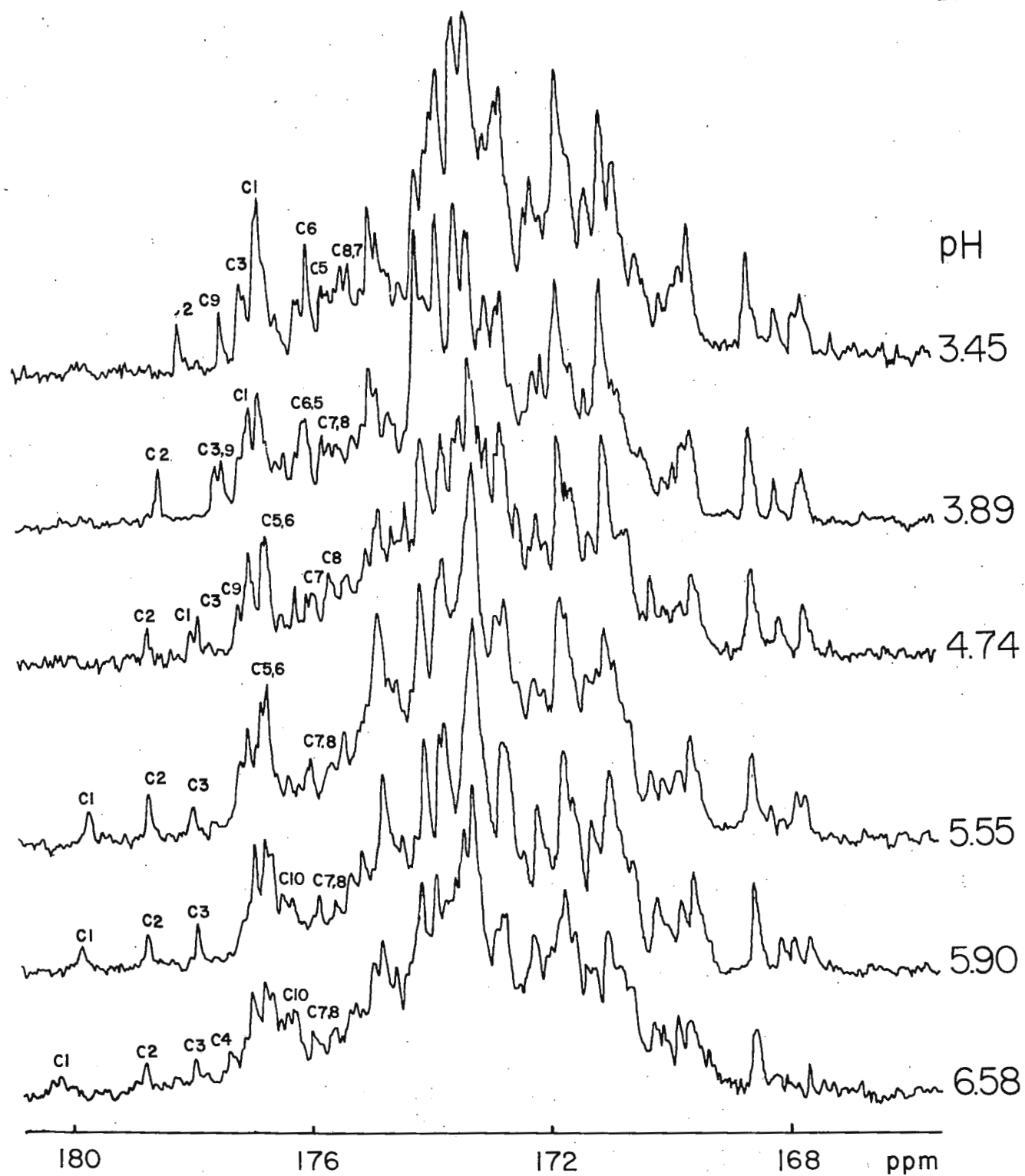
I will be on sabbatical at the Isotope Department of the Weizmann Institute, Rehovot, Israel, for a year from July, helping to set up some biochemical applications on their new Bruker WH-270.

Sincerely,

A handwritten signature in cursive script, reading "Jack S. Cohen", is written over the typed name.

Jack S. Cohen
Reproduction Research Branch
National Institute of Child
Health and Human Development

JSC:ell





March 23, 1976

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

"Carbon-13 NMR for the micro-chemist"

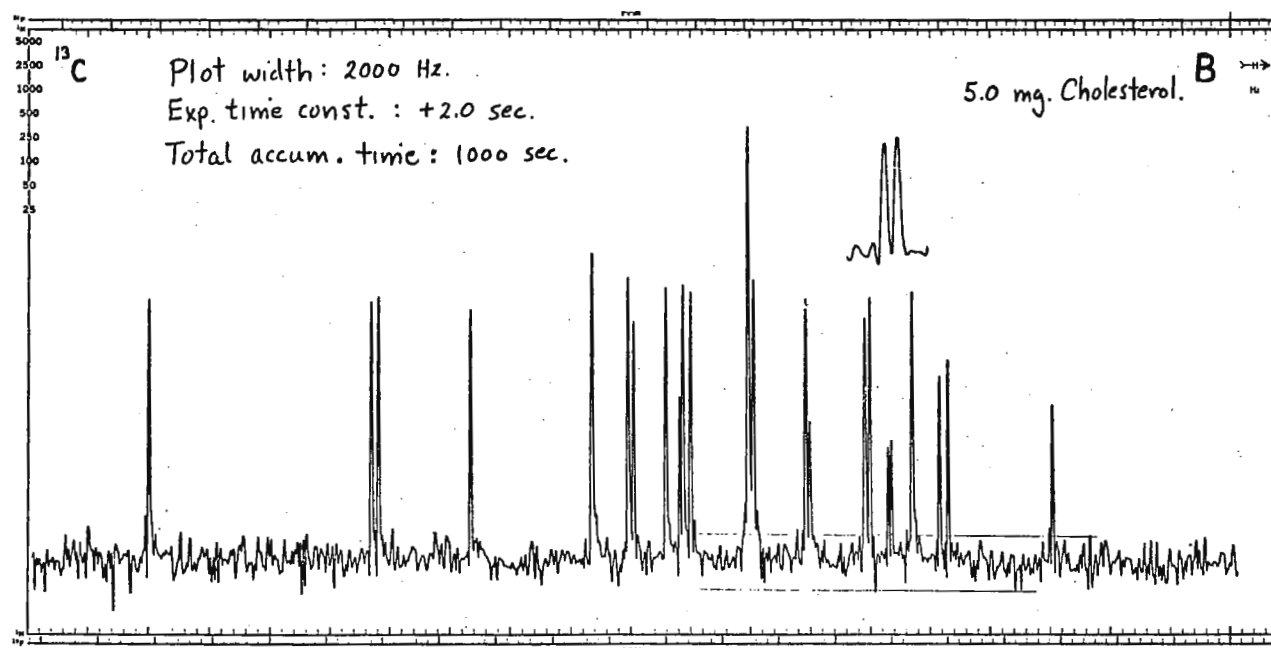
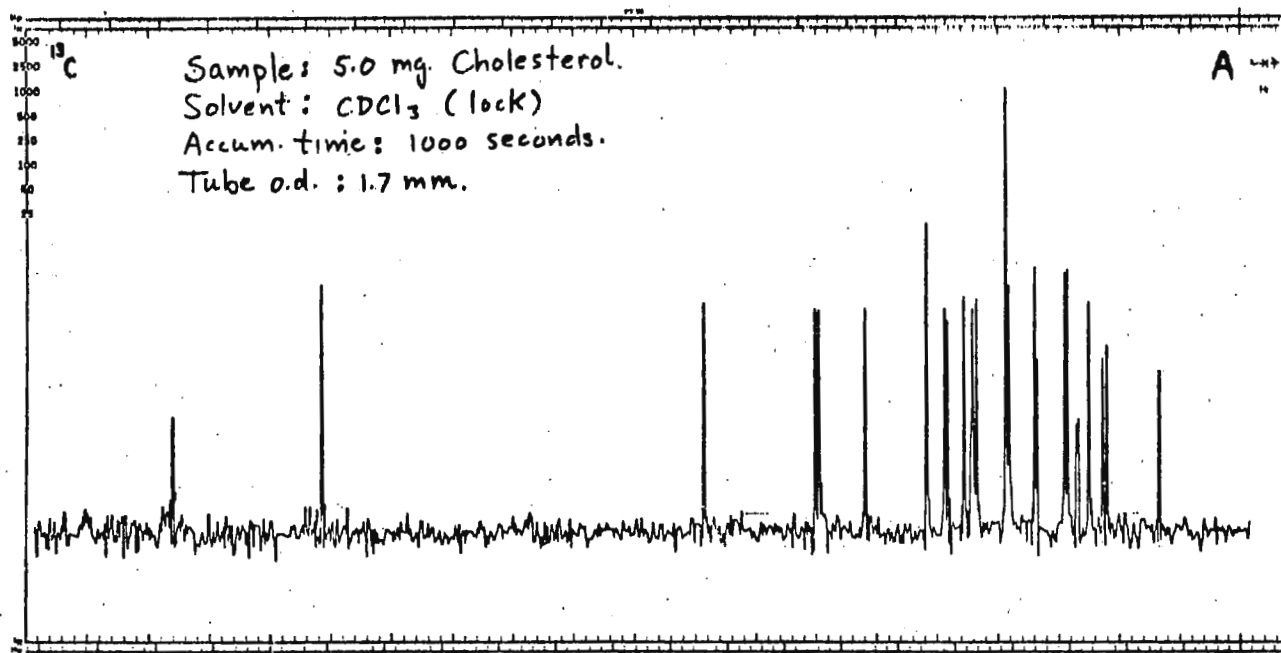
Dear Barry:

Rapid progress in instrumentation is outstripping the spread of information throughout the community of chemists who could otherwise make better use of the present capabilities of NMR spectrometers. It may be hard for your readers to believe that there are still chemists who think that 50 milligrams is necessary for a decent ^1H spectrum, and a bottle full for a usable ^{13}C spectrum, but I run into them all too often. While readers of this bulletin may already be aware of the capabilities described in this letter, they may not appreciate them enough to participate as fully in the general dissemination of this information as they might. In hopes of remedying this situation I offer the following.

For small samples with reasonable solubility in the usual deuterated solvents there is much to be gained by improving the coupling of the nuclear moments to the tuned detector circuit. Using an XL-100 spectrometer equipped with a small coil closely coupled to sample tubes of 1.7 mm o.d., 1.5 mm i.d., we have obtained the results shown in the attached spectra. Chart A shows the spectrum of 5 mg of cholesterol obtained in only 1000 seconds. The spectrum would still be very usable if only 250 seconds were devoted to accumulation of data. The latter is the scan time that most chemists think of as standard for a single-scan proton NMR spectrum. Even the most miserly of chemists can usually spare 5 mg (you get most of it back).

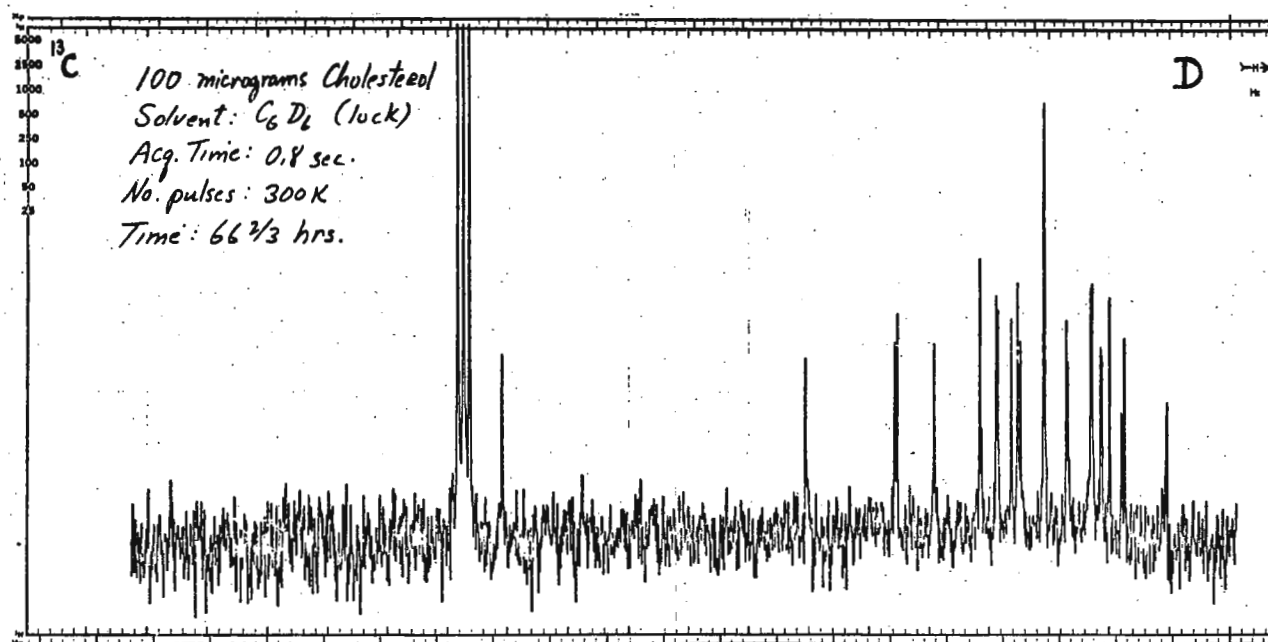
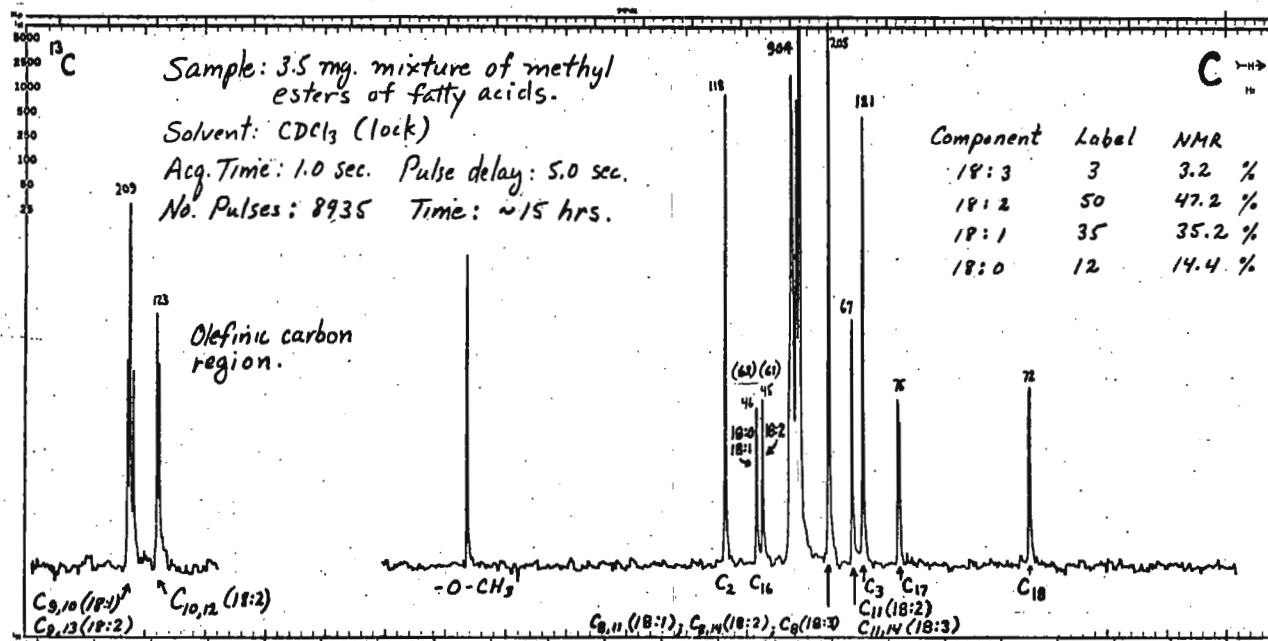
Chart B is a plot expansion that shows that such rapidly-run spectra will tolerate some resolution enhancement and resolve completely all of the spectral lines.

Chart C shows the spectrum of a mixture of fatty acid methyl esters normally used for GLC calibration. A solution of 3.5 mg in 12 μl of CDCl_3 was run for approx. 15 hrs. with 90° pulses at 6 sec. intervals. The numbers associated with the peaks are integral intensities, while assignments appear under the corresponding peaks. Since C_{16} , C_{17} , and C_{18} have more molecular motion, being at the end of the chain, they have longer T_1 's and slightly lower intensities than C_2 , C_3 and the remaining carbon atoms in the chain. The sum of the intensities of the two peaks due to C_{16} was normalized to the intensity of C_2 to correct for this difference in T_1 . Differences in NOE factors were neglected since essentially full NOE is found for most carbon atoms in these large molecules.



That the latter assumption is justified is supported by the good agreement of the composition of the sample as determined by NMR with the values on the label. Thus, a 4-component mixture can be quantitatively analyzed by ¹³C NMR, even if only a few milligrams are available.

Finally, the existence of sub-milligram samples cannot be denied or avoided indefinitely, even by the most hard-hearted and self-protective ¹³C NMR spectroscopist. Many biological applications such as metabolic studies fall into this category. Samples are often measured in mouse-days, or other equally bizarre units. A mouse-day of some products might be from 10 to 50 micrograms.



With the idea of freeing the biochemist from the drudgery of mouse culture on a large scale, I decided to determine the lower limit of sample size which could give a usable ^{13}C spectrum from a complex molecule with data accumulation over a weekend. Chart D shows the ^{13}C spectrum of 100 micrograms of cholesterol dissolved in C_6D_6 and run for 300K transients at 0.8 sec. intervals. I believe that the capability demonstrated here should make ^{13}C NMR applicable to some of these pitifully small samples resulting either from the physical size limitations of practical laboratory animals, or from the small scale of effective separation methods such as thin layer chromatography or GLC.

Sincerely,

James N. Shoolery

James N. Shoolery, Applications Chemist
 NMR Applications Laboratory
 Varian Associates
 Palo Alto, California

New 18-mm Probe for the XL-100

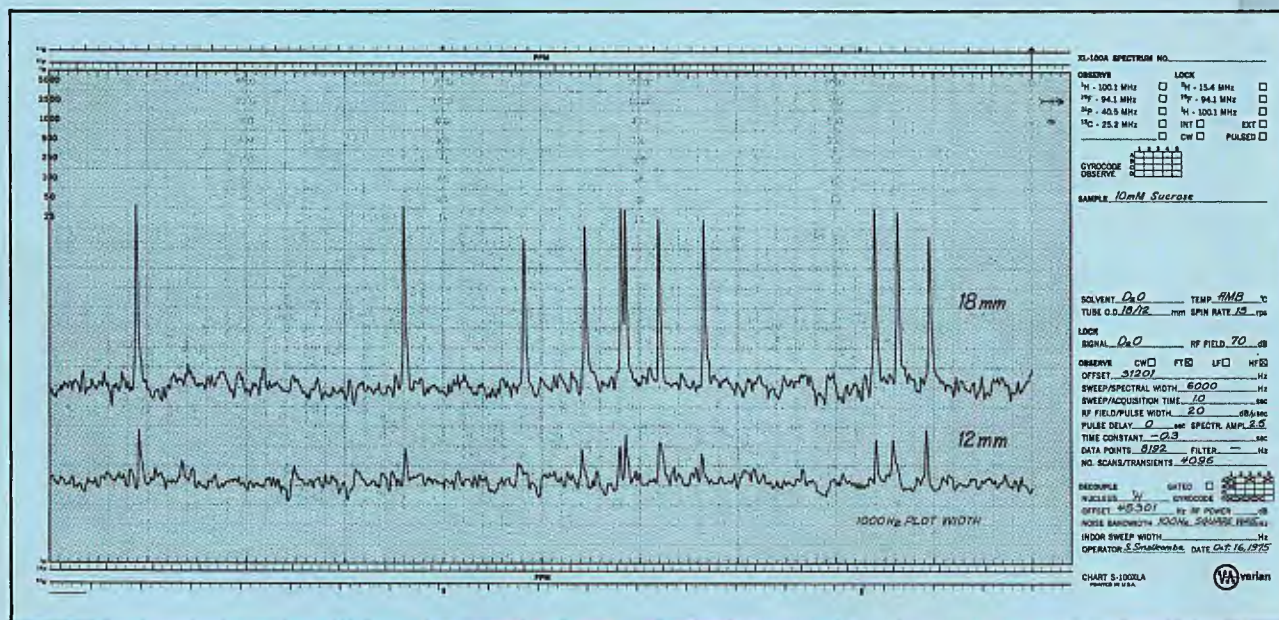
^{13}C Spectra 10 Times Faster

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!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.



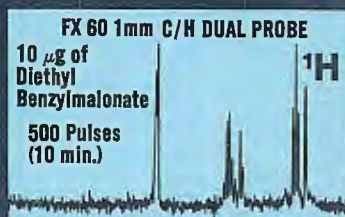
Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D_2O , one using an 18-mm sample, the other the standard 12-mm sample! Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.

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



Sample tube
shown actual size.

If you're considering the purchase of an FT NMR System. Consider JEOL's FX Spectrometer Series.



The concept behind the development of the FX Series is to provide one basic electronic system that gives each customer the option of selecting a spectrometer with the best cost / performance ratio to meet his individual FT NMR requirements.

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Since the introduction of the FX60 with the LPCS* in September 1974, we have established an enviable TRACK RECORD for reliability and performance. In addition, JEOL has introduced commercially the Dual Frequency ($^{13}\text{C}/^1\text{H}$) Probe concept for 1, 5 and 10mm VT samples, Quadrature Detection for increased performance, Digital Phase Shifters and many other innovations in our continual effort to advance *the* state-of-the-art performance.

So if you're considering the purchase of any FT NMR spectrometer, consider the present, consider the future, consider JEOL.

For further information about the FX Series
call or write . . .

*Light Pen Control System

JEOL

Analytical Instruments, Inc.

235 Birchwood Ave., Cranford, NJ 07016

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