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N-M-R Newsletter

No. 232

January, 1978

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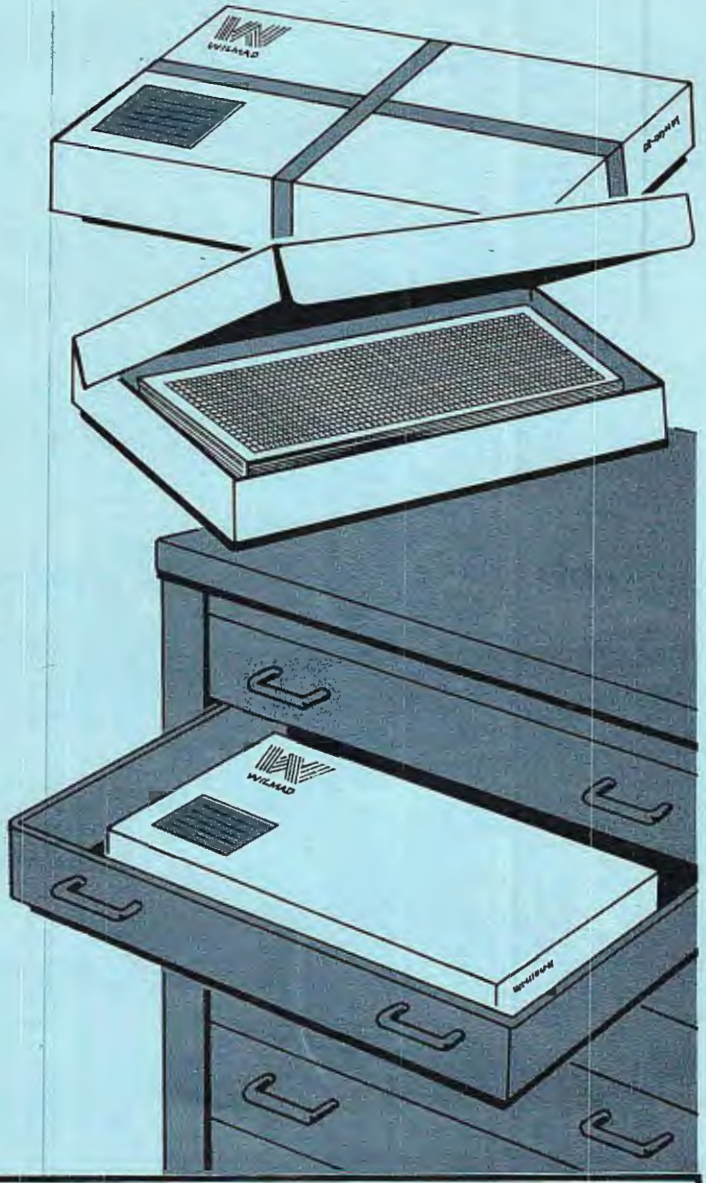

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DEADLINE DATES: NO. 233: 6 February 1978
NO. 234: 6 March 1978

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 232

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

SA/sjm

23 NOVEMBER '77

Dear Dr. Shapiro,

Variable Time Base Interface Between Pulse Spectrometer and Signal Averager

Over the last few years we have used a Bruker SXP pulse spectrometer to study a wide variety of biochemical systems by monitoring the proton relaxation of the solvent as well as the solute. A signal averager has been used to accumulate the transverse decays of magnetisation following the CPMG pulse sequence. The time base of this signal averager was initially controlled directly from the spectrometer, so that the height of each echo signal was sequentially recorded in each of its 800 memory channels.

A number of the systems studied have exhibited non-exponential decays, and a computer program was developed to resolve these complex decays into discreet exponential components, using an iterative least-squares method. It soon became apparent that valuable information was being lost at either the beginning, or the end of most decays, due to the limited time scale over which the decays could be monitored, because the signal averager was being operated with a linear time base and had only 800 memory channels.

An interface has now been developed between the spectrometer and the signal averager, so that the time base is still synchronous with the CPMG pulse sequence, but the sampling rate can now be decreased at any two preselected positions on the decay. This allows us to use short τ spacings between the CPMG pulses, so that the initial rapid relaxing component of a decay is adequately described, before the sampling rate is decreased by a factor of 2,5 or 10, depending on how quickly the relaxation rate is changing. Finally, the sampling rate is decreased further by a factor of 2,5,10,20, 50 or 100, to allow the decay to be sampled until a steady baseline is reached.

The only limitation on the time scale over which a decay can now be recorded is the minimum τ spacing produced by the spectrometer (i.e. 40 usec). This limits the most rapid relaxing components which can be adequately resolved by this method, to a relaxation time (T_2) of 100 usec. In fact, this is of little consequence, because relaxation times of 100 usec are readily obtained directly from the FID, and are accumulated using a transient recorder as an interface between the spectrometer and the signal averager.

The variable time-base interface between the NMR spectrometer and the signal averager was tested by analysing a complex decay of magnetisation containing three discreet exponential components. This was accomplished by initially preparing a 1% H_2O/D_2O solution, because this had a S/N comparable to the lowest encountered in any of our studies. Two aliquots were taken from this solution and differing amounts of copper sulphate were added to each, increasing their relaxation rates. The proton transverse relaxation times of these three solutions were individually determined to be 8.0 sec, 76.4 msec and 9.4 msec.

A composite NMR sample was prepared by separating these three solutions with concentric tubes. The complex transverse decay of magnetisation from this sample was analysed and found to require three exponential components to adequately describe it. The relaxation times of these components were 8.1 sec, 78.6 and 10.2 msec, and are in very good agreement with those determined from the individual solutions.

The circuit diagram of the interface is available on request.

Please count this as the contribution from the Unilever Research Laboratories in Europe.

Yours sincerely,

S. Ablett.

S. Ablett

University
of Strathclyde

Department of Pure and Applied Chemistry

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

23rd November, 1977

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

Dear Barry,

^{13}C-Spectra of Naturally Occurring Coumarins

Carbon-13 nmr spectrometry seems likely to prove a useful tool in unravelling the structures of naturally occurring coumarins which often occur as inseparable mixtures of closely related compounds. To illustrate this we give two examples.

Compound Ia has a spectrum summarized in the chemical shifts appended to the structure. The material to hand was contaminated by about 10% of the related compound Ib in which the isobutyroyl group is replaced by a sec-isobutyroyl group.

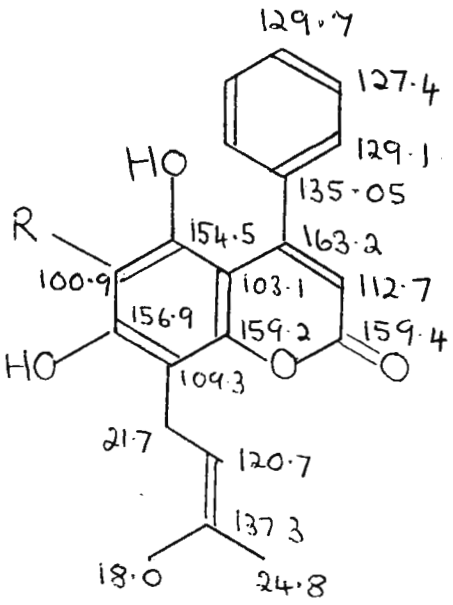
Compounds IIa and IIb occurred as an 2:1 mixture the composition of which could be only slightly altered by crystallisation. The compounds are also isomeric in the side chain. In this case, some prior hint of the situation was afforded by the presence of two low field resonances in the proton spectrum due to the hydrogen bonded phenolic OH groups, but the ^{13}C-spectrum is much more amenable to interpretation.

Yours sincerely,

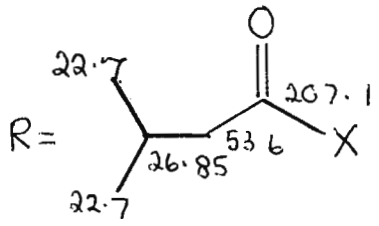
Elizabeth G. Crichton Peter G Waterman P. Bladon

E. G. Crichton* P. G. Waterman* P. Bladon

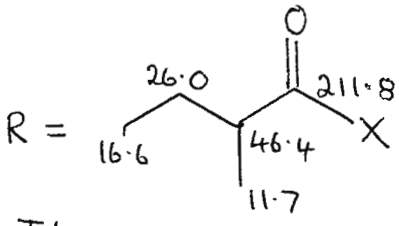
* Department of Pharmaceutical Chemistry.



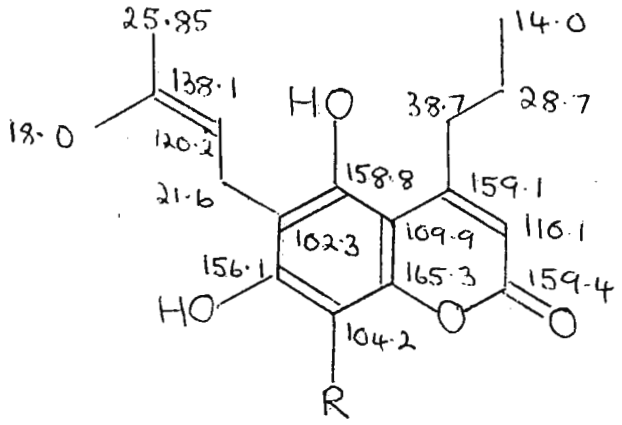
I a & b



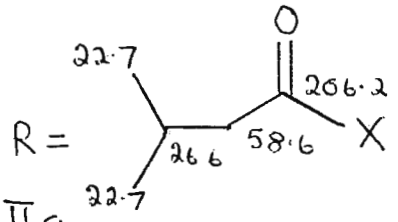
Ia



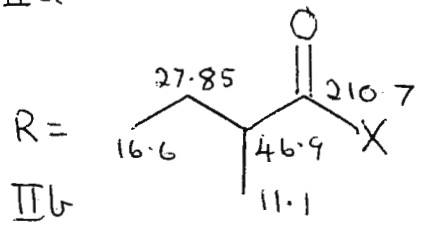
Ib



II a & b



IIa



IIb

232-5

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DÉPARTEMENT DE CHIMIE ORGANIQUE
Professeur B. ROQUES
(C N R S) E R A 07613

PARIS, Novembre 29th, 1977

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

Dear Professor Shapiro,

As usual, your blue note joins us in a critical moment : we have just received our new Bruker 270 and many problems are running long. We guess the same tremendous agitation naturally occurs in every laboratory starting in the supraconductor field.

We wish to report presently a problem we have studied, with Prof. M. Anteunis : the ^1H NMR conformational studies of L.4Hyp containing-peptides (1) and especially the "simple" L.Pro-L.4Hyp dipeptide. The 300 MHz spectrum is not enough complicated to mask the minor cis isomer in solution (note this isomer is 100 % in the crystal (2)), however, no information can be deduced about the chemical shifts and couplings, owing to the strong overlap in both trans and cis isomers.

The addition of praseodyme perchlorate (3) in water is a very efficient method for LIS experiments in the peptide field, as shown in the attached figure (a : without $Pr(ClO_4)_3$ and b with amount of LIS reagent in D_2O), thus allowing all the individual lines attributed. In order to test possible similar conformations in both the dissolved and solid states, we have simulated the spectrum (part c) with the δ values deduced from part b and a, and the ^3J constants deduced from the X-ray geometry (2), *via* a Karplus-like relation (4). The result, compared to a, is quite acceptable : this is a strong indication for close similarities between the mean ring conformations in both states.

Furthermore, the cis $\rightleftharpoons$ trans isomerism around the peptide bond surprisingly appears to be of poor influence. More details about others hypro containing oligopeptides are currently under preparation.

Sincerely yours ;

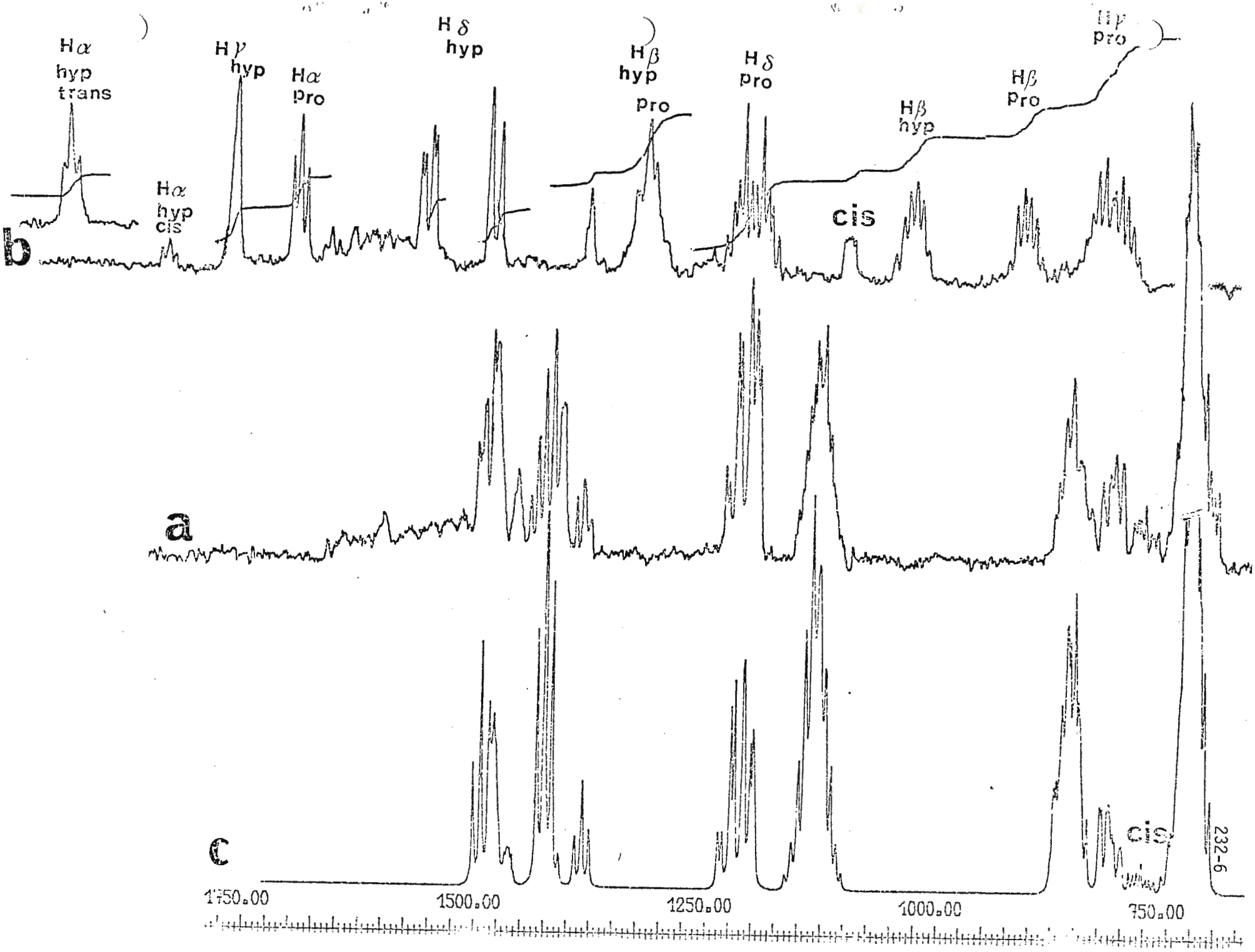
B.P. ROQUES. C. GARBAY-JAUREGUIBERRY T. PRANGE

1) T. Prangé, C. Garbay-Jaureguiberry, B.P. Roques and M. Anteunis, 1974, Biochem. Biophys. Res. Commun., 61, 104-109.

2) B. Arnoux, T. Prangé and C. Pascard, 1977, Cryst. Struct. Commun. 6, 29-32.

3) M. Anteunis and J. Gelan, 1973, J. Amer. Chem. Soc., 95, 6502-6504.

4) D.A. Torchia, 1972, Macromolecules, 4, 440-442.


Hα hyp trans
Hα hyp cis
Hγ hyp
Hα pro
Hδ hyp
Hβ hyp pro
Hδ pro
cis
Hβ hyp
Hβ pro
Hγ pro
b
a
c
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VOTRE RÉF.

VOTRE LETTRE DU

Dr. B.L. SHAPIRO
Texas A & M University
College of Science
Department of Chemistry
COLLEGE STATION, Texas 77843 U.S.A.

GRENOBLE LE 30 novembre 1977

Dear Dr. Shapiro,

In the course of our n.m.r. investigations on simple organophosphorus molecules oriented by means of liquid crystals (1) we have been interested in the $^1J(PSe)$ n.m.r. coupling constants. One of the interesting results concerning the $^1J(PSe)$ values is a high dependence upon solvent and temperature. Such a fact has already been noticed before (2). The large differences observed on the following molecules : $Se = P(CH_3)_3$, $Se = P(N(CH_3)_2)_3$, $Se = P(OCH_3)_3$, with $\Delta J \sim 70$ Hz in substituting $CDCl_3$ by $C_6D_5CD_3$, suggest a conformational effect rather than solvent effect only. The variations observed must be evaluated in terms of ΔK (reduced coupling constants) rather than ΔJ, because it expresses the nature of the true change at the electronic level. These variations are found to be large in comparison with variations observed over similar solvents and temperature range for other nuclei (HH, CH, PH).

Examples of $^1J(PSe)$ modification on $Se = P(CH_3)_3$:

$CDCl_3$	50°C	688 Hz	$C_6D_5CD_3$	90°C	729 Hz
	-50°C	658 Hz			

The problem of the origin of the change observed in $^1J(PSe)$ is also studied by means of I.R., $\delta^{31}P$, $\delta^{77}Se$ and $^3J(H\text{-}Se)$ modifications.

Sincerely,

J.B. ROBERT A. COGNE L. WIESENFELD

(1) J.P. ALBRAND, A. COGNE and J.B. ROBERT, Chem. Phys. Lett., 48, 524 (1977).

(2) W.J. STEC, A. OKRUSZEK, B. UZNANSKI and J. MICHALSKI, Phosphorus, 2, 97 (1972).

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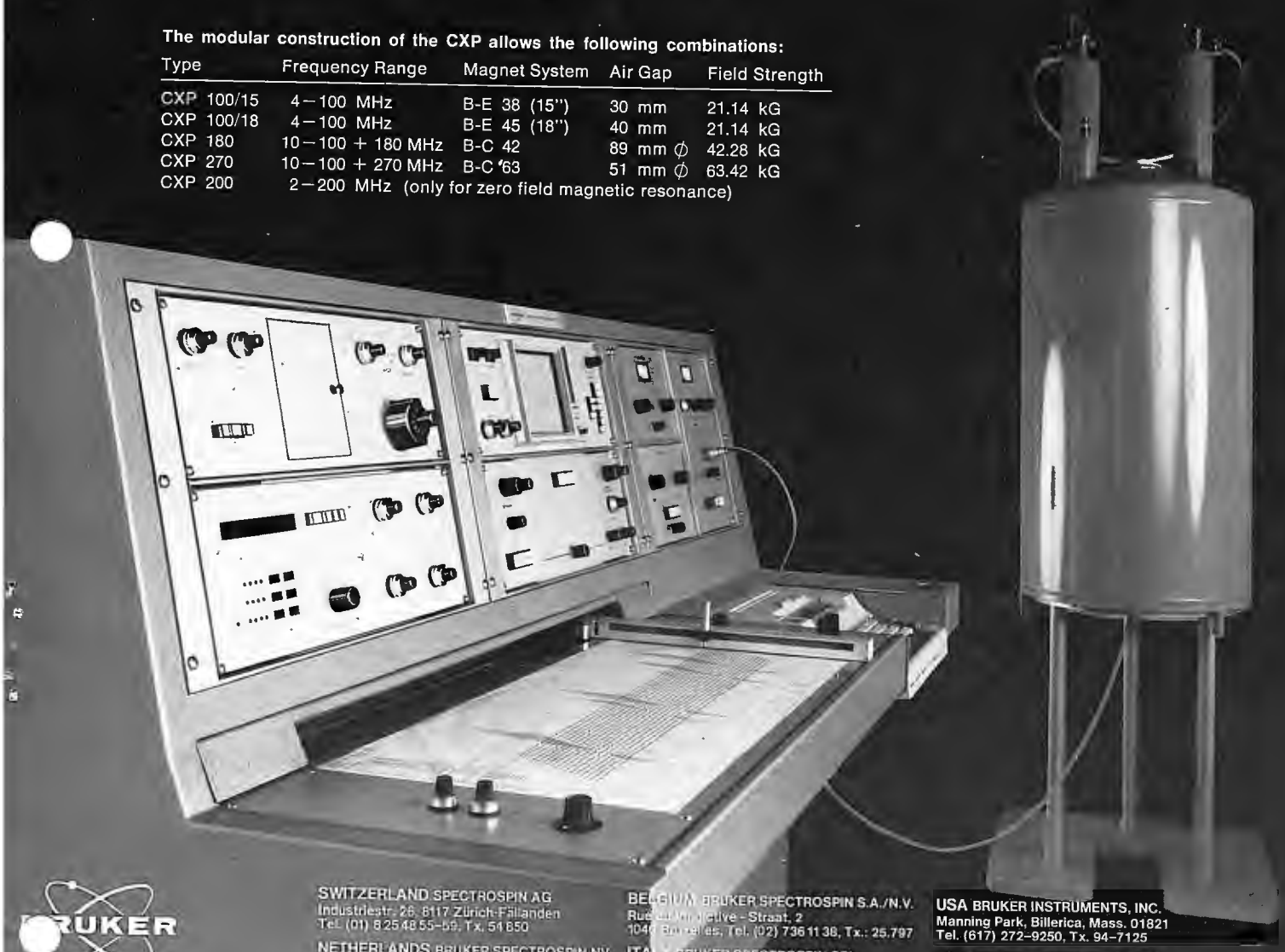
CXP 180	10 – 100 + 180 MHz	B-C 42	89 mm ϕ	42.28 kG
CXP 270	10 – 100 + 270 MHz	B-C '63	51 mm ϕ	63.42 kG
CXP 200	2 – 200 MHz (only for zero field magnetic resonance)			



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November 29, 1977

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

SPIN-LOCK AND ADRF CROSS-POLARIZATION EXPERIMENTS ON DELRIN

Dear Barry:

The procedure for cross-polarization transfer using adiabatic demagnetization in the rotating frame (ADRF) is straightforward. Following a spin lock of the protons, the ^1H rf field, H_{1I}, is slowly (compared to the ^1H inverse linewidth or T_2) reduced to zero, thereby transferring the dipolar order of the spin-lock from the applied rf field to the local dipolar fields surrounding each proton. A CP transfer can now be made during the contact time with the dual advantage that, first, no particular attention need be made to satisfying the dual spin-lock (SL) Hartmann-Hahn condition and, second, the greater one makes the ^{13}C rf field, H_{1S}, the larger the observed carbon magnetization. Finally, the carbon magnetization is observed with dipolar decoupling as before. The price one must pay for the improved sensitivity in the ADRF scheme is in the length of time required to complete the CP transfer; that is, T_{IS} (ADRF) is longer than T_{IS} (SL), usually by orders of magnitude.

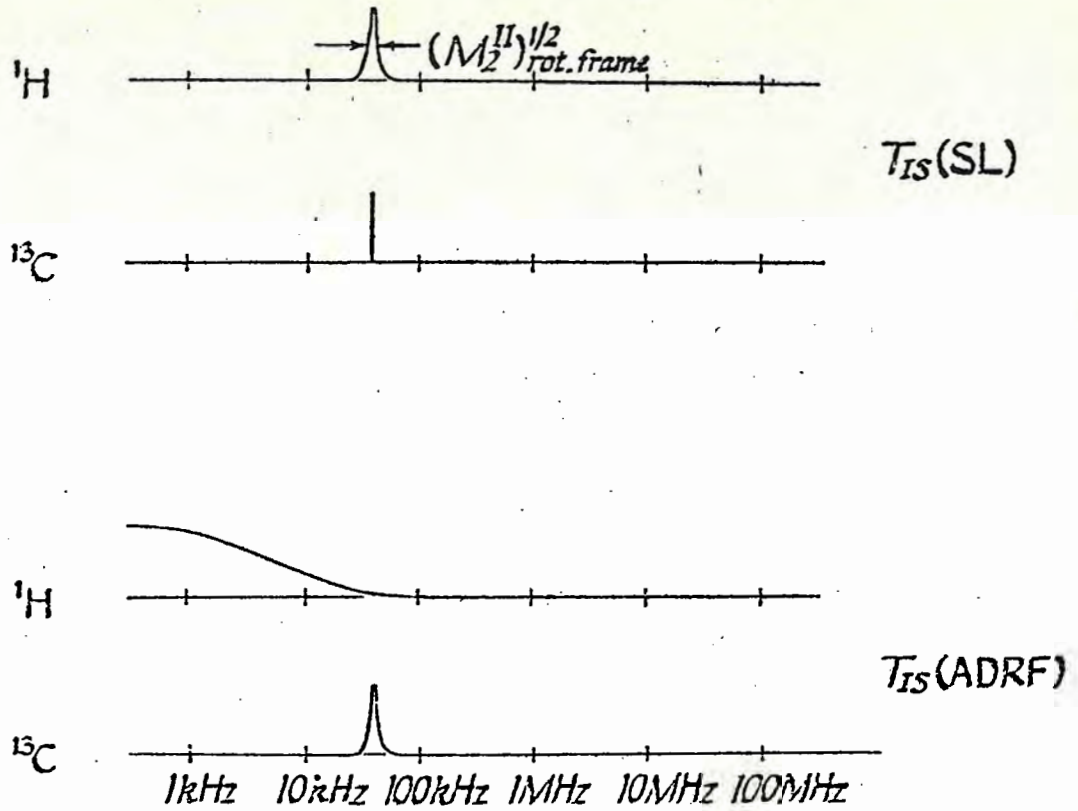
The reason for the much slower CP transfer rate in the ADRF experiment can be appreciated from examination of the figure. In the ADRF situation (second from top), despite the width of the carbon line in the absence of dipolar decoupling, the spectral overlap between I and S spin systems is limited to the tails of the two resonances. This is in sharp contrast to the effective overlap under the Hartmann-Hahn condition (top). Clearly, with a limited frequency match, the stationary components of magnetization necessary to cross-polarization are severely reduced. As a result, the CP transfer rate is slow. Demco, Tegenfeldt, and Waugh have developed a quantitative theoretical analysis which describes the dependence of the CP transfer rate on frequency mismatch in both the SL and ADRF experiments.

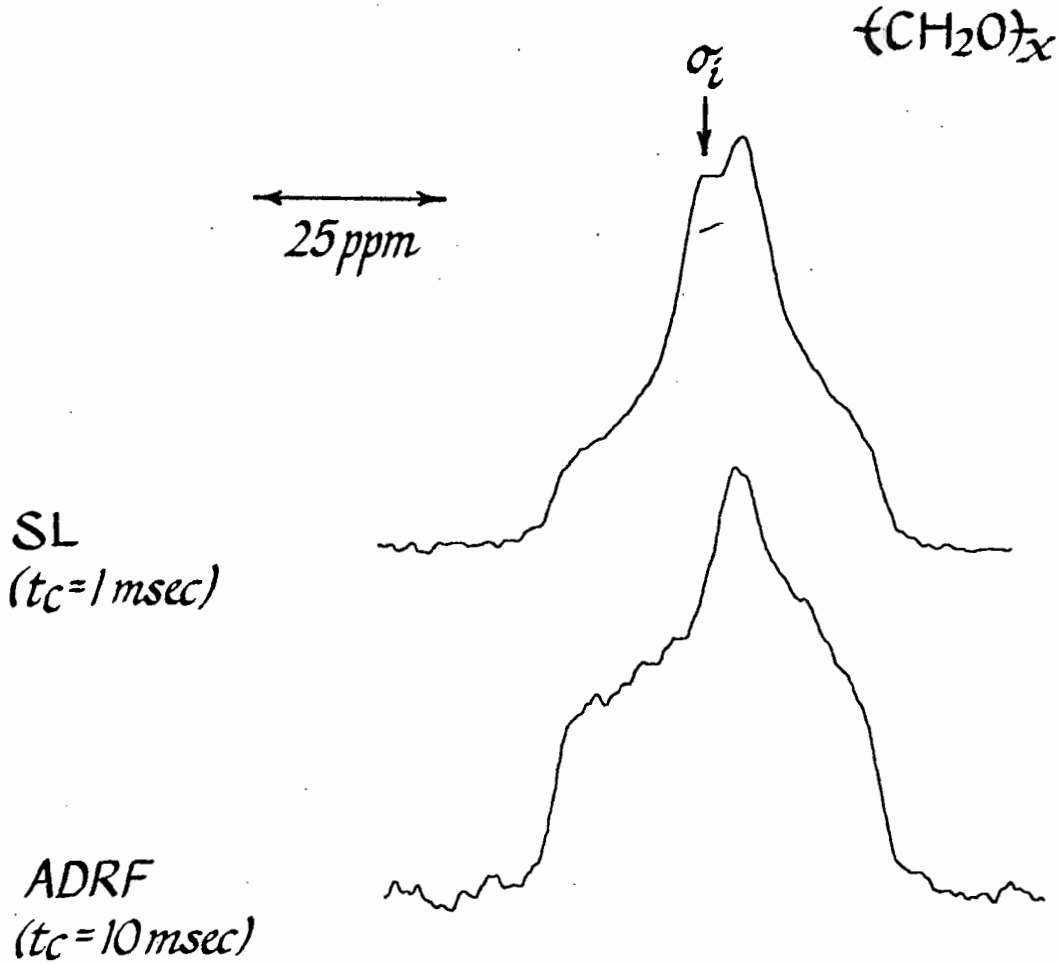
Poly(oxymethylene), or Delrin, is a partially crystalline polymer with about a 30% rubber content. In spin-lock CP experiments, the polarization transfer efficiency between protons and carbons in the rubbery phase is still good enough, despite extensive averaging of static dipolar interactions by chain motions, that a strong signal from the rubber component at the isotropic center of the CSA pattern is observed (third from top). For the less efficient CP transfer of ADRF experiments, no rubber-component signal is observed. In general, therefore, comparison of the two types of CP spectra provides a means of characterizing motionally modified CSA patterns and lineshapes, assuming of course, the ADRF experiment is indeed practical.

Sincerely

Jake Ed.

Jacob Schaefer E. O. Stejskal


^1H
$(M_2^{II})^{1/2}_{rot.frame}$
T_{IS}(SL)
^{13}C
^1H
T_{IS}(ADRF)
^{13}C
1kHz
10kHz
100kHz
1MHz
10MHz
100MHz


$(CH_2O)_x$
σ_i
25 ppm
SL
(t_C = 1 msec)
ADRF
(t_C = 10 msec)

232-11

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Department of
Chemistry

416/684-7201

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Canada

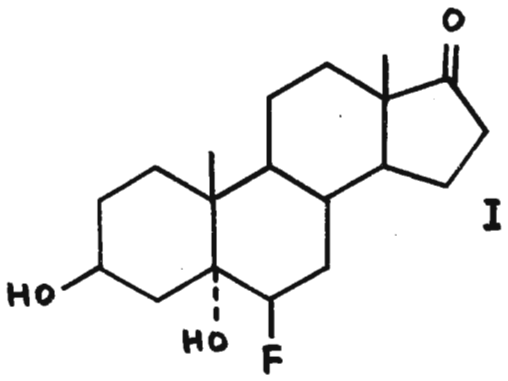
December 1, 1977.

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

Long Range ^{13}C-^{19}F Couplings

Dear Professor Shapiro:

Long range ^{1}H-^{19}F couplings are well known, but corresponding ^{13}C-^{19}F couplings where $n \geq 4$ do not appear to have been systematically investigated. In the course of our work on microbial steroid hydroxylations, we had occasion to prepare the fluoro steroids I-IV, and as a matter of routine analysis



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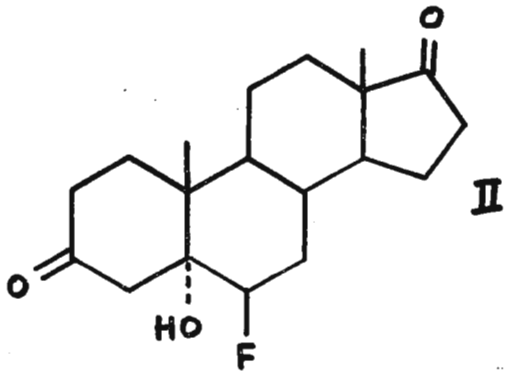

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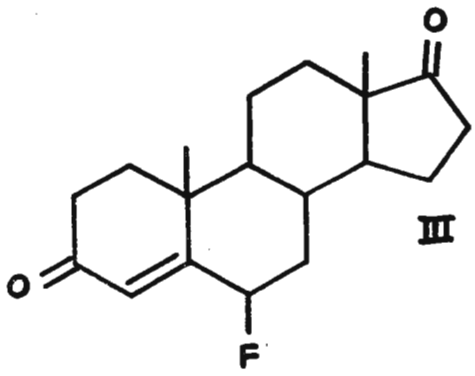

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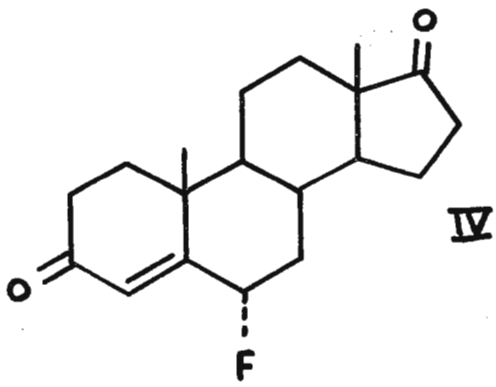

IV

recorded their ^{1}H and ^{13}C spectra (Bruker WP-60). The expected long range ^{1}H-^{19}F coupling (Cross and Landis, JACS 84, 1736 (1962)) to the C-19 methyl hydrogens was observed in I-III, and in addition we observed a significant ^{13}C-^{19}F coupling to C-19 itself (see table). The magnitude of the latter suggests the presence of a through space effect, as proposed for the corresponding ^{1}H-^{19}F coupling. We are currently investigating this phenomenon further.

Sincerely,

H. L. Holland

HLH/jh

P.S. Please credit this contribution to the account of Dr. Jack M. Miller of our Department. Sorry for the delay; our spectrometer was down for a couple of days for installation of a new disc. Your pink letter came in the middle of the problems.

Table

	δ ppm							J(X-^{19}F)Hz				
Compound	C-3	C-4	C-5	C-6	C-17	C-18	C-19	C-4H	C-6H	C-19H	C-6	C-19
I	65.0	39.8	72.5	95.1	219.5	13.4	15.4	-	50	4.4	178	9.2
II	211.6	48.9	76.3	94.8	220.7	13.8	15.5	-	49	3.6	179	9.2
III	199.6	128.8	161.2	93.1	219.8	13.8	18.5	5	50	2.2	167	<1
IV	198.4	120.0	165.3	88.0	219.5	13.7	18.1	ca 1	49	0	185	0

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December 1, 1977

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

Solvent Effects on J_{C-Pb} and Lead-207 Chemical Shifts

Dear Barry:

Solvent effects on carbon-metal coupling constants and metal chemical shifts in organometallics have been observed for some time now and the variations are usually discussed in terms of weak complex formation between the organometallic and solvent. Correlations have also been observed between solvent induced changes in one-bond carbon-metal and two-bond proton-metal coupling constants for a given compound. During our studies of organolead compounds, we have found similar correlations that may be of interest to the readers.

Carbon-lead coupling constants for the propyl carbons and lead-207 chemical shifts for tripropyllead acetate in several solvents are given in the Table. Carbon chemical shifts are ($CHCl_3$) C_1=41.6,

Solvent	δ^a	$^1J^b$	^2J	^3J
$CHCl_3$	342.2	181.9	26.8	104.9
Aniline	313.5	198.9	34.4	103.8
MeOH	274.9	239.7	39.3	112.6
DMSO	179.4	273.4	39.2	104.9
Pyridine	177.4	257.6	40.9	109.5
HMPA	103.9	306.4	41.5	114.7

[a] In ppm downfield from external Bu_4Pb.
[b] In Hz.

C_2=21.6, C_3=18.7 and vary by ∿1 ppm for all the solvents examined. There is a general increase in all the coupling constants along with an increase in the shielding of lead. A linear correlation exists between ^1J and the lead shifts with r=0.97. However, similar correlations between ^2J or ^3J and the lead shifts are not as good and neither is there a good correlation between the changes in ^1J and the changes in ^2J or ^3J.

We believe that the fact that the carbon shifts do not change appreciably with solvent while the lead shifts and carbon-lead coupling constants show large changes indicates that the observed changes are due primarily to solvent induced changes at the lead atom. Furthermore, the correlation between ^{1}J and the lead shift indicates that the same factors are responsible for the changes in both parameters. The lack of correlations between the lead shift and ^{2}J and ^{3}J could be due to different coupling mechanisms for ^{2}J and ^{3}J compared to ^{3}J.

Sincerely,

Dick

Richard H. Cox
Associate Professor

References for organomercury compounds:

1. N.K. Wilson, R.D. Zehr and P.D. Ellis, J. Mag. Res., 21, 437 (1976); M.A. Sens, N.K. Wilson, P.D. Ellis and J.D. Odom, J. Mag. Res., 19, 323 (1975).

2. V.S. Petrosyan and J.D. Roberts, Org. Mag. Res., 9, (1977).

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

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

December 1, 1977

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

Dear Barry,

MAGNITUDE CALCULATIONS ON RESOLUTION ENHANCED SPECTRA

We have been interested in employing resolution enhancement techniques in our studies involving the proton nmr of proteins. Many different methods are available: (1) convolution difference (2) negative exponential multiplication (3) sinebell multiplication and (4) trapezoidal multiplication.

An unfortunate drawback of several of these techniques is the baseline distortions introduced by the data manipulation. We have found that for certain applications that a magnitude calculation removes the characteristic dips on each side of a resolution enhanced spectrum. Some of the increased resolution is lost and the lineshape distortion expected of a magnitude calculation is introduced. However, the spectra are more pleasing to the eye and this might aid in extraction of information in some instances.

The figure shows the methyl region of BPTI. Spectrum A is the normal spectrum. Spectrum B is the same data given a negative two hertz exponential multiplication before transformation. Baseline distortion is noted only on the doublet whose original linewidth was less than two hertz; i.e. distortion is introduced when the data manipulation tries to create a line with negative linewidth. Spectrum C is the same data with sinebell multiplication (3). Here dips around each peak are noted. Spectrum D is the sinebell multiplied spectrum after a magnitude calculation. The dips are removed and a spectrum which appears to be an enhanced resolution, broad component stripped copy of Spectrum A is obtained. Spectrum E is the spectrum in which the first 600 points have been multiplied by a trapezoid function (TM in the Nicolet 1180 and 1080 software) (4). This process is sometimes preferred to sinebell multiplication when it is necessary to adjust the amount of resolution enhancement to fit the spectrum. This is often required of protein spectra with lines broader than BPTI since sinebell multiplication removes too much data in these instances. Spectrum F is the same data as in spectrum E but after a magnitude calculation. Again the dips around the peaks are removed.

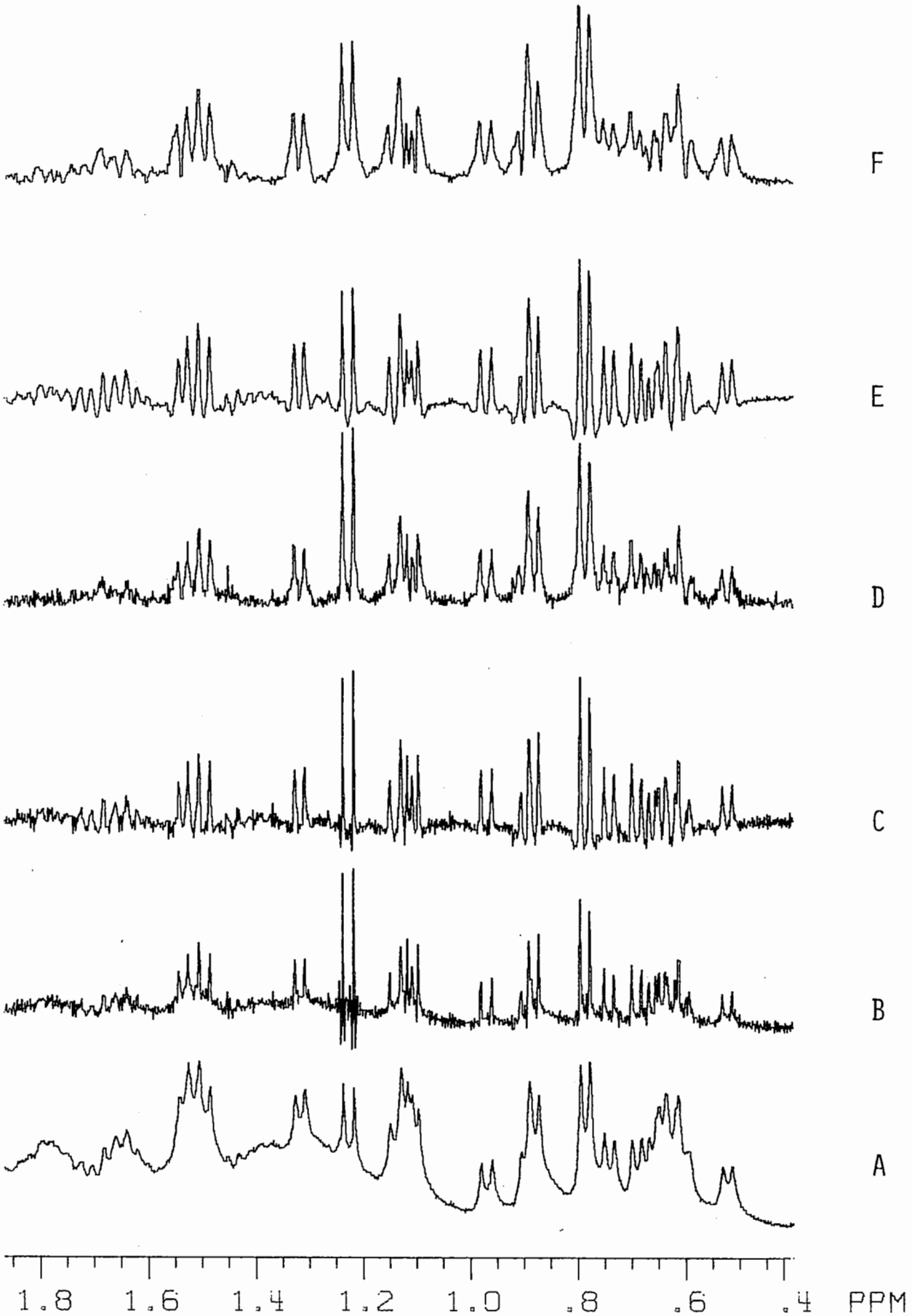
Aside from the fact that the spectra without the dips are easier to study there is another reason to remove the dips around peaks. If one were to apply successively greater TM to the data and integrate the spectral region of interest, extrapolation of this series back to TM = 0 can give a minimum indication of how much of the protein contains narrow lines.

Woody Conover Glenn Sullivan Oleg Jardetzky

Woody Conover Glenn Sullivan Oleg Jardetzky

1. I. D. Campbell, C. M. Dobson, R. J. P. Williams and A. V. Xavier, J. Magn. Res. 11, 172 (1973).
2. R. R. Ernst and W. A. Anderson, Rev. Sci. Instru. 43, 525 (1972).
3. A. DeMarco and K. Wuthrich, J. Magn. Res., 24, 201 (1976).
4. M. Gassner, O. Jardetzky and W. Conover, J. Magn. Res. submitted.

FIGURE 1: Methyl Region BPTI. A) Normal, B) Negative EM, C) Sinebell, D) Sinebell plus magnitude calculation, E) Trapezoidal, and F) Trapezoidal plus magnitude calculation.



232-17

PHYSICAL CHEMISTRY LABORATORY

OXFORD UNIVERSITY

Telephone
OXFORD
(0865–) 53322

SOUTH PARKS ROAD
OXFORD
OX1 3QZ

6 December 1977

Dear Barry,

"J-Scaling"

The time-honoured technique for assigning carbon-13 resonances by off-resonance coherent proton decoupling (1-3) is so simple and straightforward that we felt there just had to be a harder way to obtain the same result, possibly by way of some *magic pulse sequence*. Here is one possibility. Suppose we excite carbon-13 spins with an initial 90° pulse and follow their precession by measuring the signal S at the end of a variable *evolution period* t_b. A degree of confusion can be introduced by allowing free precession under proton-coupled conditions for a short time t_a, followed by proton noise decoupling for the remainder of the interval, $t_b - t_a$. (For reasons that are never properly explained, S is *observed* under coherent decoupling conditions.) The experiment is repeated many times with different settings of t_b, keeping t_a/t_b constant, and the carbon spins *think* they are coupled to protons with a coupling constant $J_{CH}\ t_a/t_b$ and pass on this false information in the form of an amplitude modulation of the signal:

$$S = S_o \cos(2\pi\delta t_b) \cos(\pi J t_a) \exp(-t_b/T_2^*)$$

for the case of one coupled proton; the expression is easily generalized. The Fourier transform subroutine, being entirely impartial, accepts this signal at face value and grinds out a spectrum with normal chemical shifts δ and linewidths $(T_2^*)^{-1}$ but grossly devalued proton-carbon splittings.

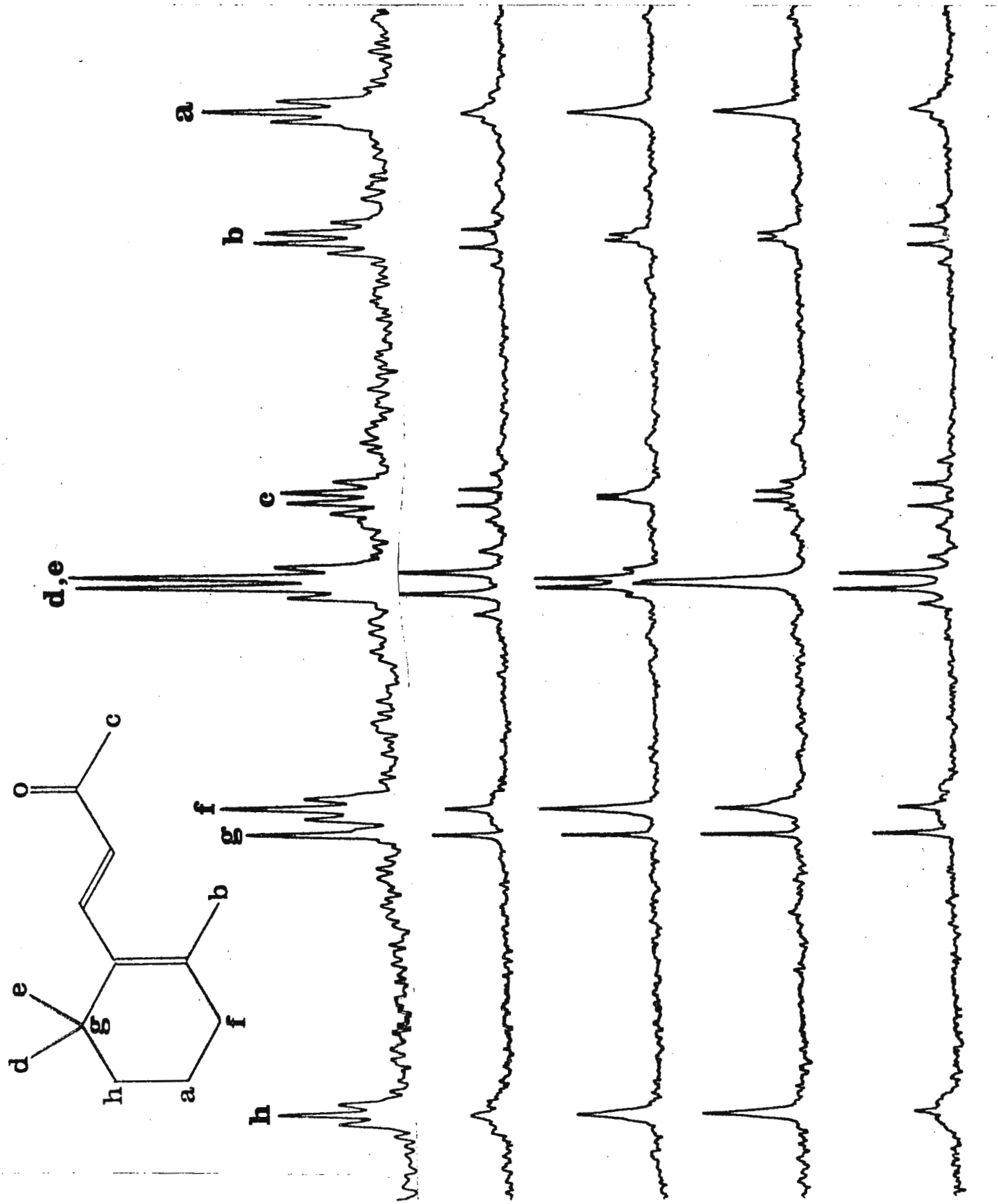
Ah, you say, but what about the lousy sensitivity when this "interferogram" is obtained one point at a time ? Well it turns out that this can all be restored to normal by yet another pulse sequence . . .

Figure 1 (top trace) shows the carbon-13 spectrum of β-ionone obtained with this recipe. Proton-carbon splittings are all scaled down by a factor of 30; consequently the long-range splittings "disappear" while the direct splittings are reduced to about 5 - 6 Hz. Imagine our consternation when we actually ran some coherent off-resonance decoupled spectra (four lowest traces) and found poorer results however we manipulated the decoupler offset. The explanation is well known to those who know these things -- the protons can be strongly coupled among themselves, and may become even more strongly coupled in the presence of the strong field H_2 (4). This is particularly noticeable for CH_2 groups which seldom show a very clear triplet structure; another problem is the anomalous broadening of the outer lines of triplets and quartets. A slightly garbled version of this story will appear in J. Magn. Resonance.

Ray Gareth Morris

Yours sincerely,
Ray Freeman and Gareth Morris.

1. Reich, Jautelat, Messe, Weigert & Roberts, J.A.C.S. 91, 7445 (1969).
2. LeRoy Johnson, Tenth Experimental NMR Conference, Pittsburgh, 1969.
3. Bremser, Hill and Freeman, Messtechnik (sic), 79, 14 (1971).
4. Wehrli and Wirthlin, *Interpretation of Carbon-13 NMR Spectra*, 1976.



SIMON FRASER UNIVERSITY, BURNABY, B.C., CANADA, V5A 1S6
DEPARTMENT OF CHEMISTRY; 291-3345

7th December 1977

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

^{31}P Magnetic Resonance Spectra of Human Aorta

Dear Barry,

We have been interested in studying several human membrane systems and report our preliminary NMR data on blood vessels. We have reconstituted the membranes from a fresh human aorta (55 year old female) in a sucrose/borate solution and present the ^{31}P spectra.

The top spectrum shows the spectrum for the lamellar suspension of the aortic membranes. One can contrast the spectrum with previous studies on phospholipid membranes (1,2). Two features stand out: first, the chemical shift tensor is smaller than previously found for homogeneous lecithin unsonicated dispersions; second, the sign of the chemical shift tensor is opposite that found for DPL liposomes and the same as that found for anhydrous DPL powder (1).

The middle spectrum follows a 10 minute sonication (11°C, N_2) of the membrane suspension. The linewidth reduces to 45 Hz indicative of small vesicles. Finally, the bottom spectrum results from EDTA treatment of the vesicles to remove ions from the solution ($\Delta\nu_{1/2}$ = 23 Hz).

Bruce J Forrest A.K. Grover Bob

B.J. Forrest A.K. Grover R.J. Cushley

1. A.C. McLaughlin et al., J. Magn. Reson. 20, 146 (1975).

2. S.J. Kohler and M.P. Klein, Biochemistry, 16, 519 (1977).

RJC:SLH
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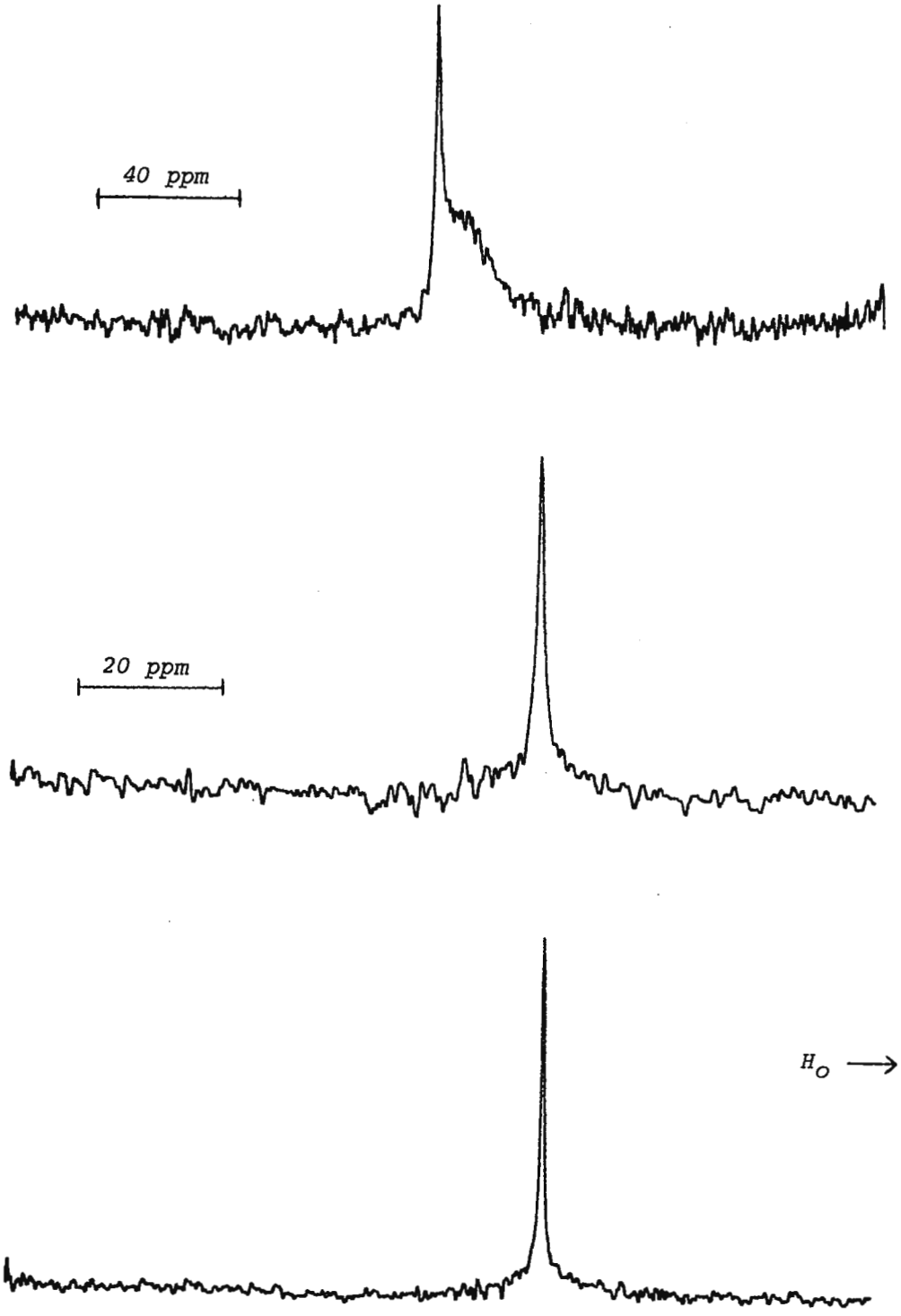
40 ppm
20 ppm
H_o ⟶

8th December 1977.

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

University of Salford
Salford M5 4WT

Department of Chemistry
and Applied Chemistry

Telephone 061-736 5843
Telex 668680 (Sulib)

Dear Barry,

A double-fitting procedure for 2-site exchange analysis

The main objective of using total lineshape analysis of systems undergoing chemical exchange is to extract the rate of exchange and hence investigate its variation with temperature. The pitfalls of such an analysis have been widely discussed and it is evident that in many cases the solution obtained may not be unique.

One problem is that the lineshape function contains terms of the type δ^2/τ, δ^2/T_2, $1/\tau T_2$ and consequently there may be some interdependence between the basic parameters. A second problem is that each of the basic parameters might be expected to have a dependence on temperature. Up to now the first problem has been ignored but some attempts to correct for the second have been made by assuming a linear temperature dependence of both T_2 and δ. Since it is normally assumed in NMR work that the correlation time varies with temperature as $\tau_c = \tau_o \exp(\Delta E/RT)$ and also that the lifetime $\tau = A \exp(-\Delta G/RT)$ it appeared to us that both of these problems might be resolved if a logarithmic approach was followed. Thus for the 5 different products encountered in a 2-site exchange problem we write

$$\ln(\delta^2/\tau) = K_1\ 1000/T + b_1 = A_1$$
$$\ln(\delta^2/T_{2A}) = K_2\ 1000/T + b_2 = A_2$$
$$\ln(\delta^2/T_{2B}) = K_3\ 1000/T + b_3 = A_3$$
$$\ln(1/\tau T_{2A}) = K_4\ 1000/T + b_4 = A_4$$
$$\ln(1/\tau T_{2B}) = K_5\ 1000/T + b_5 = A_5$$

The values of the A_i may then be determined at any temperature T from the results of the normal 'iterative' calculations. A linear regression analysis of the A_i determined over a range of temperatures then yields values for K_i and b_i. Using the latter values to define the functions at any particular temperature then allows the set of equations to be solved simultaneously for δ, τ, T_{2A} and T_{2B}.

We have applied this approach to the iterative total lineshape results earlier[1] obtained for N,N-dimethyltrichloroacetamide (DMTCA). In this example there is a very small temperature dependence of δ and a more pronounced one for T_{2A} and T_{2B} as is shown in the Figures.

It appears that the double-fitting procedure outlined here may indeed resolve some of the inherent difficulties of total lineshape calculations and we shall be looking further into this during VSD's sojourn here at Salford.

1. V.S. Dimitrov J. Mag. Resonance. 22(1976)71.

Yours sincerely,

Val Dim

Valentin Dimitrov

John Ladd.

John Ladd.

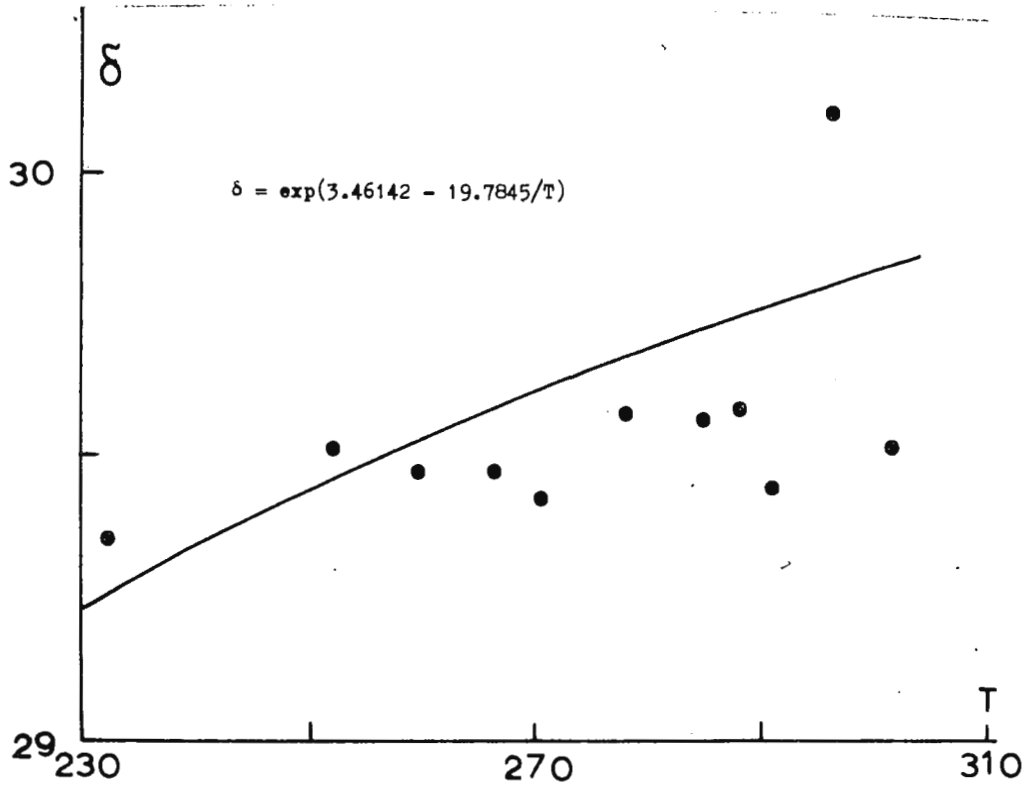

Fig. 1. Smoothed relation between δ and T. • - Total lineshape results.

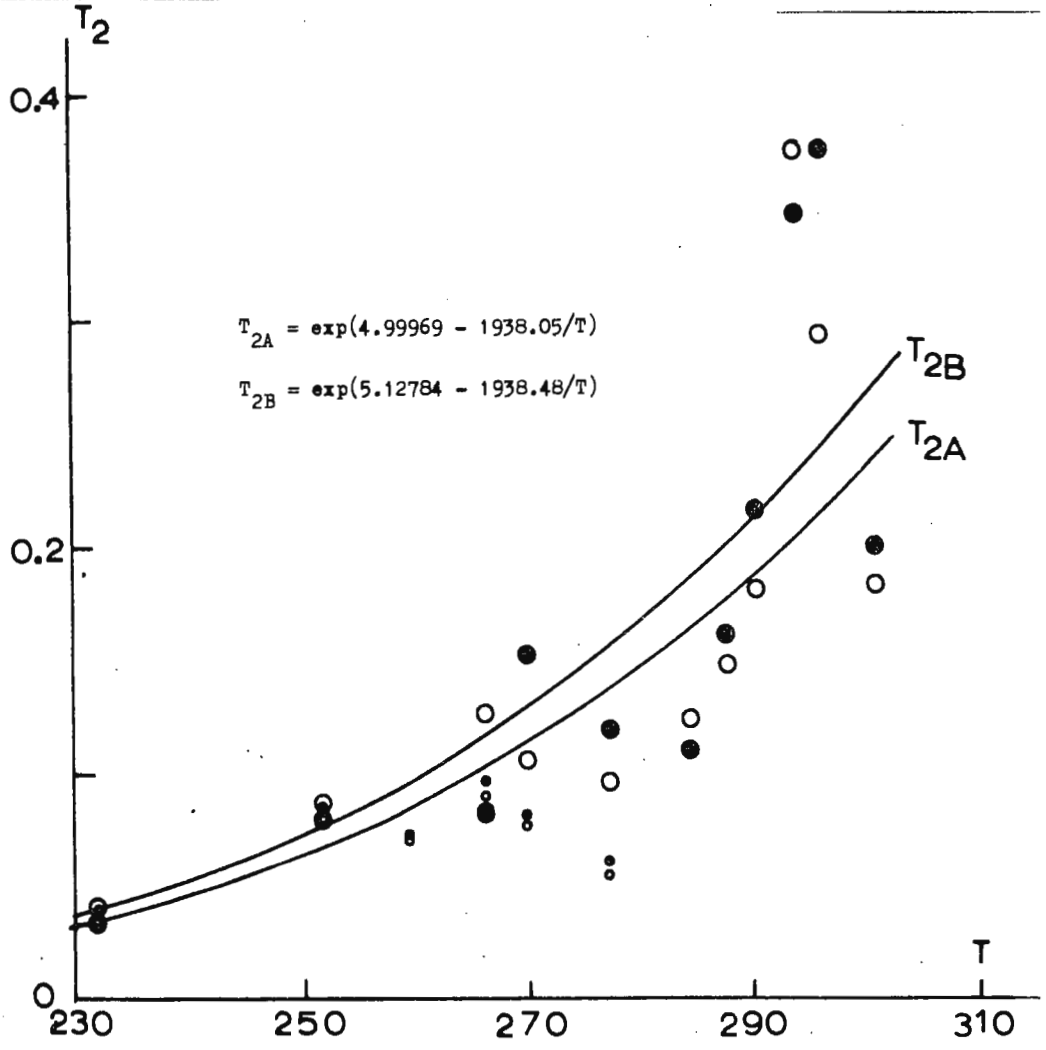

Fig. 2. Smoothed relations between T_{2A}, T_{2B} and T. O - T_2A and • - T_2B
Total lineshape results: smaller circles obtained from linewidth measurements

232-23

University of Wisconsin Madison

CENTER FOR HEALTH SCIENCES
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425 North Charter Street
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Telephone: 608/262-1416

December 28, 1977

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

Thiamine Pyrophosphate Conformation or What To Do With Your Minicomputer When Your Spectrometer Is Down

Dear Professor Shapiro:

I have recently completed a conformational analysis of thiamine pyrophosphate both in the presence and the absence of Mg^{++} via the phosphorus - proton NOE. The procedure I follow is to compute enhancements for given conformations or conformation distributions and to iterate this process until computed and experimental enhancements are congruent. For the system in question six dihedral angles must be varied and about 150 internuclear distances are computed for each different conformation. Enhancement calculations require the solution of eleven simultaneous equations (not all computed distances are used). This procedure can be programmed in BASIC for our Nicolet 1080 and about five minutes of computer time is required per test conformation. The time can be shortened by probably a factor of two by computing only those distances that are actually used in the enhancement calculations.

In the non-magnesium case the conformational distribution is about 55% the conformation in which the pyrophosphate side chain is folded over the thiazolium ring and when magnesium is present the portion of folded form increases to about 75%. I am preparing this work for publication and would be happy to provide preprints when they are available.

Sincerely yours,

Phillip A. Hart

Phillip A. Hart

PAH:jcz

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

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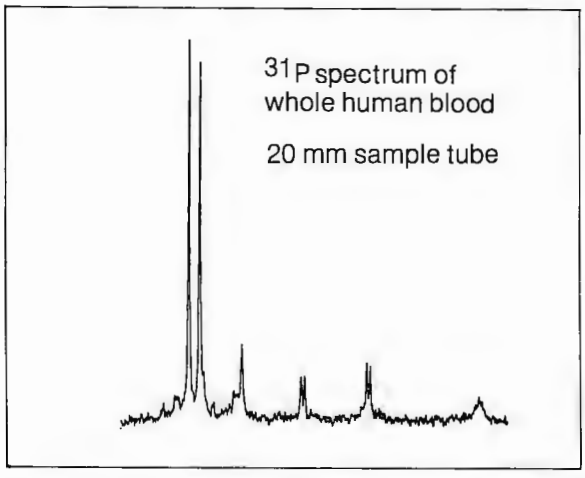

For more information or to discuss your applications, please telephone or write.

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RIJKSUNIVERSITEIT GENT

LABORATORIUM
voor
ORGANISCHE CHEMIE

B-9000 GENT, KRIJGSLAAN 271 - S 4 (België-Europa) Tel. 225715

December 8th, 1977

Prof. B.L. SHAPIRO
Department of Chemistry
Texas A&M University
College Station
TEXAS 77843 (U.S.A.)

Dear Professor Shapiro,

I would greatly appreciate if you could place the following announcement in the forthcoming issue of TAMU-NMR Newsletters.

FOR SALE :

VARIAN XL-100 12 inch wide gap NMR-spectrometer system (with extra 12 mm probe assembly) for ^{1}H(5 mm/CW,FT), ^{19}F (5 mm/CW), ^{2}H(10 mm/CW,FT) and ^{13}C(10 mm/FT), equipped with V-4421 gyrocode spin-decoupler, variable temperature unit, ^{14}N decoupling unit, SSB filter kit, 16K 620L (16 bit) computer and a cassette system "Sykes-Compu/corder 120".
The system is in excellent working condition since January 1974.
Anyone interested should write to :
Dr. F. Borremans, Laboratory of Organic Chemistry, State University of Gent, Krijgslaan 271 (S4bis), B-9000 GENT (Belgium).

Yours sincerely,

Prof. M. Anteunis.

UNIVERSITY OF BRISTOL

Telephone Bristol 24161 (Ext.)

SCHOOL OF CHEMISTRY
CANTOCK'S CLOSE
BRISTOL
BS8 1TS.

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

8th. December, 1977.

Dear Professor Shapiro,

Mercury-199 Chemical Shifts in Some Alkyl Mercury Halides

We have recently made $^{1}H-\{^{199}Hg\}$ INDOR measurements on some alkyl mercury halides with the hope of shedding some light on two intriguing features of the behaviour of $\delta(^{199}Hg)$ in dialkyl mercury compounds.

The ^{199}Hg shift in dimethyl mercury has a range of over 100 p.p.m. according to solvent, going to low frequency in the more polar media. This effect has been ascribed to coordination despite the well known reluctance of the metal in dimethyl mercury to increase its coordination. Since HgClMe is much readier to do so, we have measured its mercury shift in a comparable range of solvents. The results (Table 1) show that the overall range and ordering is similar for both compounds. There is

TABLE 1. Effect of Medium on $\delta(^{199}Hg)$

Medium	$HgMe_2$	HgClMe
Water	-	-885
Dimethyl sulphoxide	-108*	-853
Pyridine	-94*	-782
Acetonitrile	-78*	-862
Methanol	-	-856
Tetrahydrofuran	-76*	-861
Benzene	-50*	-813
Dichloromethane	-46	-814
Chloroform	-28*	-810
Hexane	+5*	
Dichloromethane + 1 equivalent $[NBu_4]Cl$	-46	-710

*From Sens et al., J.Magn.Resonance, 1975, 19, 328.

significant coordination of chloride ions to HgClMe in less polar solvents such as dichloromethane and this results in a shift to high frequency: the opposite direction to increasing polarity of the solvent. Whereas the low frequency shift of dimethyl mercury in pyridine is in keeping with the other polar solvents, HgClMe in this solvent has a particularly high frequency shift. It seems reasonable to assign the latter effect to true coordination of solvent molecules to mercury as pyridine is expected to be the best ligand out of these solvents. The natural conclusion is that the low frequency shifts of dimethyl mercury in the more polar solvents are due to some cause other than coordination (at least in the sense of chloride ions or pyridine to HgClMe).

Incidentally, it follows from the sensitivity of the mercury resonance of dimethyl mercury to the medium, that the reference shift of dimethyl mercury should refer to truly neat dimethyl mercury without any added material to provide an internal reference or lock. Using an external reference we get $\Xi(^{199}Hg)$ = 17 910 841 Hz

As early as 1959, Dessy et al. (J.Chem.Phys., 1959, 30, 1422) drew attention to the large changes in $\delta(^{199}Hg)$ to lower frequency that are produced when the hydrogens in dimethyl mercury are replaced by methyl groups ('β-effect'). For HgClR and HgBrR, the differences in $\delta(^{199}Hg)$ values are almost exactly half those for the related HgR_2 (see Table 2). The accuracy of this proportionality to the number of alkyl groups

TABLE 2 $\delta(^{199}Hg)$ for HgR_2, HgClR and HgBrR

R	HgR_2	HgClR	HgBrR
Me	-11*	-813	-915
Et	-307†	-978	-1070
Pr^i	-600†	-1128	-1202
Bu^t	-838	-1245	-
Pr^n	-213†	-947	-1039
Bu^n	-208†	-944	-1036
Ph	-745†	-1192	

*As in Table 1. †From Tupciauskas et al., J.Magn.Resonance, 1972, 7, 124.

present is surprising in view of the differences in the bonding that there must be between the two series. The smaller changes to high frequency that occur when the alkyl chain is extended from ethyl to n-propyl ('γ-effect') show a similar proportionality as do the differences between methyl and phenyl derivatives. The change from methyl to phenyl alters $\delta(^{199}Hg)$ in the same direction as increasing the number of β-carbon atoms. However properties such as the electronegativity of the organic moiety clearly change in opposite senses which makes explanations of the 'β-effect' difficult to find.

Yours sincerely,

Robin Goodfellow

R.J. Goodfellow

A few copies of the typescripts of two papers which contain details of this work are available.

232-29

Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

December 9, 1977

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

Dear Barry:

1) New Permanent B.S./M.S. NMR Position

2) Use of Microcomputers in the NMR Laboratory

1) We anticipate opening a new permanent staff position for a B.S. or M.S. having some laboratory instrumentation experience. Classified by the State of Florida as a Chemist II, the successful candidate will have responsibilities in our department nmr laboratory. Primary duties will be operation of our HX-270, HFX-90, and SEMINOLE spectrometers, and performance of routine and non-routine nmr spectroscopic service work. Other responsibilities include control of the nmr sample throughput and of the cryogenics (liquid He and N_2) for our supercon spectrometers, and some routine instrument maintenance. The Chemist II will work with Dick Rosanske, the director of the laboratory and of course with me, since I have overall responsibility as the Faculty member in charge of the laboratory.

The Chemist II will also be encouraged to interact with departmental research groups, leading to co-authoring of scientific publications.

The current annual salary range for this position is $12,653 to $16,871. Benefits include medical, vacation and non-contributory retirement plans.

I would appreciate if you would bring this position to the attention of prospective candidates. Interested parties should write to George Levy as soon as possible. We anticipate that the position will become available in February, 1978 although other starting dates may be arranged.

2) We are undertaking a new project to design a versatile Z-80 microcomputer-based hardware/software system to more fully utilize existing computers dedicated to commercial FT nmr spectrometer systems.

Our system design has several goals:

1. Maximum utilization of the existing minicomputer nmr software.

2. Effective "time sharing" of the minicomputer CPU to allow multiplexed data acquisition and processing capabilities on a Nicolet 1080 computer or other CPU not having hardware interrupt structure.

3. Production of inexpensive, portable spectral data files.

4. Minimum requirement for capital outlay.

We would like to hear of any efforts elsewhere along these lines!

Warmest regards,

Daniel Terpstra
Research Assistant

David Wright
Postdoctoral/
Systems Design

George C. Levy
Professor

Cont'd. from p. 31

As one might expect in such molecules, the various titratable groups interact to some extent. For example, the pK_a of $NH_2(1)$ is dependent upon whether $NH_2(3)$ is protonated or not (i.e., charged or uncharged). In addition, the chemical shift of any particular nucleus can be dependent upon the extent of protonation at more than one site. The latter problem is particularly troublesome in the ^{13}C spectra; and as a result, pK_a values derived from ^{13}C spectra are frequently very misleading. This problem is particularly acute in tricyclic aminoglycosides such as tobramycin. In our experience, ^{15}N spectra give much more reliable pK_a values.

Manuscripts reporting the details of these studies are presently in various stages of preparation.

Sincerely,

LILLY RESEARCH LABORATORIES

Douglas E. Dorman, Ph.D., Jonathan W. Paschal
Physical Chemistry Research

DED/JWP:vr

LILLY RESEARCH LABORATORIES

DIVISION OF ELI LILLY AND COMPANY • INDIANAPOLIS, INDIANA 46206 • TELEPHONE (317) 636-2211

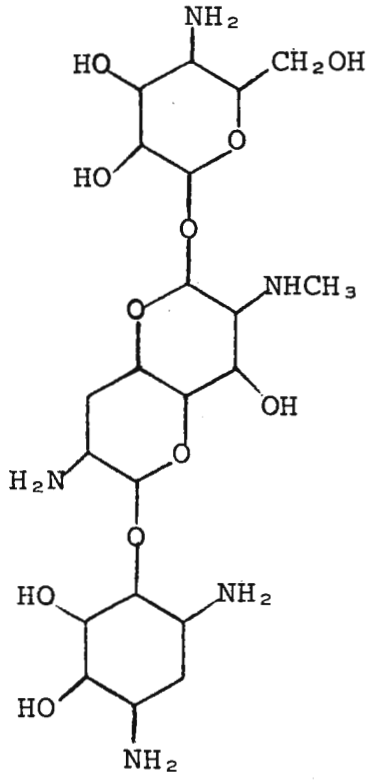
December 15, 1977

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

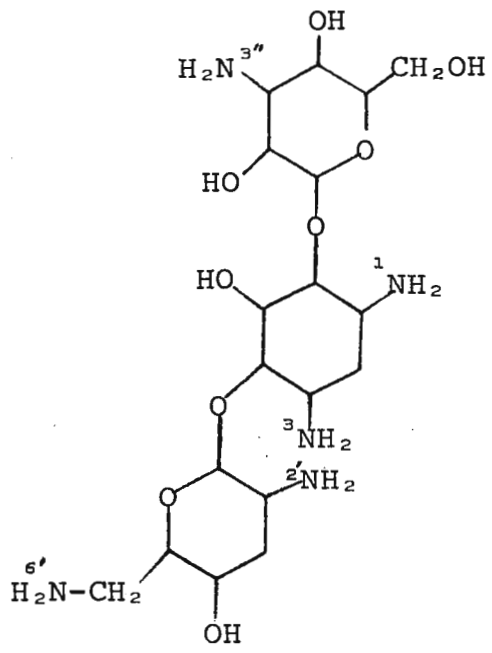
Dear Professor Shapiro:

pH-Dependent Spectra of Aminoglycosides

We have had a lot of fun continuing our investigation of the pH dependence of the ^{13}C and ^{15}N nmr spectra of aminoglycosides. These dependences have been used by many workers to determine the pK_a's of the individual amine groups of these antibiotics. We now have enough data to urge caution in such determinations.



Apramycin



Tobramycin

Cont'd. on bottom p. 30

TECHNISCHE HOGESCHOOL DELFT

Laboratorium voor Technische Natuurkunde

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

U.S.A

Uw kenmerk | Uw brief van | Ons kenmerk | Lorentzweg 1, Delft 8, telefoon (015) 133222 toestel: 786601

December 12, 1977

Onderwerp

On Line Disc Oriented Data Acquisition and Time Averaging.

Dear Professor Shapiro,

Our home-built 7 Tesla hr-n.m.r. spectrometer is equiped with a HP 21M20 minicomputer, and the fast HP7905 disc.
One third of the disc storage of 15 M byte is used for data acquisition and time averaging purposes.
The time averaging can either be done in single - (16 bits) or double precision (32 bits). This gives us the possibility to sample and time average up to a total of 2.5 M 16 bits words, or 1.25 M 32 bits words.

The time averaging, with the interactive usage of the disc storage, can be done on-line up to a sampling frequency of 45 kHz in double precision.
By this it is possible to sample spectra with a width of up to 22.5 kHz, without dynamic range or resolution limitations.
The principle of the data acquisition is discussed on the basis of fig. 1.
Data coming into the computer from the A.D.C. are divided into "A.D.C. blocks" with a number of points which fits in 68 millisec.
A number of A.D.C. blocks with in total 6K data is called a "full block".
During the last A.D.C. block of a full block, the double precision data which correspond with that full block (12K 16 bits words) are read from the disc into a buffer in the main memory. Parallel with reading we can add the first half of the full block to the just read double precision data with a microprogrammed subroutine.
During the first A.D.C.-block of the following full block, the second half of data is added, and parallel the double precision data are written back to disc.

Technische Hogeschool Delft

Geadresseerde: Prof. Shapiro | Ons kenmerk: | Datum: December 12, 1977 | Blad:

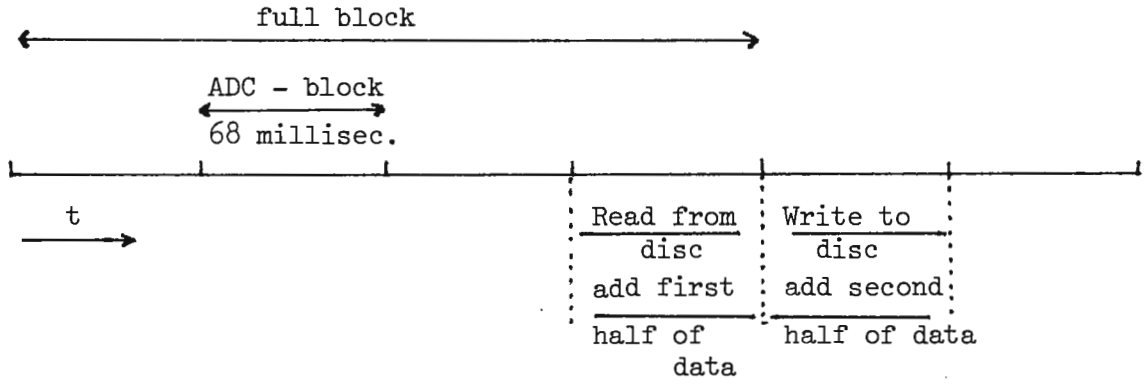


fig. 1 The basic principle of the data-acquisition and -reduction.

As is clear from the above the sampling frequency can be $\frac{6144}{68*10^{-3}*(2+N)}$, with N = 0,1,2,....., where $\frac{6144}{2+N}$ must be an integer.

In fig. 2 the C-13 spectrum of acetophenone (60 volume % deutereted aceton) is shown. The spectrum resulted from a fourier transformation of 128K data points, obtained from a FID experiment (sampling rate 45 kHz, acquisition time 2.1 sec.).
Fig. 2b is an enlargement of the aromatic region Ar of fig. 2a.
Fig. 2c is an enlargement of fig. 2b, containing a meta and ortho multiplet.

Yours sincerely,

Ir. A.F. Mehlkopf A. Bax.

Please credit this contribution to Prof. J. Smidt.

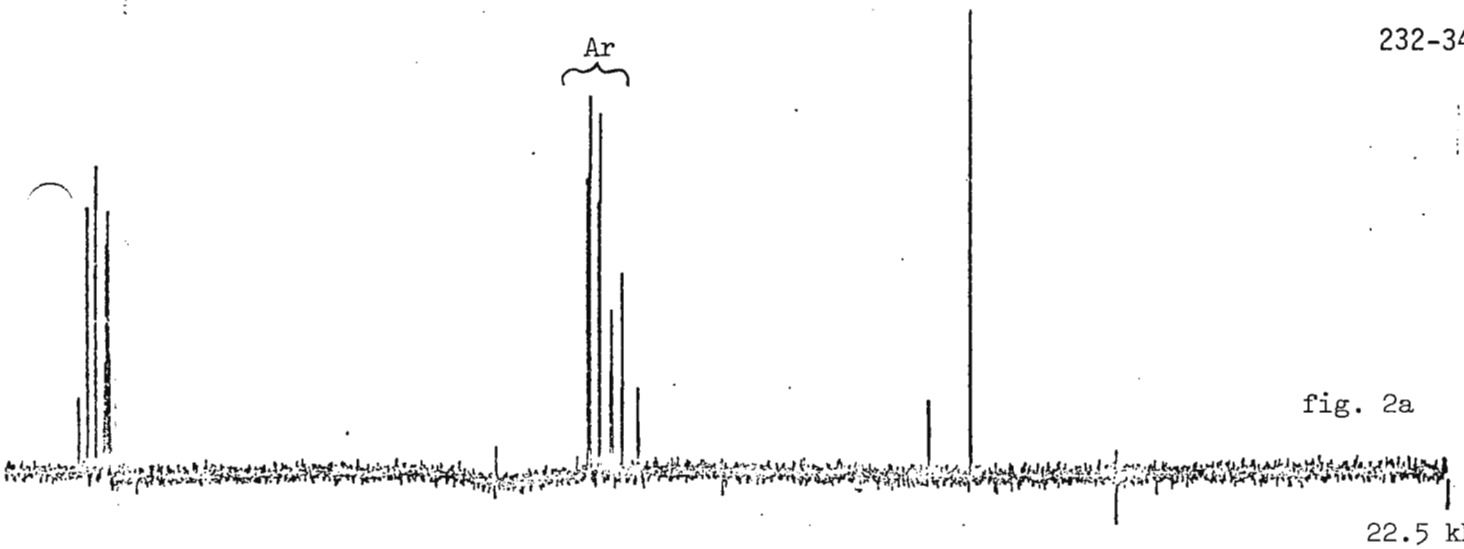


fig. 2a

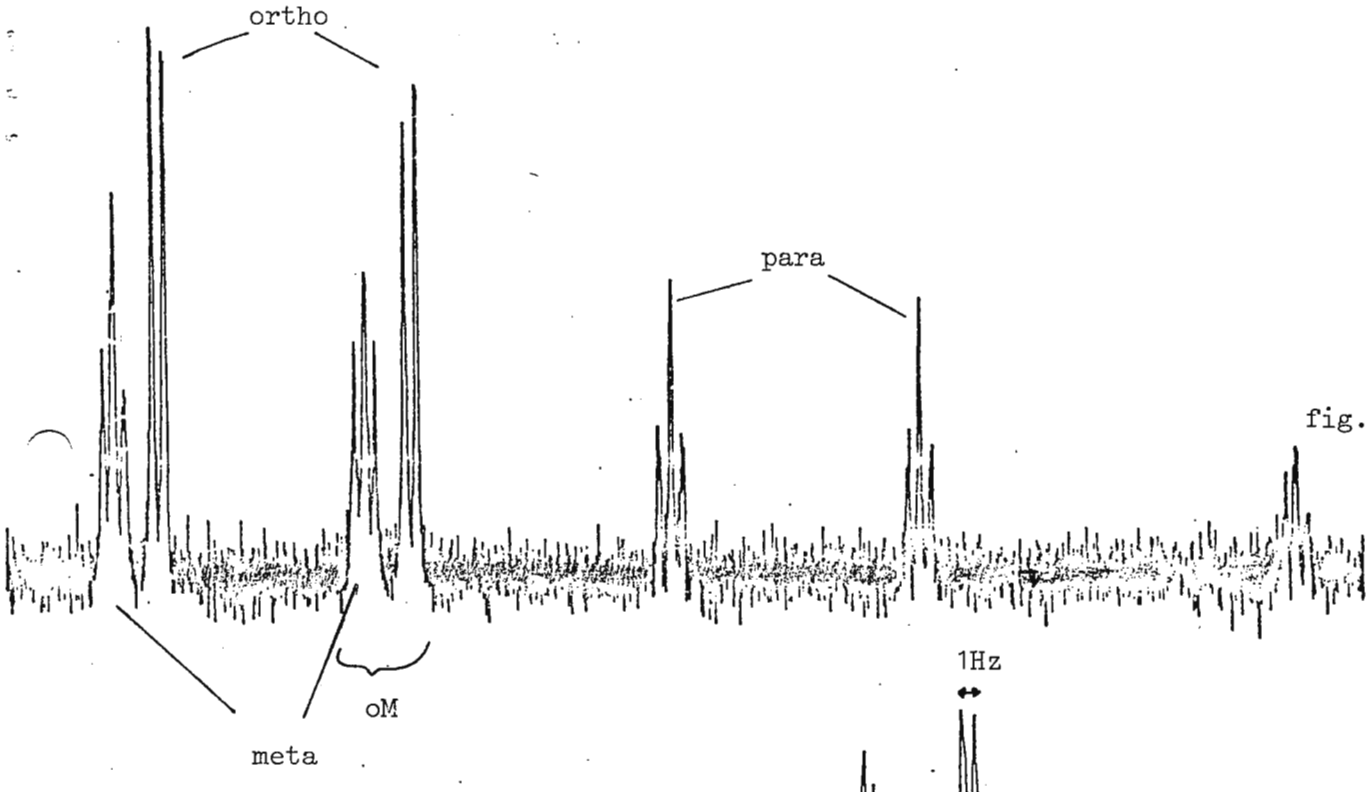


fig. 2b

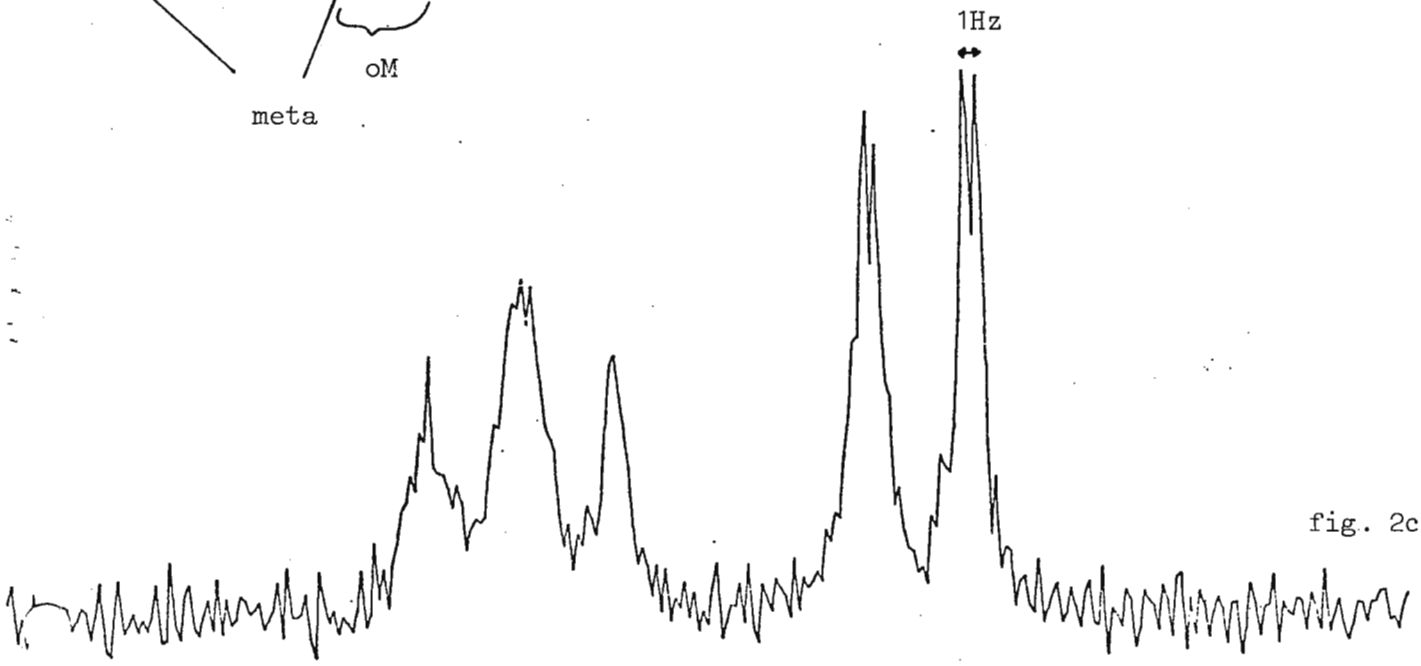


fig. 2c

232-35

מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE
REHOVOT · ISRAEL רחובות · ישראל

ISOTOPE DEPARTMENT מחלקת איזוטופים

December 15, 1977

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

Dear Prof. Shapiro:

We have recently become interested in the application of NMR of alkali and alkaline earth metals to study ion transport through vesicular membranes. The difficulty here lies in the similarity of the chemical shift and relaxation rate of the nuclei inside and outside the vesicular media. To discriminate between the resonances in the two compartments, we made use of the negatively charged relaxation agent $Gd(EDTA)^-$. Trace A in Fig. 1 shows the ^{23}Na signal in a phosphatidylcholine vesicular suspension containing sodium ions. Trace B in this figure is obtained after adding a small amount of $Gd(EDTA)^-$ to the solution. There is a pronounced broadening of the sodium resonance but no separate signal due to the less abundant sodium ions within the vesicular compartment can be seen. To bring out this weak signal, we employed a $180°$-τ-$90°$ pulse sequence with $\tau \sim T_1^{ex} \ln 2$ where T_1^{ex} is the T_1 of the extra-vesicular sodium ions (in the presence of the relaxation agent). In this way we minimized the signal of the outer sodium and could accumulate sufficient FID traces following the $90°$ pulses to render the inner sodium visible. Its signal after fourier transformation is depicted in trace A of Fig. 2. The other traces in this figure show the effect of adding increasing amounts of the sodium ionophore monensin. There is a clear broadening of the signal which is interpreted in terms of enhancement of the rate of transport across the membrane. We are currently studying the mechanism of this transport process for other alkali as well as alkaline earth ions.

Sincerely yours,

Hadassa Degani

Hadassa Degani

Gabriel A. Elgavish

M.B. Please credit this letter to Dr. R. Poupko's account.

HD/sn

CABLE ADDRESS: WEIZINST (Israel) מען למברקים: PHONE: 951721 טלפון: TELEX: 31934 טלקס:

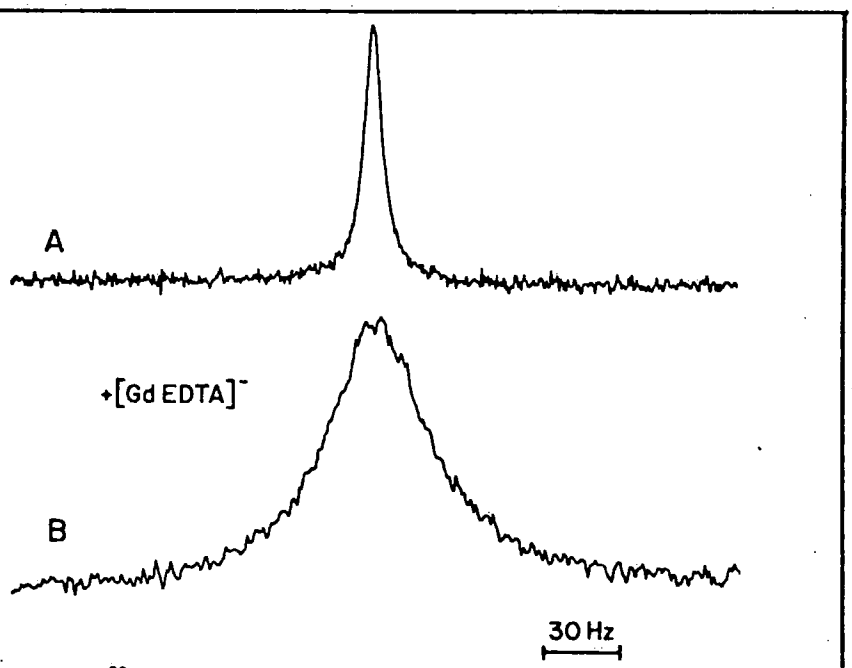


FIG. 1 (A). ^{23}Na NMR SIGNAL IN A SUSPENSION OF 10% EGG LECITHIN VESICLES (PREPARED BY SONICATION) CONTAINING 150 mM NaCl AT p^2H 9.4 AND 28°C; (B). SAME AS (A) AFTER ADDITION OF 11.6 mM Gd(EDTA)⁻.

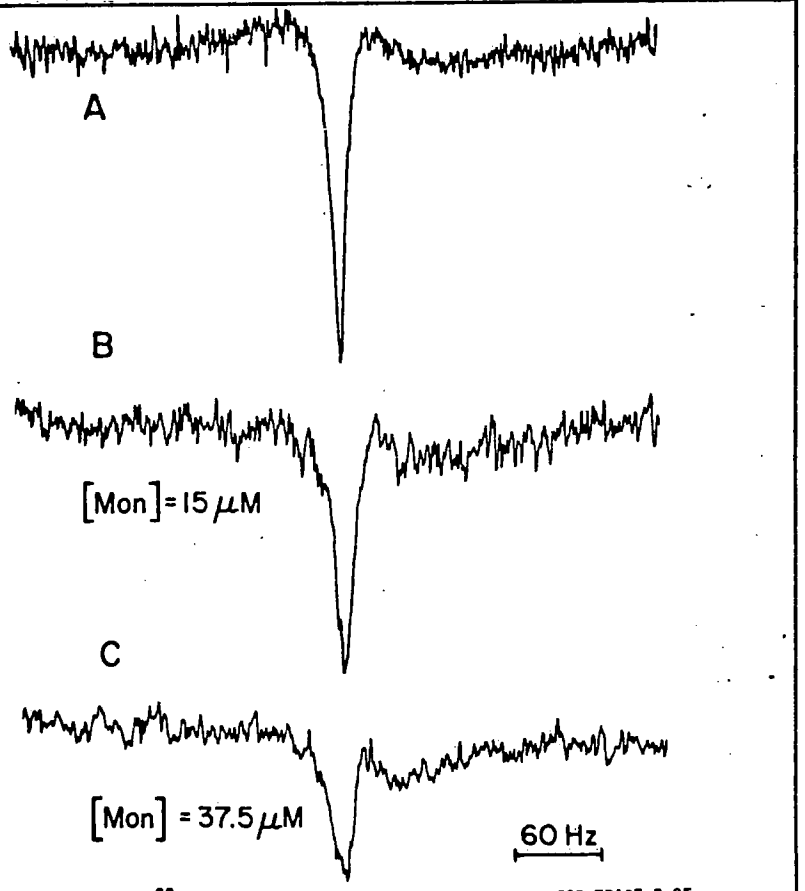


FIG. 2 (A). THE ^{23}Na SIGNAL IN THE SAME SOLUTION AS USED FOR TRACE B OF FIG. 1 USING THE 180°-τ-90° SEQUENCE (τ=4 MSEC, 7500 TRANSIENTS). (B) AND (C) SAME AS (A) AFTER ADDING THE INDICATED AMOUNTS OF MONENSIN.

232-37

NAVAL RESEARCH LABORATORY
WASHINGTON, D.C. 20375

IN REPLY REFER TO:
6110-1004:RDB:hlw

20 December 1977

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

Dear Barry:

Title: Spin Locking Protons Using Nicolet Technology Corporation Software with the Nicolet 1180 and 293A Pulse Programmer.

We have been reconfiguring our home-built FT NMR spectrometer in order to carry out proton spin locking experiments in liquids. Our data system consists of a Nicolet 1180 with a Nicolet 293A Pulse Programmer. The necessary proton channel RF phases are generated as follows: The 100 MHz RF signal is split by a quadrature power splitter, giving two signals with a 90° phase difference. Each of these signals is further split by a 180° power splitter. The resulting signals are passed through double balanced mixers used as attenuators and combined using power splitters/combiners. The appropriate attenuator is turned on by decoding the 293A output levels 0,1,2 and 5 and using current drivers to supply current to the IF part of the mixers. Amplitude balance for the four phases is achieved by adjusting the current with variable resistors. Exact phase balance is achieved with variable capacitors at the inputs of the various phase splitters. These adjustments are facilitated with a vector voltmeter, such as the Hewlett-Packard Model 8405A.

The RF phase selection procedure of the data system requires between 90 and 100 μs, whereas our hardware is capable of resetting phase in about 2 μs. One problem came to light while attempting to use the Nicolet Technology Corporation software to program the pulse sequence we required. According to the NTC software instruction manual two intervals in a pulse sequence which generate interrupts cannot be adjacent. It also happens that an interrupt is generated in the interval prior to a pulse to set its phase. This means if we wait for the phase change to occur between 2 pulses, a 100 μs delay

would be required between the pulses. We have discovered, however, that if these rules are ignored in a suitable way, phase changes can be made to occur when we want them (within ±2 μs) provided the total pulse length in the inital RF phase is greater than about 100 μs. Using the NX command in the NTCFT program allows writing a program for a tailored pulse sequence. The following program works for proton spin locking experiments on liquids where the 90° flip requires >100 μs.

```
#1   P1/0,S
#2   P2/0
#3   P3/1
#4   A
#5   D2,A
#6   D5,X
```

By setting the P1 equal to 0.032 μs, the P2 equal to 20 μs and P3 equal to a spin locking time of a few ms, a 90° phase change in the RF will occur 90 μs into P3. The length of the RF pulse with 0° phase will thus be 110 μs. A "glitch" in the RF is observed at the end of P2 and when the phase change takes place, but for liquids on our spectrometer this has not been a problem.

Please credit this contribution to the subscription of Bill Moniz.

Sincerely yours,

Richard D. Bertrand

Richard D. Bertrand
Polymer Diagnostics Section
Code 6110
Chemistry Division

232-39

Department of Industry
LABORATORY OF THE GOVERNMENT CHEMIST
Cornwall House Stamford Street London SE1 9NQ UK
Telegrams Govchem London
Telephone 01-928 7900 ext 649

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

Your reference

Our reference

Date 21 December 1977

Dear Professor Shapiro, re Locking Capillaries

We have been examining a wide range of highly viscous samples by FTNMR spectroscopy including lumps of food, swollen polymers and (intentionally) viscous materials. In the latter category, we include samples run at controlled viscosity for the purpose of sensitivity enhancement through reduction of T_1[1,2]. With field-frequency lock on deuterium in the sample and use of the deuterium signal for resolution shimming, C-13 or P-31 FTNMR spectroscopic performance was degraded. With viscous materials, C-13 and P-31 resolution (and thus signal-noise ratio) often is not so much limited by sample environment as by the deuterium lock hunting. Therefore, we obtained the locking signal from non-viscous deuterated materials in coaxial capillaries. We found that it was essential to match the polarity and magnetic susceptibility of the deuterated material with the sample, and this led to construction of a series of colour-coded capillaries (Table).

These capillaries were constructed from borosillicate glass of wider diameter than commercial NMR capillaries so as to give greater lock signal-noise ratio, and also to give sufficient strength for them to be pushed forcefully through rubbery materials. The hook (see Figure) allows easy removal and the lower coaxial spacer also serves as a convenient vortex suppresser. This range of capillaries also permits high temperature operation, and prevents contamination of samples. For P-31 FTNMR work, tetrasodium cyclo-tetraphosphate[3] gives a convenient up-field reference point clear of almost all phosphate signals and can give direct P-31 shimming of the sample by observation of the free induction decay. We have also obtained direct C-13 shimming by observation of 1-(C-13) sodium acetate in D_2O in a capillary; this has the advantage of a long T_1 that suppresses the otherwise strong signal during rapid pulsing of viscous samples.

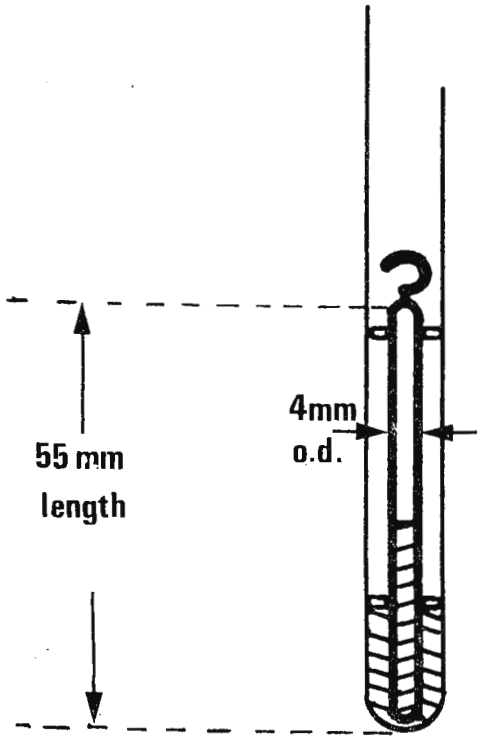
Yours

Ian O'Neill Brian Stuart

1 M L Jozefowicz, I K O'Neill and H J Prosser, Anal Chem, 49, 1140 (1977).
2 I K O'Neill et al, presented at 3rd European EENC Denmark 1977.
3 I K O'Neill and M A Pringuer, Anal Chem, 49, 588 (1977).

TABLE Contents of locking capillaries

Deuterated material	Dye	Colour	Intended sample range
Benzene-D_6	Oil yellow	gold	aromatics
Napthalene-D_8	none	white crystals	high temp. aromatics
Bromobenzene -D_5	Hansa	yellow-green	high temp. halogenated aromatics, esp dichlorobenzene
Dimethylsulfoxide -D_6	Xylene red	fluorescent pink	polar organics
Ethylene glycol-D_6	Turquoise blue G8	Turquoise	high temp. polar organics
D_2O	none	colourless	aqueous(neutral)
IM NaOD/D_2O	Ponceau red 6R	blood red	aqueous (alkaline)
IM DCl/D_2O	Indigo carmine	dark blue	aqueous acid hydrolysates(1)
IM H_3PO_4/D_2O	Rosaniline hydrochloride	flesh pink	aqueous acid, P-31 work
0.2M c-$(NaPO_3)_4$ /D_2O	Ponceau red 6R + Indigo carmine	purple	aqueous P-31 work; muscle reference



232-41

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Recherche Océanographique

Professor B. L. SHAPIRO

Department of Chemistry
Texas A & M University

COLLEGE STATION Tex. 77843 USA

N/ Ref 77 12 782 CB/MCH

V/ Ref

Wissembourg le 21.12.1977

More (?) on Ethyl Benzene

Dear Prof. Shapiro,

This short note is dealing with rather trivial a matter as Ethyl Benzene is concerned.

As everybody knows, this compound is widely used as test sample for ^1H sensitivity test. I would like to stress also a resolution test via the ethyl moiety, i.e. the appearance of second order splittings when focusing on the methyl resonance.

Under hight resolution conditions, the methyl group triplet does appear as shown in the attached figure (spectrum a), ran on a WH 90.

This pattern is not due to a fancy computer behaviour during F.T. calculations as one can judge from the corresponding computed spectrum (spectrum b) taking into account the well known (δ, J) parameters for ethyl benzene CH_2 - CH_3 group - (A_2B_3 system).

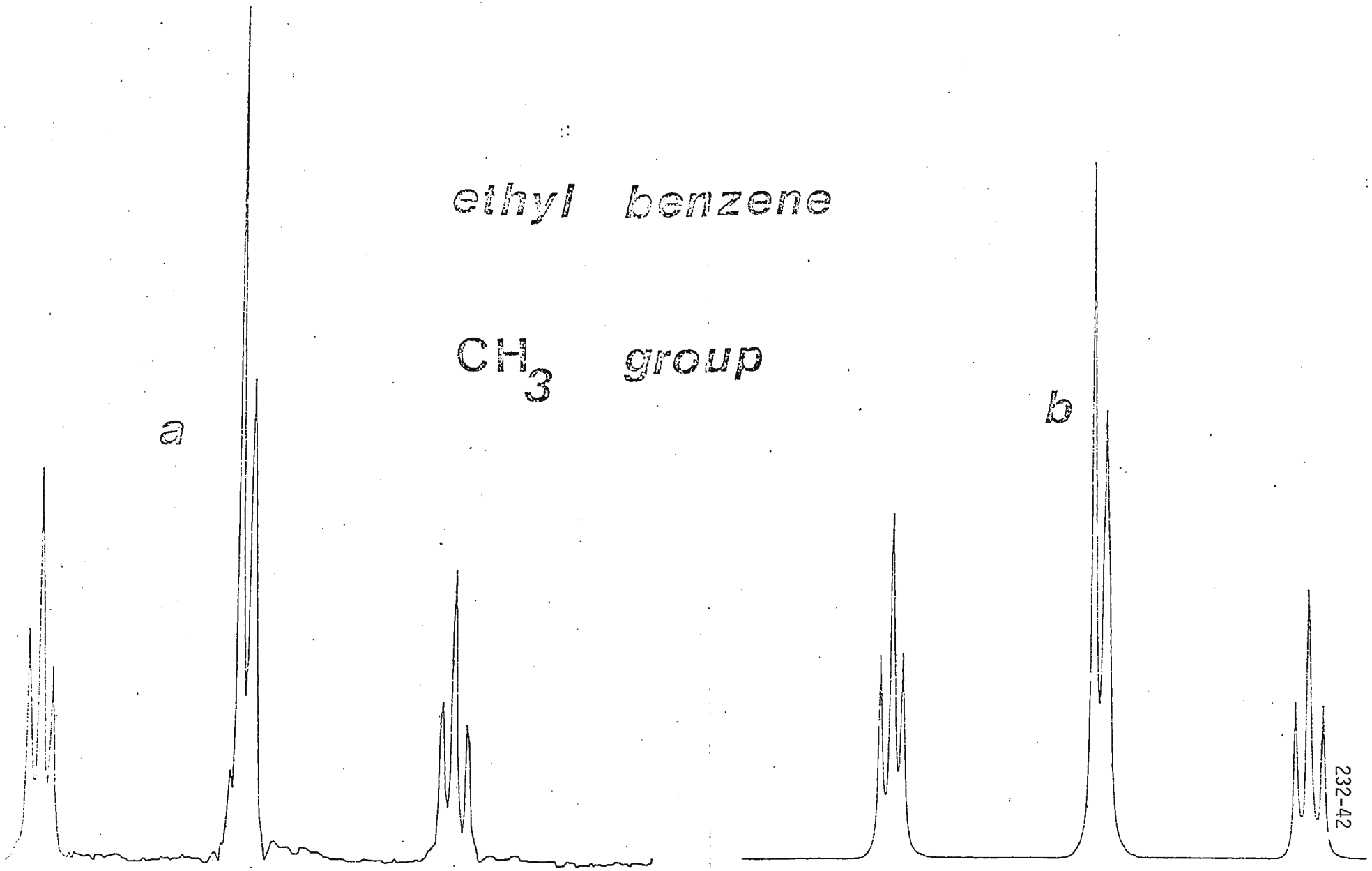
On the other hand, a few exemplars of the proceedings from the last seminar we organized in Wissembourg on "exotic" nuclei are still available. I shal be happy to forward a copy to anyone interrested in.

Sincerely yours,

C. BREVARD

ethyl benzene

CH_3 group



232-43

UNIVERSITY OF STOCKHOLM
ARRHENIUS LABORATORY
Physical Chemistry

29 December 1977

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

Title: Determination of NOE Factors Using the Dynamic Overhauser Enhancement Technique Combined with a Non-Linear Least Squares Fitting Procedure

Dear Dr Shapiro,

One of the projects at our laboratory involves ^{13}C T_1 studies of the internal motion of methyl groups. This requires accurate determination of the dipolar relaxation times, T_1^{dd}, which implies measurements of both the total spin-lattice relaxation times, T_1, and the nuclear Overhauser enhancement (NOE) factors, $1 + \eta$. In the course of this work, we have found that the precision of T_1 determination, using the fast inversion recovery method, was in general much better than the precision in the conventional gated decoupling measurements of the NOE factors. Therefore, we have become very interested in developing an improved technique for accurate NOE measurements.

In our search for such a technique we have turned to the dynamic NOE (DNOE) experiments, which allow following the signal intensity as a function of the time τ during which the NOE is being built up. The basic sequence of the technique is $(PD\text{-}\ \tau\text{-}90^{o}\text{-}AT)_n$. During the delay time $PD \simeq 10T_1$ the decoupler is switched off and the spin system is allowed to equilibrate. During the remaining part of the sequence the decoupler is switched on and the NOE build-up during τ is monitored by the analytical 90^{o} pulse. The signal intensity as a function of τ, $S(\tau)$ may be written

$$S(\tau) = S(0)[\eta + 1 - \eta\exp(-\tau/T_1)] \qquad (1)$$

If sufficiently many $S(\tau)$ values are measured, eq.(1) may be used to obtain $S(0)$, η and T_1 by means of a non-linear least squares fitting procedure. Further, if T_1 is known from an independent experiment, a two parameter ($S(0)$ and η) fitting procedure may be used. The DNOE technique, used together with this type of procedure for data analysis, has several important advantages compared to repeated conven-

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tional measurements of $S(0)$ and $S(\infty)$. First, the length of the longest τ is not of critical importance. Second, most of the $S(\tau)$ values measured contribute to the determination of both $S(0)$ and $S(\infty)$. Third, the probable error in determination of η may conveniently be defined by any standard criterion of the non-linear regression method.

We have applied this technique for the NOE measurements for a variety of test cases and as a practical tool in our internal motion project. The results have in general been very satisfactory. All the measurements have been carried out using a Varian XL 100 spectrometer. The series of measurements with variable τ have been performed in automatic mode using standard Varian disk system software. For the case of ^{13}C resonances, our experience shows that the DNOE technique for determination of T_1 is clearly inferior to the fast inversion recovery (FIRFT) method (it is much more time consuming and gives a smaller dynamic range) and that the η value determined from the two-parameter fitting of eq.(1) is not very sensitive to the choice of T_1. For dilute solutions, we have therefore found it practical to perform a FIRFT experiment for T_1 first and than to use this value in evaluating the DNOE experiment for η.

Predominantly dipolarly relaxed ^{15}N and ^{29}Si nuclei provide a rather spectacular case where application of simultaneous measurement of η and T_1 using the DNOE pulse sequence and least-squares fitting of eq.(1) may be practical. Here, the NOE factor is large and negative, which means that the dynamic range (and consequently, precision) of the DNOE and FIRFT experiments become similar. We have verified this statement experimentally by performing measurements on the ^{15}N signal in ^{15}N-enriched aniline. For the same number of transients, the standard deviations in the T_1 obtained by both methods were the same. The fact that the DNOE experiment is more time consuming is a disadvantage, but it is at least partly offset by the advantage of obtaining both the values necessary for calculation of T_1^{dd} in a single experiment.

Yours sincerely

Jozef Kowalewski Anders Ericsson

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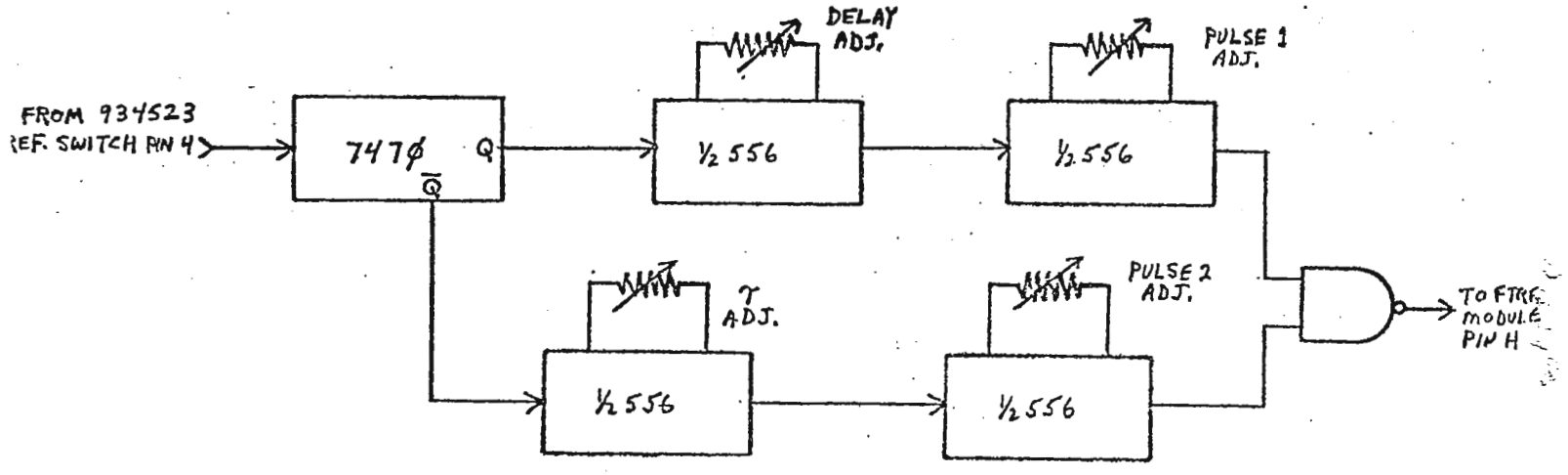
December 9, 1977

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

Modification of XL-100 for T_1 Measurements Without FT

Dear Barry:

The transmitter pulse timing on the XL-100 is normally under software control and thus cannot be continuously varied while one is observing the FID on the scope. One disadvantage of this is that for measurement of water T_1 relaxation rates, which can be obtained precisely from the null point in the 180°-τ-90° pulse sequence without Fourier transformation changes in pulse widths and τ-intervals must be repeatedly entered via the teletype in discrete values. We have developed an alternative to this time consuming approach with a simple two-pulse sequencer which provides continuous independent external control of pulse widths and delays. The device contains five inexpensive integrated circuits and several passive discrete components. The circuit is mounted on a Vector-board and housed in a Vector-Pak box which is mounted to the blank panel above the FT control module. A simplified logic diagram is shown below. Details of the circuit will be supplied upon request.



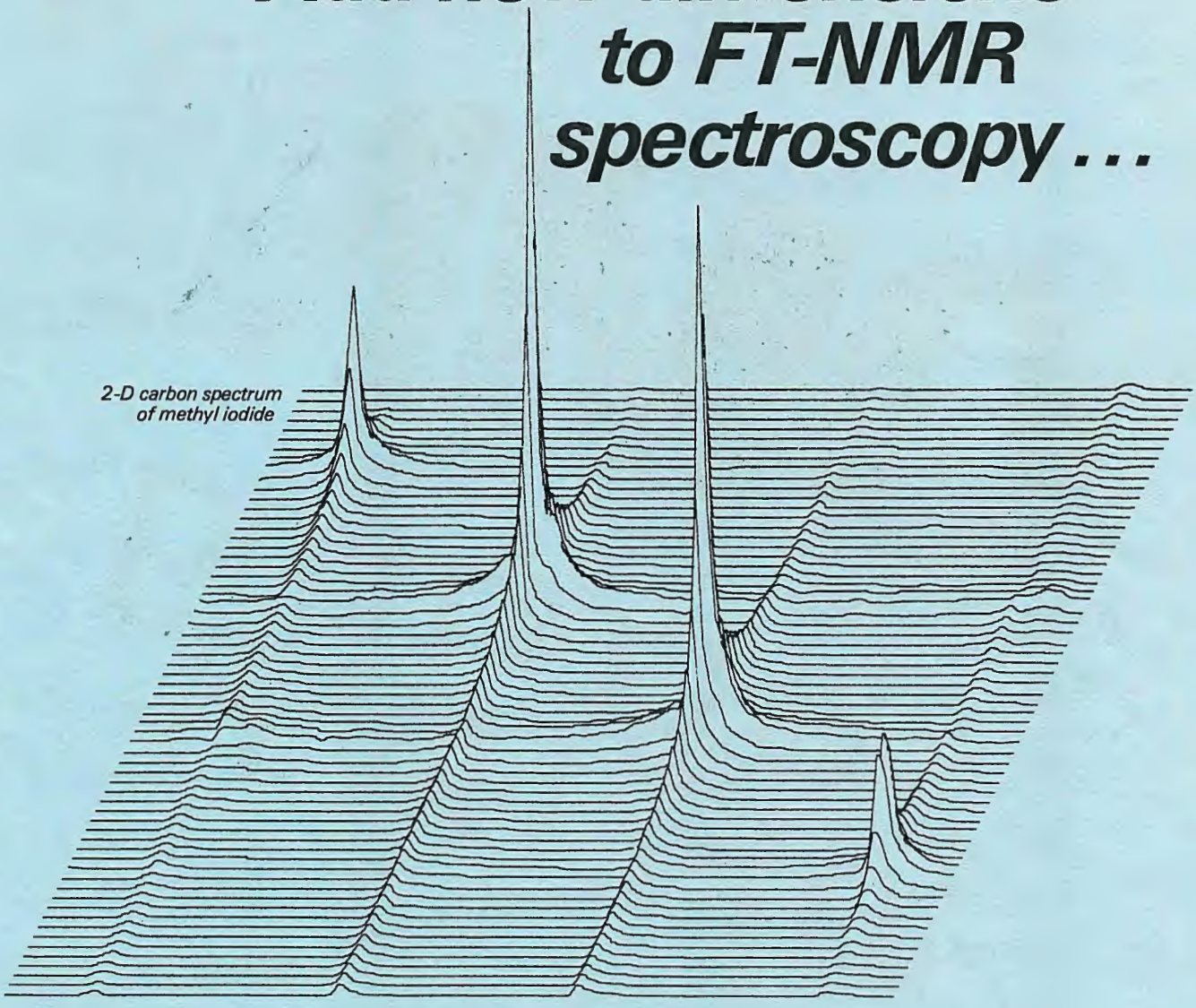
Sincerely yours,

Sol Alstein

SA/sm

Please credit this contribution to Al Mildvan's account

Add new dimensions to FT-NMR spectroscopy . . .



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