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Newsletter

No. 196

January, 1975

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Deadline Dates: No. 197: 7 February 1974
 No. 198: 3 March 1974

All Newsletter Correspondence, Etc. Should Be Addressed To:

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

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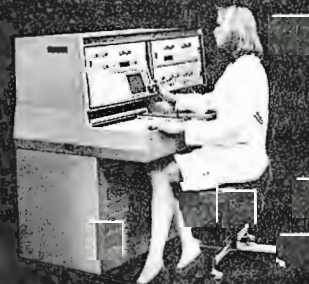
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Professeur R. FREYMANN

Paris, le 7 NOVEMBRE 1974

Professeur Bernard L. SHAPIRO
 Department of Chemistry
 Texas A and M University
 College Station

TEXAS 77843

RF/GK-74/192

Cher Professeur SHAPIRO,

Dans le cadre d'une étude spectroscopique portant sur des cycloalcanes et des hétérocycles saturés comprenant de trois à six chaînons (1) (2), nous avons étudié, par R.M.N., les actions intermoléculaires de ces composés : a) sur les protons du Tétraméthylsilane ; b) sur les protons de leurs groupements α -CH₂.

Les résultats obtenus, rassemblés Tableaux I et II et illustrés par les Figures 1 et 2 ($\Delta\delta$ exprimé en p.p.m.), indiquent que les composés étudiés - sauf (CH₂)₅O et (CH₂)₂NH - ont des effets pratiquement identiques sur les protons du T.M.S. et sur les protons des groupements α -CH₂.

Dans le cas des cycloalcanes, on observe un "effet de cycle" maximum $\Delta\delta = +0,3$ p.p.m. pour C₃H₆, valeur qu'il est intéressant de rapprocher de $\Delta\delta$ (T.M.S.) = +0,5 p.p.m. mesurée pour C₆H₆ dans les mêmes conditions expérimentales.

Les graphiques relatifs aux éthers cycliques et aux cycloalcanes, présentent la même allure, bien que les valeurs $\Delta\delta$ ne soient pas identiques. Il n'en est pas de même dans le cas des sulfures et des amines.

Ces résultats montrent également que les caractéristiques électroniques d'un cycle sont modifiées par la présence de liaisons intermoléculaires (ex. liaison Hydrogène), et mettent en évidence, par rapport aux cycloalcanes, l'existence d'une action intermoléculaire propre à l'hétéroatome.

Croyez, Cher Professeur SHAPIRO, en mes sentiments très cordiaux.


 R. FREYMANN


 J. LE BRUMANT


 M. SELIM

Références.

- (1) J. LE BRUMANT, R. FREYMANN, M. SELIM
- (2) J. LE BRUMANT, Thèse PARIS (1974)
- (3) E. LIPPERT, H. PRIGGE Ber.Buns.Phys.Chem. 67, 415 (1963)
- (4) H. SAITO et Coll., J.A.C.S 89, 6605 (1967)

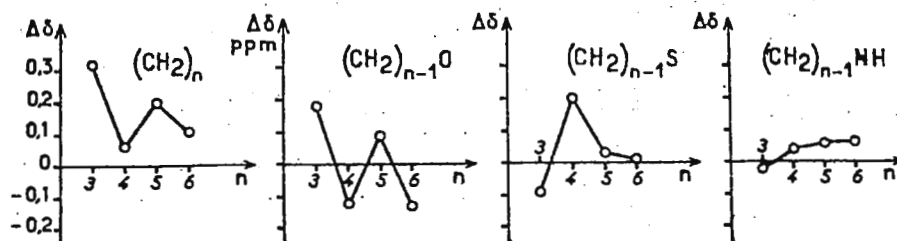


Fig. 1. — Action sur le TMS.

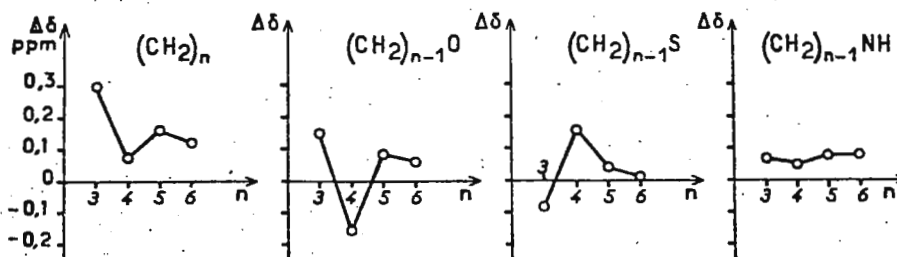
Fig. 2. — Action sur α -CH₂.

TABLEAU I
Action sur le TMS

δ (α -CH ₂)	TMS	TMS ext.			δ (α -CH ₂)	TMS	TMS ext.		
	int.	δ_2 me- suré	δ'_2 (^a)	$\Delta\delta =$ $\delta_1 - \delta'_2$		int.	δ_2 me- suré	δ'_2 (^a)	$\Delta\delta =$ $\delta_1 - \delta'_2$
	δ_1 me- suré					δ_1 me- suré			
(CH ₂) ₃ (^b)	0,24	-0,08 (^c)	-0,07	+0,31	(CH ₂) ₂ S.....	2,28	2,42	2,37	-0,09
(CH ₂) ₄ (^c)	1,96	1,52 (^c)	1,90	+0,06	(CH ₂) ₂ S..... (^d)	3,43	3,33	3,23	+0,20
(CH ₂) ₅	1,53	1,23	1,34	+0,19	(CH ₂) ₂ S.....	2,76	2,81	2,73	+0,03
(CH ₂) ₆	1,45	1,23	1,34	+0,10	(CH ₂) ₂ S.....	2,56	2,55	2,55	+0,01
(CH ₂) ₂ O... (^c)	2,58	2,25 (^c)	2,40	+0,18	(CH ₂) ₂ NH... (^d)	1,39	1,41	1,41	-0,02
(CH ₂) ₃ O... (^c)	4,65	4,27	4,77	-0,12	(CH ₂) ₂ NH... (^d)	3,56	3,31	3,52	+0,04
(CH ₂) ₄ O... (^c)	3,63	3,42	3,54	+0,09	(CH ₂) ₂ NH... (^d)	2,76	2,64	2,70	+0,06
(CH ₂) ₅ O... (^c)	3,36	3,22	3,49	-0,13	(CH ₂) ₂ NH... (^d)	2,71	2,56	2,64	+0,06

(a) Après correction de susceptibilité;

(b) Mesure effectuée à -67°C.

(c) Mesure effectuée à -15°C.

(d) Pointé proposé par Lippert et Prigge (3)

TABLEAU II
Action sur α -CH₂

δ (α -CH ₂)	δ_1 ds CCl ₄	δ_2 pur (^a)	$\Delta\delta =$ $\delta_1 - \delta_2$	δ (α -CH ₂)	δ_1 ds CCl ₄	δ_2 pur (^a)	$\Delta\delta =$ $\delta_1 - \delta_2$
(CH ₂) ₃	0,22	-0,07 (^b)	+0,30	(CH ₂) ₂ S.....	2,29	2,37	-0,08
(CH ₂) ₄	1,98	1,90	+0,07	(CH ₂) ₂ S.....	3,39	3,23	+0,16
(CH ₂) ₅	1,50	1,34	+0,16	(CH ₂) ₂ S.....	2,77	2,73	+0,04
(CH ₂) ₆	1,46	1,34	+0,12	(CH ₂) ₂ S.....	2,56	2,55	+0,01
(CH ₂) ₂ O...	2,55	2,40 (^c)	+0,15	(CH ₂) ₂ NH...	1,48 (^d)	1,41	+0,06
(CH ₂) ₃ O...	4,62	4,77	-0,15	(CH ₂) ₂ NH...	3,57	3,52	+0,05
(CH ₂) ₄ O...	3,63	3,54	+0,08	(CH ₂) ₁ NH...	2,78	2,70	+0,08
(CH ₂) ₅ O...	3,55	3,49	+0,06	(CH ₂) ₃ NH...	2,72	2,64	+0,08

(a) repère TMS externe (valeur corrigée).

(b) Mesure effectuée à -70°C.

(c) Mesure effectuée à -15°C.

(d) voir (4)

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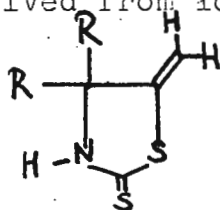
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November 30, 1974

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

Title: Temperature dependent long range coupling

Dear Professor Shapiro,

In the last year our analytical department has been equipped with two new NMR spectrometers, namely a Bruker WH60 for FT ^{13}C and a Bruker HX90E for cw proton and phosphorus work. The HX90E has been augmented with a Hewlett Packard 5105A frequency synthesizer which is phase locked to the 10 MHz clock output of the spectrometer. This addition has proved to be invaluable in several respects, be it trouble shooting or general operation, as triple irradiation and heteronuclear INDOR experiments. With such a system we are obviously able to do much more than what is usually understood by "analytical" work. It is good sometimes to verify the validity of certain "rules", and to establish structures independently of them. Recently we have been interested in stereochemical information derived from long range couplings. Several compounds of the type



have been kindly provided to us by Dr. J. D'Amico. We have observed that the two upfield transitions (for $\text{R}=\text{CH}_3$; the downfield transitions for $\text{R}=\text{C}_2\text{H}_5$) of the AB spectrum due to the olefinic protons were split by a 0.8 Hz long range coupling with the proton on the nitrogen. A NOE experiment carried out with a degassed 3% CDCl_3 solution showed a 15 % enhancement for the low field (B) proton, and a negligible enhancement for the upfield (A) proton when the methyl group protons were irradiated. This confirmed the zigzag rule in this case. Furthermore, the planarity of the zigzag path was well established by the identical ^{13}C shifts of the methyl group carbons; it is presumably due to rapid N inversion (1). At temperatures close to 60° C

the longrange coupling disappeared, probably because of rapid proton exchange on nitrogen. At lower temperature, one would expect the nitrogen inversion to slow down and the H-N-C-C-C-H pathway therefore no longer to be averaged out to planarity. This should affect the long range coupling markedly. Unfortunately, the compound crystallized out of the solution at about -30°C in CDCl_3 as well as in CD_2Cl_2 (the two only solvents in which a splitting³ was observed, after several hours). Nevertheless, a decrease of ^5J by about 30%, accompanied by a strong broadening of the A resonance, was observed even at this relatively high temperature. A line shape study is now in progress. Meanwhile, we are also looking for a better solvent.

Please credit this contribution to the Monsanto subscription.

Sincerely

P. A. Berger

P. A. Berger

C. C. Deatherage

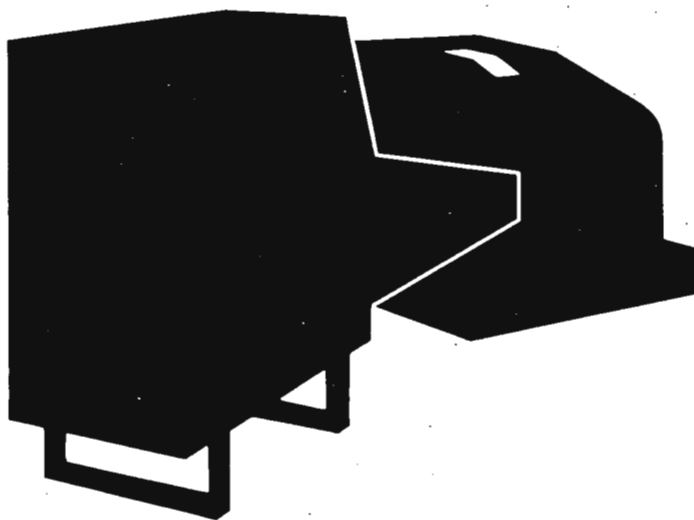
C. C. Deatherage

(1) J. B. Lambert, W. L. Oliver, Jr., J. Am. Chem. Soc., 91, 7774 (1969)



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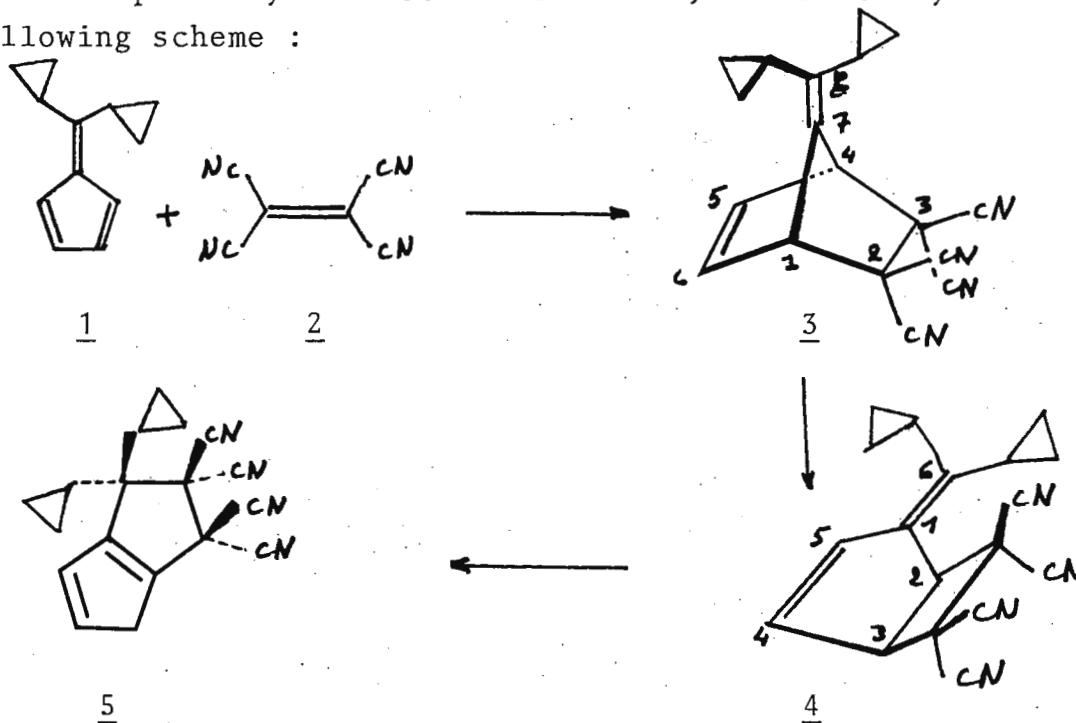
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College of Science
College Station, Texas 77843

December 2, 1974

Reactional cascade; J.I. Musher; preprint available.

Dear Barry,

We recently investigated the addition reaction of tetracyanoethylene(2) to dicyclopropyl-6,6-fulvene(1). It takes place by a "cascade" reaction, described by the following scheme :



where the second and third steps have been proven to occur via zwitterionic intermediates.

The structures of the successive adducts were elucidated on the basis of pmr, cmr and homonuclear INDOR.

Among the interesting spectral features :

- the cmr spectrum of 3, the difference of chemical shift between carbons 7 and 8, 5.2 ppm, is remarkably low, compared with molecules with similar skeleton; e.g.

	Δ	<u>reference</u>
<u>6</u>	104	1
<u>7</u>	59.7	2
<u>8</u>	52.4	2

This indicates, in the case of 3, a lack of polarization - hence of stabilization - of the exocyclic double bond by homoconjugation with the endocyclic one.

- in the case of adduct 4, $^1J_{CH}$ have been determined for positions 2 and 3, i.e. at the ring junction. Their values, ca. 157 and 167 Hz, are rather high and indicate a good deal of strain in 4.

This work was done in collaboration with André Cornélias.

We mourn the untimely death of Jeremy I. MUSHER. To his outstanding qualities of enthusiasm, wide-ranging skills, and a critical bent, he added during his last years obstinate courage in the face of grave illness. He had a beautiful talent for friendship and for enjoying the best in life, which many of your readers will long remember, together with his gifts and accomplishments as a scientist.

Preprint available : "Orientational Correlation Times for Globular Hydrocarbons as Neat Liquids", J. Grandjean and P. Laszlo, Mol. Phys. (in press).

Warmest regards,



Pierre Laszlo

PL:nd

References :

- 1) M.T. Reetz, R.W. Hoffmann, W. Schäffer, A. Schweig, Angew. Chem. Int. Ed., 12, 81 (1973).
- 2) K. Tori et al., Tetrahedron Lett., 327 (1974).



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

2nd. December 1974

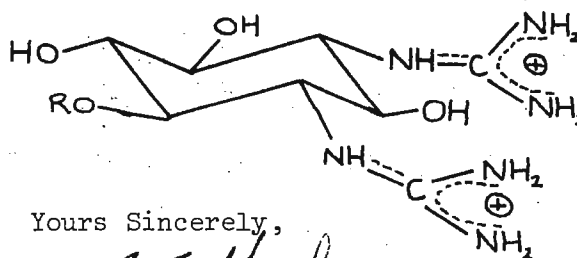
Dear Professor Shapiro,

^{15}N NMR at the Natural Abundance Level.

In response to your request we present some typical ^{15}N spectra, some obtained before our last letter on Viomycin (No.182, 1973), the others after. Since we occasionally adopt a purist stance, our efforts are mainly directed towards ^{15}N nmr at the natural abundance level and without Tl reagents. The spectra illustrate the resolution and S/N we are currently obtaining with our Bruker HFX-13 (^{15}N @ 9.12 MHz) in the FT mode. They were obtained with ^1H noise decoupling but without the advantage of an exponential weighting function on the FID before transformation. We use an approx. 30° throb* and a 0.4 sec. throb repetition time. All spectra shown, except Ac-Gly-Ala are "magnitude" and contain no phase information, but for Ac-Gly-Ala the negative ^{15}N - $\{^1\text{H}\}$ NOE is apparent. The "X" in each of the upper two spectra marks coherent noise from our time-share ^2H lock.

We were pleased to see that cis and trans N-formyl-L-proline are well resolved (this spectrum was obtained long ago by Alistair White in 1972), and also the good resolution on the guanidinium nitrogens of streptomycin sulphate:-

Please credit this
contribution to Ed
Randall's group.



Yours Sincerely,

G.E. Hawkes

G.E.Hawkes.

* We understand this term is in vogue in certain parts of the U.S. and

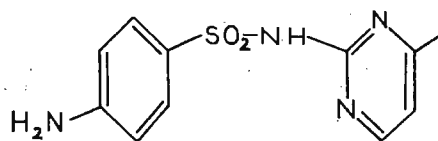
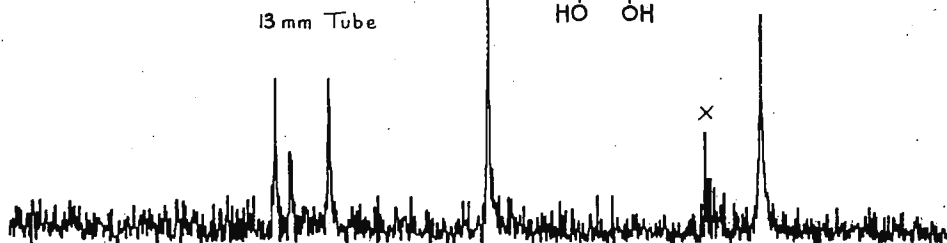
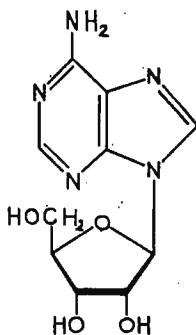
ADENOSINE

1.2 M / (CD₃)₂ SO

128,752 PULSES

14.6 HOURS

13 mm Tube



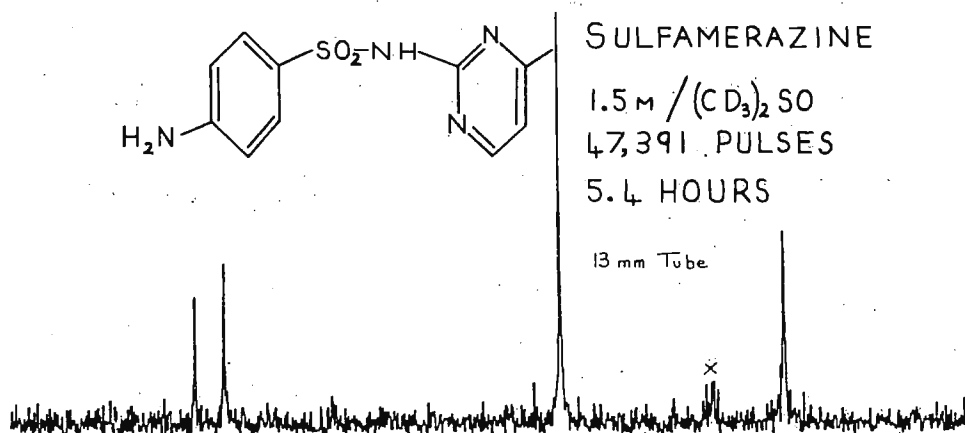
SULFAMERAZINE

1.5 M / (CD₃)₂ SO

47,391 PULSES

5.4 HOURS

13 mm Tube



250

200

150

100

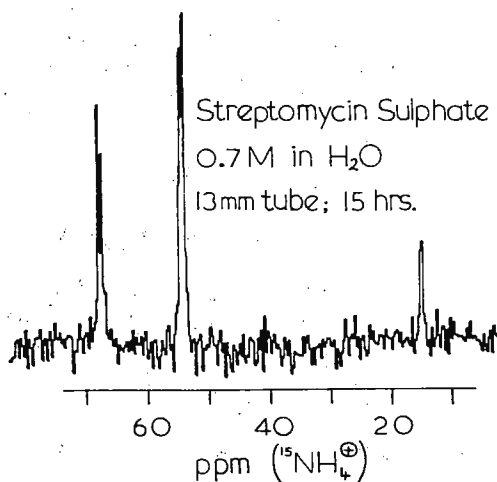
50

p.p.m. (¹⁵NH₄⁺)

Streptomycin Sulphate

0.7 M in H₂O

13 mm tube; 15 hrs.

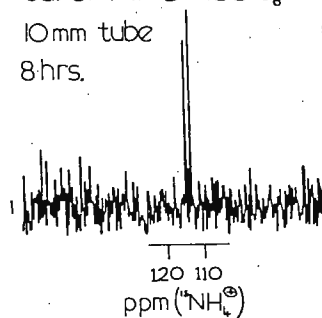


60

40

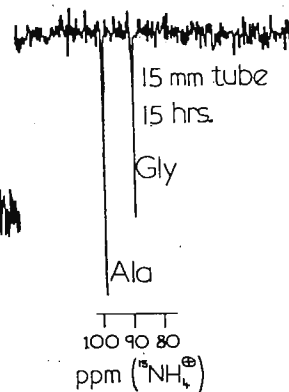
ppm (¹⁵NH₄⁺)

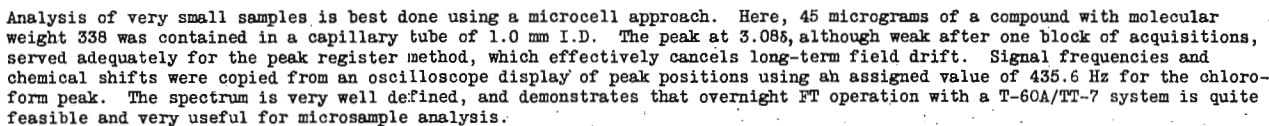
N-Formylproline
ca. 3 M in DMSO d₆
10 mm tube
8 hrs.

120 110
ppm (¹⁵NH₄⁺)N-Acetylglycyl-
L-alanine1 M in DMSO d₆15 mm tube
15 hrs.

Gly

Ala

100 90 80
ppm (¹⁵NH₄⁺)



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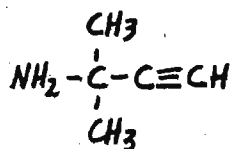
December 3, 1974

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

Dear Barry,

PROTONATION OF PROPARGYLAMINE

We have developed an interest in the effect of protonation of aliphatic amines and would like to share our recent experience with 1,1-dimethylpropargylamine with your readers in hopes that they can help us better understand the observed effects.



	¹ H-nmr ^a				¹³ C-nmr ^a		
	free base	HCl salt	$\Delta\delta^b$		free base	HCl salt	$\Delta\delta^b$
CH_3	1.28	1.57	-0.29	CH_3	31.8	27.2	+4.6
$\equiv\text{CH}$	2.91	3.68	-0.77	N-C	44.6	46.8	-2.2
-----				$\equiv\text{C}-\text{C}$	92.5	83.8	+8.7
				$\equiv\text{CH}$	69.2	75.7	-6.5

^a Chemical shifts are reported in ppm downfield from internal TMS.

^b Negative sign indicates downfield shift upon protonation.

The same DMSO- d_6 solutions were used for both the ¹³C- and ¹H-nmr spectra. The ¹³C-nmr analysis was facilitated by an ORSFD experiment.

The ¹³C-chemical shifts demonstrate the alternation of downfield and upfield shifts as recently reported by Morishima and coworkers (JACS, 95, 165 (1973) including the large upfield β -shifts which are now used diagnostically for assignments (Wenkert and coworkers, JACS, 96, 3300 (1974)). The substantial downfield γ -effect observed, however, appears to be unique to this system.

Also most interesting is the downfield shift experienced by both proton centers — especially the substantial magnitude at the distant acetylenic proton. After protonation the chemical shift of this proton is quite untypical (cf. Jackman and Sternhell, p. 193).

Our facilities here at Abbott have been recently expanded to include an XL-100-15A/TT-100 Spectrometer system which is in the final (we hope) stages of installation.

Best wishes,

Rich

Richard S. Egan, Ph.D.
 NMR Lab D-482



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Professor Bernard L. SHAPIRO

Department of Chemistry

Texas A&M University

College of Science

College Station, Texas 77843

COI GM/mg

Vert le Petit, le Dec. 10, 1974

Dear Barry,

I suppose that your pink reminder is still in the lot of mail left standing by after our long postal strike (more than six weeks). I don't wait for it (too long is too long) and, to content your appetite, I propose some edible and drinkable stuff made from water-filled cellulose acetate membranes.

You know that the available literature is rather abundant on the state of water in ion-exchange resins (see f.i. W.J. Casey and D.J. Pietrzyk, Anal. Chem., 45, 1404 (1973) ; L.S. Frankel, ibid, 45, 1570 (1973) and earlier references) but not in the case of non-ionic resins used for reverse osmosis. In this case, only Loeb - type membranes have been studied by low- or high- résolution proton NMR (V.V. Mank, D.D. Kucheruk and F.D. Ovcharenko, Dokl. Phys. Chem., 199, 729, (1971) ; S. Krishnamurty, D. McIntyre E.R. Santee and C.W. Wilson, J. Polym. Sci., Polym. Phys., 11, 427, (1973) ; V.V. Mank and D.D. Kucheruk, Colloid J. U.S.S.R., 35, 1000, (1972)). As in such rather porous membranes, water mainly exists as "free water" filling the pores, what is observed is by no means representative of the interaction water-ions-polymer : it is not surprising that the authors quoted above find no appreciable difference for the state of water between membranes contacted with saline solutions and the corresponding liquid solutions. This fact is consistent with the estimate made by Frommer et al. (J. Appl. Polym. Sci., 17, 2263 (1973)) of the ratio of free - to - polymer "bound" water from free decay experiments : it is more than 10/1. To study in better conditions the interaction water-ions-polymers, it is

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necessary to exclude this free water - by some means not perturbing too much the equilibrium of the bound water (experiments are in progress in that direction) - or to avoid its presence by working on densified membranes (for which Frommer et al. find no practically detectable free water). By using FT proton techniques, it is quite possible to observe the very low amount of water existing in such membranes and to obtain variable-temperature data.

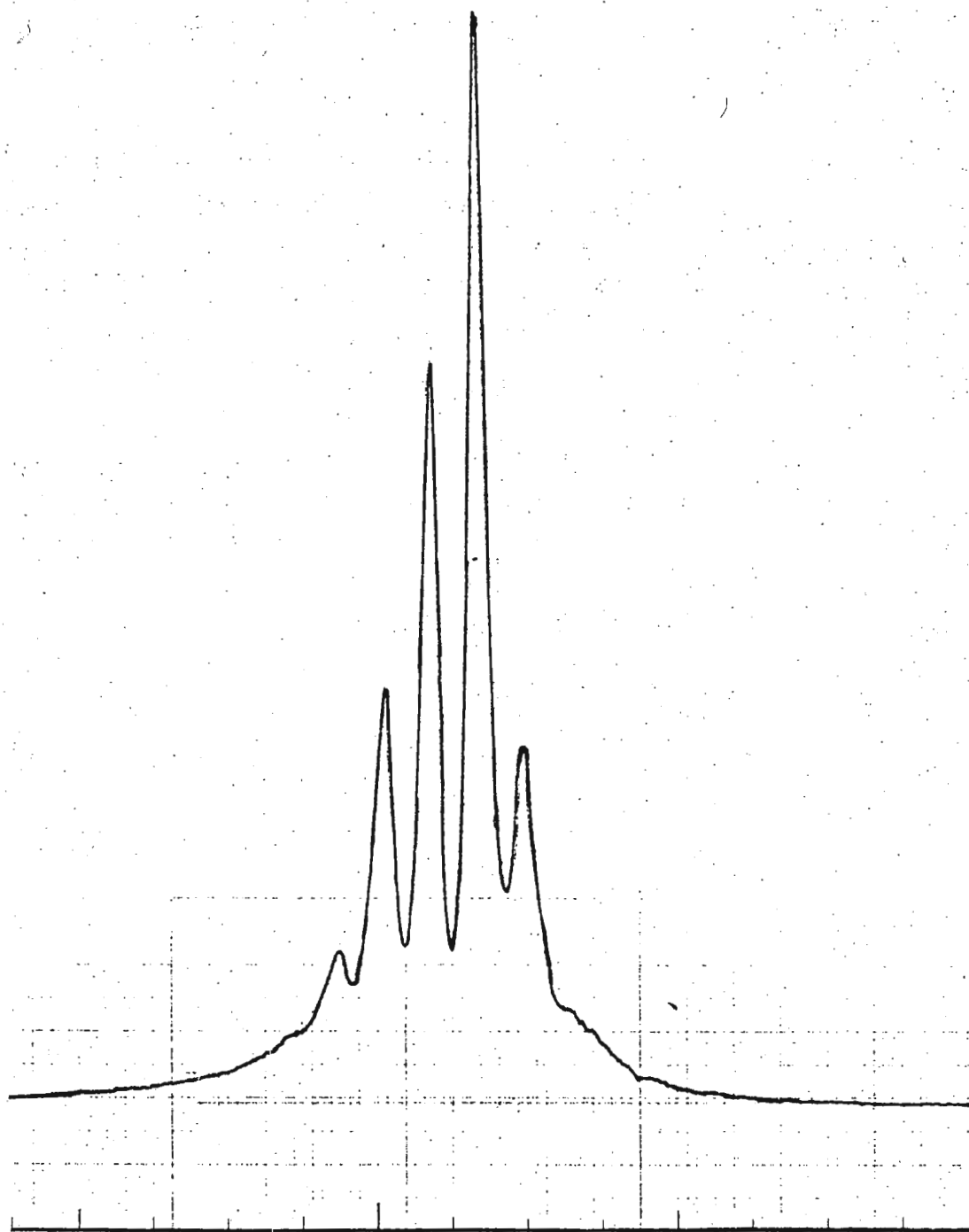
Grossly speaking, membranes equilibrated with H_2O or D_2O show a rather broad line (ca. 100 to 300 Hz at half-height at room temperature) : the temperature change of its linewidth follows an Arrhenius type law down to $-20^\circ C$ and activation parameters are obtained in this way for the mobilization of water. They are ca. 3 kC/m for dense membranes with no heat-treatment, more than 4 kC/m for heat-treated membranes (half an hour at $85^\circ C$) ; for comparison's sake, activation energies for the self-diffusion in liquid water are 4.5 kC/m at room temp. and 11 kC/m at -31° (K.T. Gillen, D.C. Douglass and M.J.R. Hoch, J. Chem. Phys., 57, 5117 (1971)).

This is not astonishing. It is much more surprising to find a rather well defined structure when membranes have been contacted with saline solutions. The following figure is just an example of what appears for rather large temperature ranges. Experiments made with various salt concentrations and D_2O instead of H_2O seem to prove that this phenomenon is not a pure artifact. We are trying to correlate its appearance with other physico-chemical data before attempting to propose an explanation with relevant peak assignments.

With very best regards and
Season's greetings,



G. MAVEL



FT proton spectrum at 20°C of water in a dense homogeneous cellulose-acetate membrane contacted (3.5 days) with a 1 % NaCl aqueous solution.

(The membrane has been rolled and inserted in a tube filled with carbon tetrachloride to dewet imbibition water). The major peak appears at ca. 3.5 ppm (downfield respect to TMS) and has a linewidth of 40 Hz.
1 cm = 139 Hz.

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Professor B.L. Shapiro

Nov. 29th, 1974

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

C-13 NMR of 500 μ gr. Cholesterol by 2 ϕ Capillary

Dear Barry:

Recent inflation is terribly bad. We nmr peoples are susceptible to this desperate inflation. This is a part of reasons for our strong intention to build the capillary probe for C-13 nmr.

In the designation of the capillary insert, its filling factor and quality value of the coil are of the most important. Our coil insert has 25% as the filling factor for the capillary sample tube with 1.2-1.3 mm in inner diameter. Probe is also designed so as to spin the sample by wind wheel. The circuitry of the receiver system in the probe is double-tuned with D-2 internal lock signal. Intensity of deuterium signal due to CDCl_3 solvent is strong enough to keep nmr locked for over-night (~14 hrs.)

A spectrum of 50% ethyl benzene is obtained at 25 MHz by Jeol PFT-100 spectrometer without crystal filter. Two other cholesterol spectra are run with crystal filter (5 KHz of BW) for S/N improvement by factor $\sqrt{2}$.

We can expect from the results 3-4 times of S/N improvement achieved for a fixed amount of the sample by use of the capillary probe compared with the results of 10 mm standard probe. We believe that the C-13 capillary probe will be routinely usable for a few mgr of the sample like cholesterol without any difficulty of sampling and thereby that it will tempt you clinical chemist, organic chemist, biochemist and so on.

Sincerely Yours

H. Shindo K. Ishibitsu 風原富

H. Shindo K. Ishibitsu and T.C. Farrar

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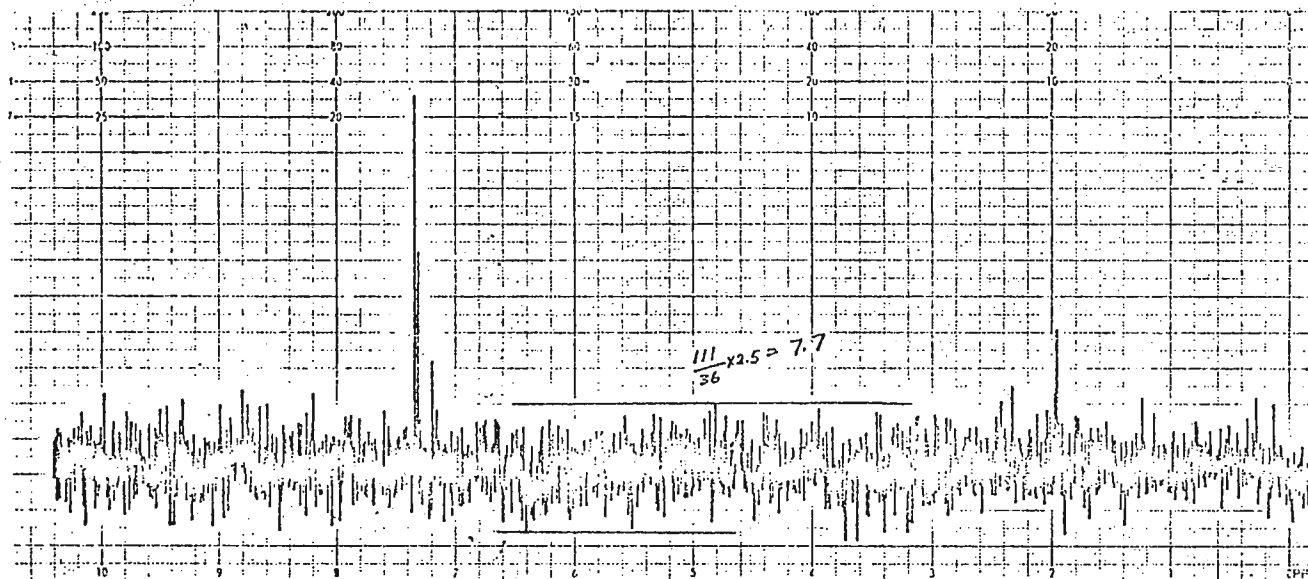


Fig. 1. 50% ethyl benzene C-13 spectrum at single pulse. Sample volume is 20 μl .

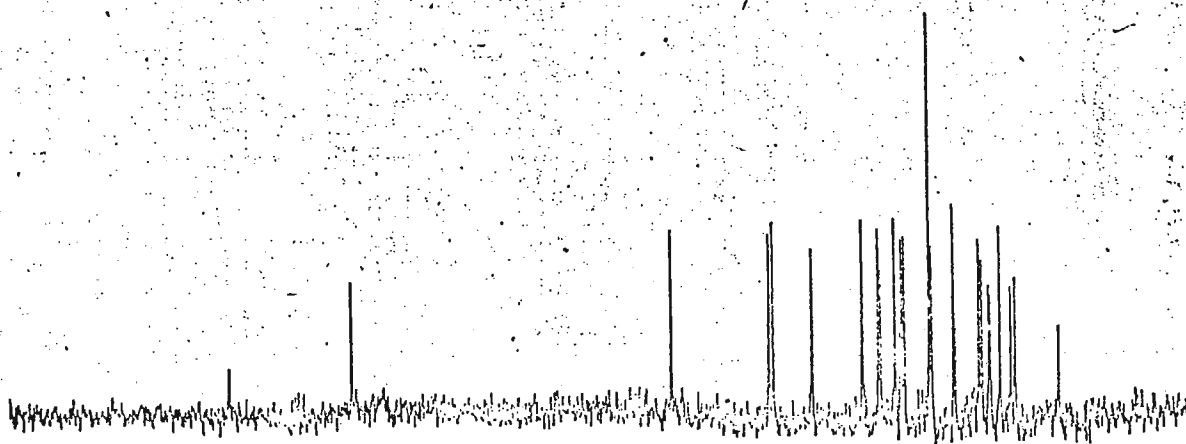


Fig. 2. C-13 nmr spectrum of 2 mgr/20 μl cholesterol in CDCl_3 . for 8000 scans (2 hrs.)

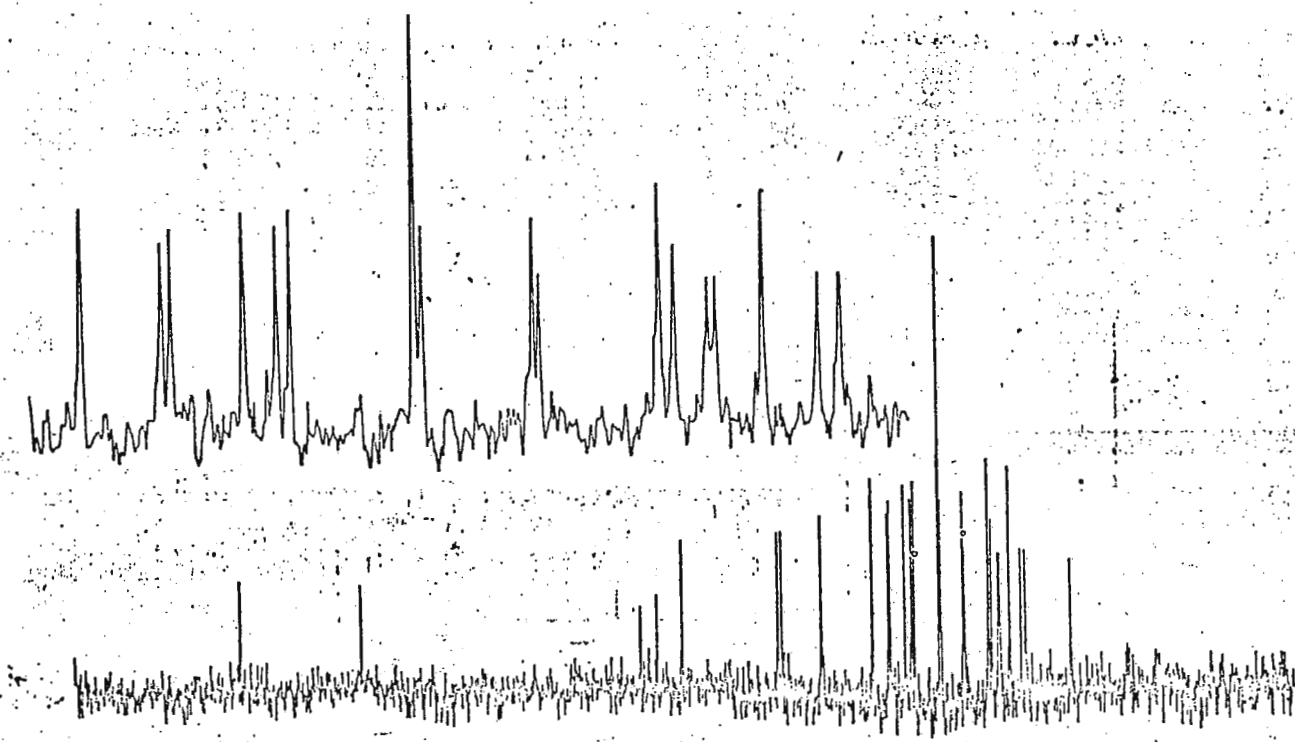


Fig. 3. C-13 spectrum of 500 μ gr/20 μ l cholesterol in CDCl₃ for 32000 scans (8 hrs.).

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Professor B. L. SHAPIRO

Texas A & M University

College of Science

College Station

Texas 77843 (USA)

N/Réf. 74 12 914 CB/MCH

Wissembourg, le 3.12.1974

V/Réf.

NMR meeting, reprints available

Dear Professor Shapiro,

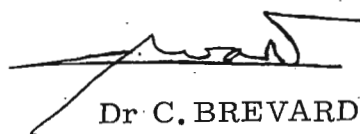
We have been hit by a nice postal strike and your blue invoice arrived in Wissembourg with rather long a delay time !

For the first contribution of BRUKER France to your NMR letters, I propose to the interrested readers a reprint of the plenary lectures and communications from a seminar we organized last october on "molecular motions studied by high resolution NMR".

Contributed lectures were given by Prof. PTAK, LEMANCEAU, MARTIN and LEHN, together with short communications.

On the other hand, our applications lab is now running with a HX 90 E (^1H , ^{13}C , ^{31}P , ^{29}Si , ^2D , ^{14}N and ^{43}Ca , CW and Fourier) and there will be some "windows" left to record spectra for people interrested in.

Sincerely yours,


Dr C. BREVARD



Laboratorium
für anorganische Chemie
Eidg. Technische Hochschule
Zürich

8006 Zürich, December 16, 1974
Universitätstrasse 6

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

Re: POSITION AVAILABLE

Dear Prof. Shapiro,

In light of a recent revision of the status of postdoctoral fellows in Switzerland, I am pleased to advise your readers that a position for a postdoctoral research assistant is now available in our Institute. The studies will deal with the applications of ^{195}Pt nmr (direct observation) to problems in platinum chemistry and will be conducted using our Bruker HX-90 (FT) Spectrometer. Compensation of the order 35.000 SFr.

Interested parties should contact me as soon as possible.

Sincerely,

Dr. P. S. Pregosin

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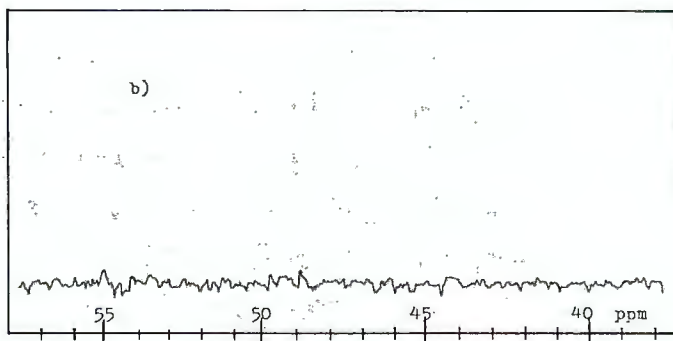
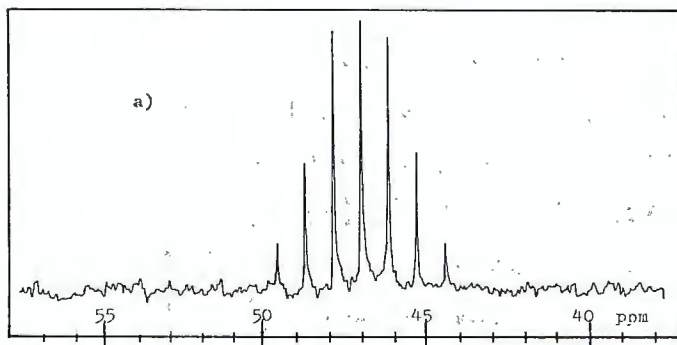
In Fourier transfer ¹³C NMR spectroscopy, the signal-to-noise ratio, and thus spectrum quality, is often limited by the strongest signal. In a normal sample, there is much more of the solvent present than there is of the substance under test. For this reason, the solvent signal is frequently much stronger than the sample signal; thus the solvent tends to limit the sensitivity and usefulness of ¹³C NMR measurements.

Fourier transform techniques increase the sensitivity of NMR spectroscopy to such an extent that the natural content of ¹³C (1.1%) is often sufficient to provide ¹³C solvent signals that mask the ¹³C signals of the sample.

In order to minimize the solvent signal, E. Merck has developed a new class of Uvasols, in which the ¹³C content is less than 10% of the natural level. These are compounds with ¹²C content of from 99.93 to 99.95%. In addition, these Uvasols are synthesized with a deuteration degree of more than 99.5% in order to eliminate possible Overhauser amplifications in proton-noise de-coupled spectra which could increase solvent-signal

amplitudes by a factor of as much as three and which, therefore, could mimic a higher level of ¹³C than is actually present. Preparation techniques allow the synthesis of many different solvents. For example, chlorinated ¹²C methanes (CCl₄, CDCl₃, CD₂Cl₂), ¹²C methanol, and ¹²C methyl halogenides, non proton solvents such as ¹²C dimethylsulfoxide, ¹²C dimethylformamide, ¹²C tetramethyl urea, ¹²C acetic acid and its derivatives and others in which the carbon atoms in a molecule have the same ¹²C isotope content. At the present time, five ¹²C solvents are commercially available from EM Laboratories.

Figure 1 compares the NMR spectrum of methanol with natural ¹³C content (a) and the spectrum of methanol containing only 5% of the natural ¹³C content (b). Both spectra were obtained under identical measuring conditions with a Varian XL-100 NMR spectrometer. Spectrum (a) shows the septet of the CD₃ group at 47.05 ppm with a ¹³C-²H spin coupling of 22 Hz in the region between 40 and 55 ppm relative to TMS. In spectrum (b), the same region is practically signal-free.



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¹²CCl₄ MW 153.81

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Prof. Dr. B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843
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17. Dez. 74

Betreff

Dear Barry,

recently we reported on our preliminary results with an interactive computer system for mutual assignment of substructures and ^{13}C -nmr-subspectra/1/. The process of developing various approaches for computer-aided interpretation of nmr-spectra can be optimized by empirically comparing the results of different search strategies using the same data-collection. In the course of this work we are now testing an algorithm which seems adaptable also to ^1H -nmr, where certainly a computer-search system will be more helpful and widely applicable though probably less efficient in some cases.

Comparing the features of two spectra (reference and query), we feel that not only the similarity of their features is important but that the similarity of less frequent features is a more relevant information for the structure elucidation than a similarity of "normal" (or "trivial") features. As described by Naegeli and Clerc/2/ for their program OCETH we assign different numerical values to the different similarity matrices. However, in our approach we calculate these values from the frequency of these features. In the most simple case of coding yes (1) or no (0) for the presence of a feature in a certain range we obtain the "basic matrix" which is later expanded to include other characteristics:

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Prof. Dr. B.L. Shapiro

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17. Dez. 1974

Betreff

		0	query	1
reference	0	$A - 2\ln(1-W)$		$-B - \ln W - \ln(1-W)$
	1	$-C - \ln W - \ln(1-W)$		$D - 2\ln W$

W is the probability of finding a certain feature and it can be easily seen that a frequent feature is connected with a relatively low number of positive points for identity (1,1), whereas non-identity (0,1 or 1,0) yields a relatively high value of negative points (A, B, C and D are positive constants).

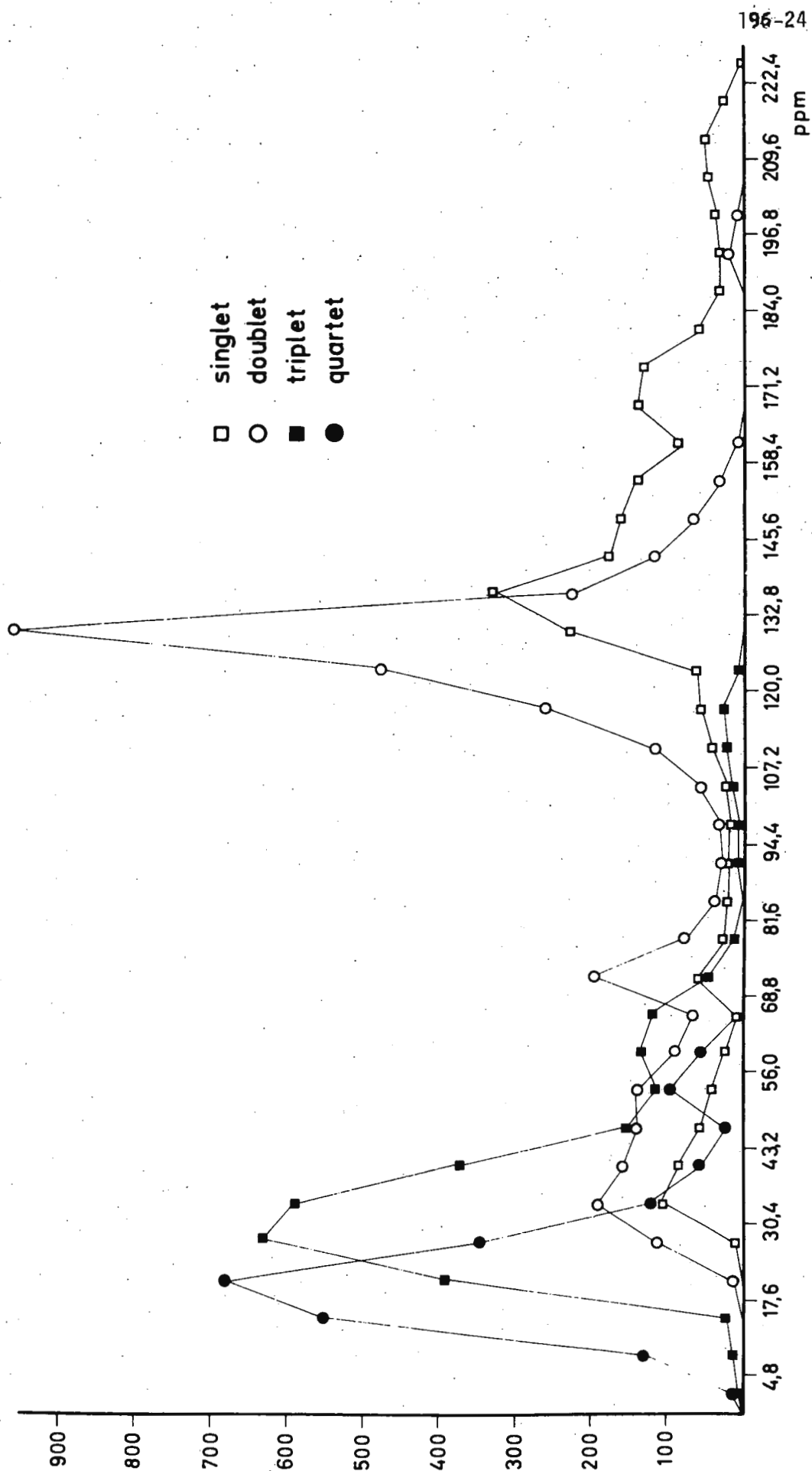
A byproduct of these considerations is the attached graph with the distribution of the features singlet, doublet, triplet, and quartet over the range of frequencies in ^{13}C -nmr based on 1088 references. I presume this might be of interest also to those readers of the newsletter still relying solely on their intuition when interpreting nmr-spectra.


(W. Bremser)

- References: /1/ W. Bremser, M. Klier and E. Meyer, Org. Magn. Res. in press
/2/ P. Naegeli and J. Clerc, Anal. Chem. 46, 739 A (1974)

Short title: Frequency distribution of features in ^{13}C -nmr-spectroscopy

Number of lines
within 6.4 ppm



UNIVERSITY OF COLORADO
BOULDER, COLORADO 80302, U.S.A.

DEPARTMENT OF CHEMISTRY

December 6, 1974

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

Dear Barry:

RE: ^{35}Cl T_2 Measurements from Free
Induction Decays

Recently, we have been studying the broadening of the $^{35}\text{Cl}^-$ resonance in the presence of the ferric ion, and the perchlorate ion. In such studies the acquirement of resolution is paramount. Thus, a narrow spectrum width (100-500 Hz) is desired. However, to acquire this desired width means that the acquisition time for one transient (≈ 2 sec for 2K datapoints) becomes much longer than the repetition time (.06 to .1 sec). Therefore, the limiting time factor is the rate at which data can be processed into the computer.

The observed linewidth and the decay of the FID are functions of the transverse relaxation time, T_2^* . So that the linewidth width and T_2^* can be determined from the FID, instead of the transformed spectrum. In addition, the acquisition time is no longer determined by the requirement of a narrow spectrum width, thus acquisition time can be decreased considerably.

The FID of a single species decays with a characteristic time constant T_2^* define by eq. (1),

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma\Delta H_0}{2} \quad (1)$$

Where T_2 is the "natural" transverse relaxation time and the second T_2^* term takes into account the inhomogeneity of the external magnetic field. The intensity of the FID can be described by eq. (2),

$$I(t) = I_0 e^{-t/T_2^*} \quad (2)$$

if the pulsing frequency, ω_p , is equal to the resonant frequency, ω_i , of the species of interest. T_2^* can be obtained by plotting the $\ln I(t)$ vs time. However, we have found that the T_2^* values obtained by this method are not very reproducible. The reason being that if ω_p is not exactly equal to ω_i , the FID will contain a very low frequency cosine component.

Professor Barry L. Shapiro

December 4, 1974

As a result, we have set the pulsing frequency slightly different from that of the resonant frequency, which improves the reproducibility. In this case, the intensity of the FID is given by eq. (3).

$$I(t) = I_0 \cos(\Delta\omega t + \delta) e^{-t/T_2^*} \quad (3)$$

where $\Delta\omega = (\omega_p - \omega_j)$ and δ is a phase factor. In fact, eq. 3 can be expanded to describe the FID of 2 or more species as:

$$I(t) = \sum_j I_{0j} \cos(\Delta\omega_j t + \delta_j) e^{-t/T_{2j}^*}$$

all species

where j represents the j th resonant species.

By applying a non-linear least squares fit to the data points that describe the FID, (along with initial educated guesses for the T_{2j}^*) the values for the T_{2j}^* 's can be determined.

In our studies we have been able to obtain the T_2^* for Cl^- in the presence of ClO_4^- . By using the above method, spectrum acquisition time is decreased and the transverse relaxation times of different species which have large chemical shift differences can be determined simultaneously.

Please credit this to the University of Colorado subscription.

Sincerely yours,

Dale R. Holecek

Dale R. Holecek

DRH:eag



UNIVERSIDAD DE BUENOS AIRES
FACULTAD DE CIENCIAS EXACTAS Y NATURALES

Buenos Aires, December 10th.1974.

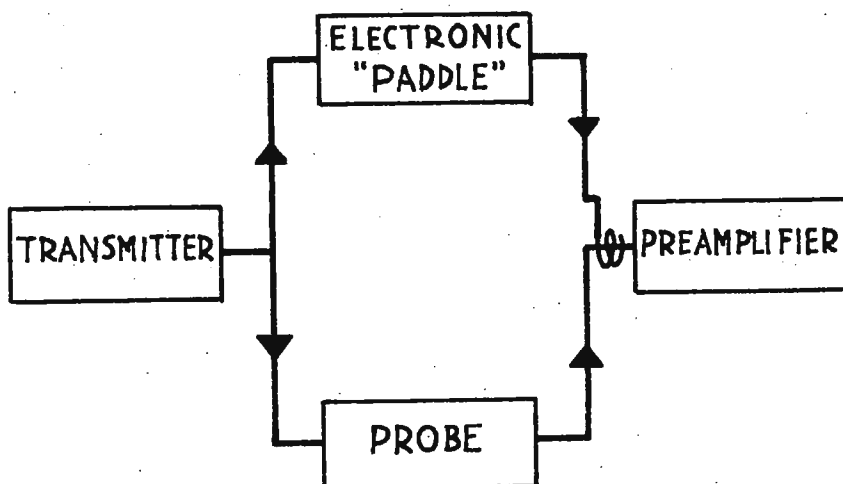
Mr. Bernard L. Shapiro
Texas A.& M. University.
College Station
Texas 77843
USA.

Title: Electronic Paddles.

Dear Dr. Shapiro:

While we here dream about a F.T. spectrometer and prepare the necessary steps for a time sharing system, we built a small gadget which eases a little the work of the operator of our venerable DP-60 (converted to something like the HA-60) by sparing him the need of frequent adjustments of the probe leakage with the paddles, particularly when doing variable temperature work or when a sample proves to have an abnormally high magnetic susceptibility, which is not rare. The only modifications to the probe (or rather the preamplifier, which is a home built improved cascode) is a small hole and an extra BNC connector.

We have an auxiliary circuit connected as shown in the figure:

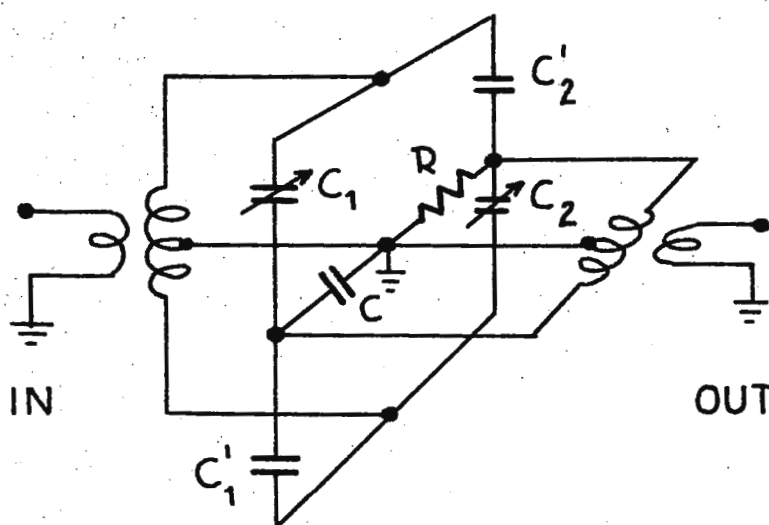




UNIVERSIDAD DE BUENOS AIRES
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- 2 -

The circuit of the "electronic paddles" itself is shown in the next figure:



where $R = 27$ ohms and $C = 100$ pF. C_1 and C_2 are 15 pF air capacitors. C'_1 and C'_2 are 15 pF ceramic trimmers. The balun transformers are wound on ferrite cores. For 60 MHz each coil has two turns. C_1 and C_2 are driven with good quality planetary reduction drives.

The bridge is initially adjusted without the probe. With both air capacitors at mid-range the trimmers are adjusted until a good null is obtained. After this, the probe is attached and adjusted in the usual way. Though, the fine paddles can be forgotten.

This work was basically the job of one of us. (R.L.).

R. Lembo

V.J. Kowalewski.

P.S. Thanks for the remainder!

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UNIVERSITY OF SOUTH FLORIDA

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DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813: 974-2571

December 17, 1974

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

Dear Barry:

Recently, we have been studying the conformations of various sulfur-containing compounds *via* the use of lanthanide shift reagents. During these studies, we came up with an interesting set of results which may be of use to others.

With the exception of thioethers, the compounds we examined exhibited no LIS whatsoever. The LSR's employed were $\text{Eu}(\text{fod})_3$, $\text{Pr}(\text{fod})_3$, and $\text{Dy}(\text{fod})_3$. Relative concentrations of LSR to substrate were taken up to about 0.5 moles LSR/mole substrate.

The most obvious application of these observations lies in the fact that there is now a simple means of distinguishing sulfides from disulfides: the former experience LIS, whereas the latter are *totally inert* toward shift reagents. Our results are summarized in the table below.

<u>Compound type</u>	<u>Examples tested</u>	<u>LIS</u>
R-S-R'	Tetrahydrothiophene	Substantial
R-S-S-R'	1) Benzyl disulfide 2) <i>tert</i> -butyl disulfide	NONE NONE
$\begin{array}{c} \text{S} \\ \\ \text{R}-\text{C}-\text{S}-\text{R}' \end{array}$	$(\text{C}_6\text{H}_5)_2\text{HCSSCH}_3$	NONE
$\begin{array}{c} \text{S} \\ \\ \text{R}-\text{C}=\text{S}-\text{S}-\text{R}' \end{array}$	1) <i>tert</i> -butyltrithio- phenylperacetate 2) <i>tert</i> -butyl-4-biphenyl- trithioacetate	NONE NONE

Sincerely yours,

Milton D. Johnston, Jr.
Assistant Professor

George R. Jurch, Jr.
Associate Professor

Suggested title: LIS OF SOME SULFUR-CONTAINING COMPOUNDS

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20th December, 1974.

School of Science

Ref:

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

Dear Professor Shapiro,

^{13}C Isotropic Shifts in Some Fe(III) Tris-Dithiocarbamate Complexes

I have just moved to Griffith University from the University of New England and wish to begin my own contribution to the TAMU newsletter.

The School of Science has bought a HX-90 spectrometer with ^1H , ^{13}C , ^{15}N , ^{19}F , and ^{31}P capabilities; the system will be installed early next year. This should provide more than an adequate instrumental backup for the magnetic resonance research we plan to undertake in the School.

To add a bit more meat to this first letter I have enclosed results of some ^{13}C chemical shifts we (Tony Gregson and I) have measured on some Fe(III) Tris-dithiocarbamates complexes. These are interesting compounds as depending on the alkyl group (see structure) they are either high-spin ($S = \frac{5}{2}$) or low-spin ($S = \frac{1}{2}$) or undergoing spin interconversion¹. (Further details of this work will soon appear in Chem.Phys.Letts. and a preprint is available upon request.)

Our isotropic shifts are listed in the Table. Shifts were computed using the chemical shift of the same carbon in the appropriate diamagnetic Co(III) complex as reference. Also listed are the line-width (in Hz) and the ratio of the linewidth-to-shift ($\Delta H_{1/2}/\sigma_{\text{iso}}$) in Hz/ppm.

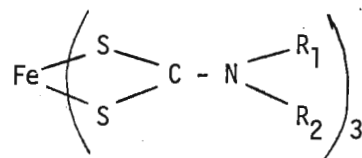
Although ^{13}C contact shift are difficult to interpret we have concluded that the reduction in magnitude of σ_{iso} and its change in sign (- to +) as the $S = \frac{1}{2}$ form of these complexes is favoured to be evidence of increased metal-ligand π -bonding in the low-spin complexes relative to the high-spin form². It is interesting to note that $\Delta H_{1/2}/\sigma_{\text{iso}}$ is much larger in the low-spin complexes; this result is somewhat contrary to that normally expected for high- and low-spin Fe(III) complexes³.

Yours sincerely,

D. Doddrell

1. R.M. Golding, W.C. Tennant, C.R. Kanekar, R.L. Martin and A.H. White, J.Chem.Phys., **45** (1966)2688.
2. R.R. Eley, R.R. Myers, and N.V. Duffy, Inorg.Chem., **11** (1972) 1128.
3. H.A.O. Hill and K.G. Morallee, J.Amer.Chem.Soc., **94** (1972) 731.

Table Carbon-13 and Proton Isotropic Shifts^a in Some Iron(III) Tris-Dithiocarbamate Complexes.



R₁ and R₂ are the alkyl groups in the appropriate secondary Amine

Amine ^b	<u>C_α</u>			<u>C_β</u>			<u>H_α</u>			<u>H_β</u>		
	σ _{TMS} ^{Fe}	σ _{TMS} ^{Co}	σ _{iso}	σ _{TMS} ^{Fe}	σ _{TMS} ^{Co}	σ _{iso}	σ _{TMS} ^{Fe}	σ _{TMS} ^{Co}	σ _{iso}	σ _{TMS} ^{Fe}	σ _{TMS} ^{Co}	σ _{iso}
diisopropyl (u = 2.41)	-38.5 (130) ^c	-50.6	+12.1 (10.7) ^d	-56.1	-20.9	-35.2	-3.6	-4.6	+1.0 (+12.1) ^f	0.0	-1.4	+1.4 (-25.1) ^f
dicyclohexyl (u = 2.55)	-21.7 (130) ^c	-60.3	+38.6 (3.4) ^d	-57.9	-31.0	-26.9	e	e	e	e	e	e
diisobutyl (u = 3.77)	-218.6 (80) ^c	-57.0	-161.6 (0.5) ^d	-104.3	-27.8	-76.5	-25.4	-3.5	-21.9 (+7.4) ^f	-3.4	-2.2	-1.2 (+63.8) ^f
morpholine (u = 4.02)	-411.6 (90) ^c	-46.4	-365.2 (0.25) ^d	-173.5	-66.8	-106.7	-30.8	-3.8	-27.0 (+13.5) ^f	-2.4	-3.8	+1.4 (+76.2) ^f
piperidine (u = 4.09)	-397.1 (120) ^c	-47.5	-349.6 (0.34) ^d	-86.5	-26.0	-60.5	-29.0	-3.8	-25.2 (+13.9) ^f	-0.4	e	e
dimethyl (u = 4.19)	-372.5 (120) ^c	-38.5	-334.0 (0.36) ^d				-49.6	-3.2	-46.4 (+7.2) ^f			

amine ^b	<u>C_α</u>			<u>C_β</u>			<u>H_α</u>			<u>H_β</u>		
	$\sigma_{\text{TMS}}^{\text{Fe}}$	$\sigma_{\text{TMS}}^{\text{Co}}$	σ_{iso}	$\sigma_{\text{TMS}}^{\text{Fe}}$	$\sigma_{\text{TMS}}^{\text{Co}}$	σ_{iso}	$\sigma_{\text{TMS}}^{\text{Fe}}$	$\sigma_{\text{TMS}}^{\text{Co}}$	σ_{iso}	$\sigma_{\text{TMS}}^{\text{Fe}}$	$\sigma_{\text{TMS}}^{\text{Co}}$	σ_{iso}
diethyl (u = 4.37)	-384.3 (50) ^c	-42.8	-341.5 (0.15) ^d	-109.0	-12.6	-96.4	-39.4	-3.7	-35.7 (+9.6) ^f	-1.0	-1.3	+0.3 (-321.3) ^f
di-n-butyl (u = 4.53)	-338.9 (80) ^c	-49.5	-289.4 (0.28) ^d	-114.4	-30.3	-84.1	-36.4	-3.6	-32.8 (+8.8) ^f	-1.2	e	e
pyrrolidine (u = 5.83)	-567.8 (185) ^c	-49.2	-518.6 (0.36) ^d	-242.8	-25.7	-217.1	-81.8	-3.7	-78.1 (+6.6) ^f	-6.2	-1.9	-4.3 (+50.5) ^f

^aIn ppm, computed via $\sigma_{\text{iso}} = \sigma_{\text{TMS}}^{\text{Fe}} - \sigma_{\text{TMS}}^{\text{Co}}$ where $\sigma_{\text{TMS}}^{\text{Fe}}$ and $\sigma_{\text{TMS}}^{\text{Co}}$ are the chemical shifts from TMS of the appropriate carbon or proton in the Fe and Co complexes, respectively. + = upfield; - = downfield. ^bValues in parenthesis are the magnetic moments (in BM) of complexes taken from ref. 2a. ^cValues in parenthesis are the linewidths at half-height in Hz. ^dValues in parenthesis is the ratio of the linewidth to shift, $(\Delta H_{1/2}/\sigma_{\text{iso}})$, in Hz/ppm. ^eThe complexity of the spectrum precluded a simple analysis to yield the chemical shifts. ^fValues in parenthesis is the ratio of $\sigma_{\text{iso}}^{\text{C}}/\sigma_{\text{iso}}^{\text{H}}$.

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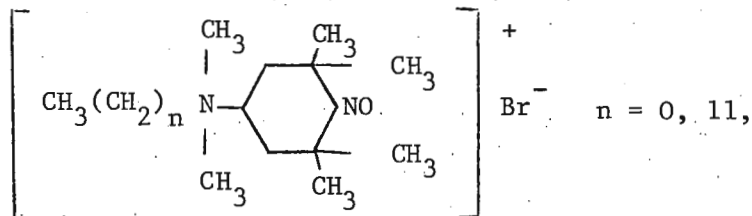
Dr B L Shapiro,
Dept. of Chemistry,
Texas A & M University,
College Station,
Texas 77843,
U.S.A.

16 DEC 74

Dear Dr Shapiro,

SPIN-EXCHANGE AND THE "CONCENTRATION-INDUCED" DISCREPANCY BETWEEN
NMR AND EPR MEASUREMENTS OF HYPERFINE COUPLING CONSTANTS

Recently we did some Knight Shift measurements in order to determine the proton hyperfine coupling constants of nitroxide I. Spectra of concentrated aqueous solutions of I(n=0) and of I(n=11) were recorded at



95 + 2°C on the Varian 220 MHz NMR spectrometer operated by TNO, Delft, the Netherlands. The spectra were analysed by standard techniques¹, yielding the coupling constants $a_{\text{CH}_3} = -0.43 \pm 0.02\text{G}$, $a_{\text{CH}_3} = -0.30 \pm 0.03\text{G}$ for the n = 11 compound and $a_{\text{CH}_3} = -0.44 \pm 0.02\text{G}$, $a_{\text{CH}_3} = -0.31 \pm 0.02\text{G}$ for the n = 0 compound.

These coupling constants were used, in conjunction with a program written by C.S. Johnson², to computer-simulate the EPR spectra of a dilute solution of I(n = 11). The coupling constants were varied by up to 10% of their value (in steps of 0.001G) in attempts to better approximate the experimental spectrum. The best approximation obtained is shown in the accompanying figure.

The computer program used was designed to consider hyperfine lines of the same width. Freed and co-workers³ have shown that, when the strongest nuclear spin-dependent relaxation processes are due to exchange, in the slow exchange region the width of each hyperfine line depends upon the degeneracy of that line:

$$\delta_M - \delta_M(0) = \frac{2}{\sqrt{3}} W_{\text{HE}} \frac{N-2D_M}{N}$$

Here $\delta_M - \delta_M(0)$ is the increase in the width of the M^{th} hyperfine line caused by exchange at frequency W_{HE} , D_M is the degeneracy of the M^{th} line, and N is the total number of transitions. It is probable that a substantial proportion of the linewidth of the $2 \times 10^{-5}\text{M}$ solution of I(n = 11) shown in the figure has been caused by Heisenberg spin exchange (extrapolations from Freed's³ data for di-t-butyl nitroxide in dimethoxyethane indicate that 0.36G is the exchange contribution to the total linewidth expected for a $2 \times 10^{-5}\text{M}$ solution). By assuming that exchange was taking place, and by scaling the widths of the more intense peaks (those containing more than 10% of the intensity of the most intense

proton hyperfine line) accordingly, it was possible to greatly increase the correspondence between the experimental and the simulated spectra. The postulate that exchange is present in the system was strengthened by the observation that in more concentrated solutions where hyperfine structure was not observed, the minimum measured envelope linewidth was less (1.4G vs 1.7G) than that predicted from increasing the proton hyperfine linewidths, using the hyperfine coupling constants shown in the figure. This is consistent with a reduction in the separation of the proton hyperfine lines due to exchange.

These observations indicate that electron spin exchange in dilute solutions may cause observed EPR spectra to differ from those predicted from Knight shift measurements.

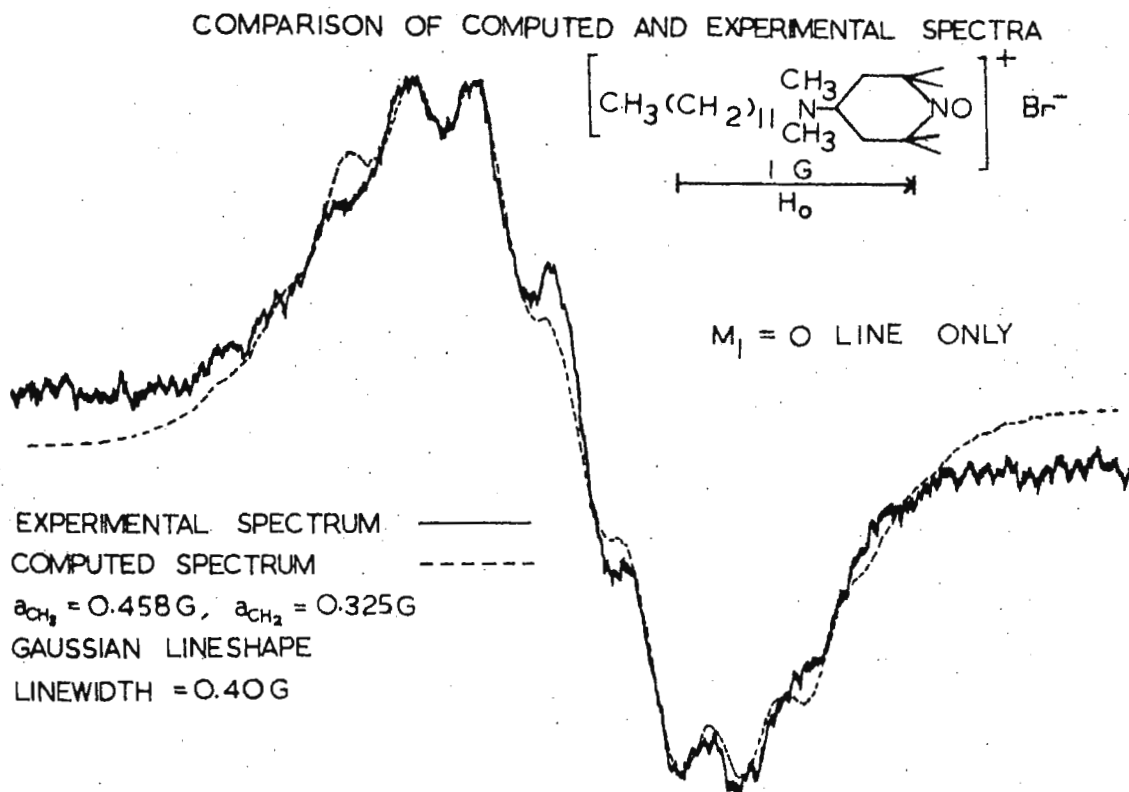
Yours sincerely,

Kay Fox

K K FOX

References:

1. R.W.Kreilick, J.Chem.Phys. 45, 1922 (1966).
2. R.Chang and C.S.Johnson,Jr., J.Chem.Phys. 41, 3272 (1964).
3. M.P.Eastman, R.G.Kooser, M.R.Das, and J.H.Freed, J.Chem.Phys. 51, 2690 (1969).



Department of Chemistry

YORK
UNIVERSITY

FACULTY OF SCIENCE

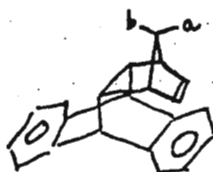
4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

December 19, 1974

Dear Dr. Shapiro,

Aromatic Shifts in ^{13}C and ^1H Spectra

The chemistry of proximal π -bond system is being investigated by a colleague here¹. Some of the compounds developed seemed likely candidates for estimation of ^{13}C aromatic ring shifts. Two examples are shown:-



I



II

Thus in compound I the olefinic carbons are directly over the inner edge of the nearest aromatic ring and in compound II the CH_2 group occupies such a position. From molecular framework models estimates of ring to proton and carbon distances can be made. Using the various tables² of ring current effects, estimates of the magnitude of the aromatic shift can be made. The shift contributions for both rings can be summed as shown in the Table, using the data of Johnson & Bovey. Comments on the estimates compared to experimental shifts are given.

Assuming that bond geometries per se are not greatly changed in the two derivatives (which seems reasonable) a rather better degree of correspondence between estimated and observed shifts would be anticipated. Proton (a) of the CH_2 group seems to be satisfactorily accounted for in this manner, and if one is willing to stretch a few tenths of a ppm so are the protons of the olefin group.

Grossly in error are a proton (b) and the carbon atoms. Proton (b) finds itself rather tightly jammed into the π -electron cloud of the ring in compound II. If one assumes that this causes a repulsion of the $1s$ electron away from the proton then a deshielding effect is superimposed on the ring shielding effect, accounting perhaps for the grossly overestimated shift of this proton. The electron drift should end up

Dr. Shapiro
Tamu Newsletter

December 19, 1974

on the carbon atom, whose shielding does indeed seem to be grossly underestimated by the ring current shift alone.

In the case of the olefinic carbons, a CNDO calculation has suggested that the π -cloud of the ring and the olefin interact in such a way as to increase electron density around the olefinic carbon atoms. This interaction seems to have a minimum at around 2 to 3 Å. We are currently attempting to refine the calculation on this and related systems, and also to estimate charge densities in the CH_2 groups when it moves into and away from the influence of the ring π -cloud.

There does seem to be some caution necessary, however, in interpreting proton shifts at such short ranges. The data also indicate yet again how difficult it is to find good model systems for ring-current effects in ^{13}C spectroscopy³.

	olefin	Proton shift ppm		Carbon shift ppm	
		a	CH_2 b	olefin	CH_2
Compound 1	1.9	0.3	0.05	1.5	0.2
Compound 2	0.34	1.1	6.8	0.2	1.2
Estimated shift (upfield)	1.6	0.8	6.7	1.3	1.6
Experimental shift.	1.2	0.6	1.52	10.0	13.1
Comments on estimate.	fair	OK	over	under	under

1. D.N. Butler and R.A. Snow, Can.J.Chem. 50, 795 (1972).

2. C.E. Johnson and F.A. Bovey, J.Chem.Phys. 29, 1012 (1958).

D.W. Haigh and R.B. Mallion, Org.Mag.Res. 4, 203 (1972).

3.e.g. R.DuVerner and V. Boekelheide, Proc.Nat.Acad.Sci. 71, 2961 (1974).

Yours sincerely,

C.E. Holloway D.E. Axelson

C.E. Holloway

D. E. Axelson

CEH, DEA:pc

HARVARD UNIVERSITY
DEPARTMENT OF CHEMISTRY

12 Oxford Street
Cambridge, Massachusetts 02138
U.S.A.

December 21, 1974

A NEW APPROACH TO DIFFERENCE SPECTROSCOPY;
CORRELATION SPECTROSCOPY ON THE XL-100

Dear Barry,

^1H NMR has proved an extremely useful tool in the study of the interactions of small molecules and proteins. Typically, changes in the spectrum of the small molecule induced by addition of the protein are used to monitor both the extent and the nature of the binding.

In many cases it would be desirable to carry such studies to concentrations at which the small molecule is substantially bound to the protein. For example, consider the question of resolving one-step from two-step binding in the interaction of an inhibitor and an enzyme:



Since the two-step binding (2) offers the possibility of observing chemical exchange broadening even when all the inhibitor is bound to the enzyme, one may be able to distinguish between the two mechanisms by using low enough concentrations.

At such concentrations, however, enzyme resonances will provide considerable interference with attempts to measure most parts of the typical inhibitor spectrum. The simplest answer to this problem is to subtract off a spectrum of the enzyme taken under similar conditions. Unfortunately, changes induced in the enzyme spectrum upon binding of the small molecule are often of the same order of magnitude as the changes in the spectrum of the inhibitor, and will in many cases render the resultant difference spectrum useless.

Accordingly, we have developed the technique of preparing two samples, identical except for the deuteration of the inhibitor at selected positions in the molecule. The difference between spectra taken of such matched samples will now be a true difference spectrum, consisting only of the resonances of the selected positions. Using this technique, usable difference spectra have been produced of samples equimolar in inhibitor and enzyme.

Typical difference spectra are seen in Figure 1. A) is a spectrum of a sample containing 5.9 mM NAG₂ and 2.9 mM lysozyme; B) is identical with the exception of the deuteration of the two acetyl groups of NAG₂; C) is the difference spectrum showing clearly the (largely) unshifting non-reducing end acetyl resonance together with the shifted and broadened resonance of the reducing end acetyl group.

In the experiments we have been doing we felt it desirable to use H₂O as a solvent, both to closely represent the *in vivo* conditions and also to facilitate comparison with temperature-jump studies which had to be performed

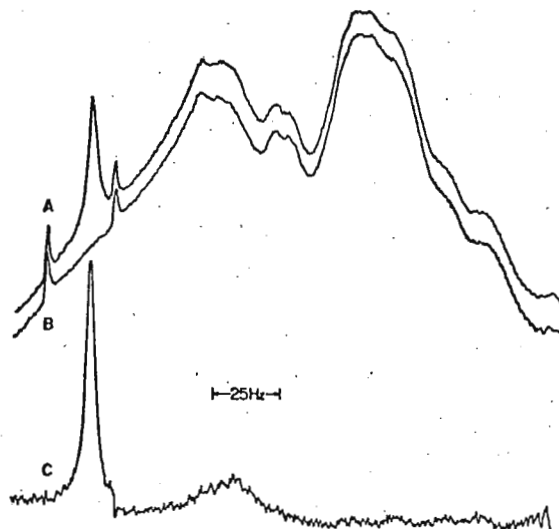


FIGURE 1. Typical difference spectroscopy experiment (see text).

in H_2O . Of the several techniques available for producing spectra in H_2O , we thought correlation would best suit our needs and accordingly modified our XL-100 to perform such an experiment.

In normal XL-100 operation, the position of the recorder arm, digitally determined, is used to drive a digital-to-analog converter (DAC) which in turn drives a voltage-controlled oscillator (VCO), which in conjunction with the sweep offset knob and sweep width button determines the frequency range swept. To convert to correlation operation, we provide (via a switch) an alternative voltage input to the VCO, that voltage being provided by a 14-bit DAC in the Varian 620i computer. The computer DAC is set to produce an output of 5V for a 10,000 step input, corresponding to the recorder arm. The frequency may now be stepped across the desired range by the software. Spectra were improved by rewiring relay K1 on the Attenuator Interface of the RF Module to allow the computer to switch the rf level to 0 dB during the retrace.

The output of the spectrometer is available in several locations, but we found it both convenient and desirable to take the output from across the "DC observe" switch on the "Power control and scope selector" panel. This (relatively) unfiltered output was passed through a low pass filter (Ithaco #4215) and then through a homemade box providing both amplification and DC offset capabilities, allowing for full usage of the dynamic range of the computer's analog-to-digital converter (of which one of the four multiplexed ports is unused). Synchronization of frequency sweep with data acquisition is inherent since the computer is controlling both functions.

Production of software for both data acquisition and correlation was tedious, but straightforward. Unfortunately, the intimate connection between our software and our hardware configuration (particularly our Computer Operations Linc Tape) precludes our sharing it with others.

John Baldo, now departed for Bristol, was an important partner in this work.

Sincerely,

Steve

Steve Patt

Brian

Brian Sykes

P.S. — We do offer this software tidbit for users of XL-100 program 16KVFT 994100-@ 20615: The routine for printing out the hertz-per-point produces incorrect values. To correct this problem, change locations 5562 through 5564 to 5001, 170323, 170323, 30046.



December 27, 1974

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

Dear Professor Shapiro:

Observation of Slow Proton Exchange Between a Carboxylic Acid
and Its Salt

We have discovered recently that the fluorine-19 spectrum of perfluorobutyric acid and sodium perfluorobutyrate in acetone indicates that exchange between the protonated and non-protonated moieties is slow on the nmr time scale below -100°C . Splitting of the signal of the CF_2 adjacent to the carboxyl is particularly pronounced, the relative size of the absorptions in the low temperature spectrum being proportional to the relative amounts of acid and base present. Temperature also has a substantial effect on the chemical shifts. As may be seen in the figure, coupling between the methyl group and the CF_2 group adjacent to the carboxyl is greater than is coupling between the methyl and the central CF_2 group.

As far as we are aware, slow exchange on the nmr time scale between carboxylate anions and carboxylic acids has not previously been observed, although Olah and co-workers have found slow exchange at low temperatures in the proton spectrum of diprotonated carboxylic acids.¹

The spectra were recorded with the Fourier transform method. The methyl peak and a signal of hexafluorobenzene used for an internal lock were allowed to fold over into open portions of the spectrum and are not shown. Concentrations were about 8×10^{-3} for both the salt and the acid.

Sincerely,

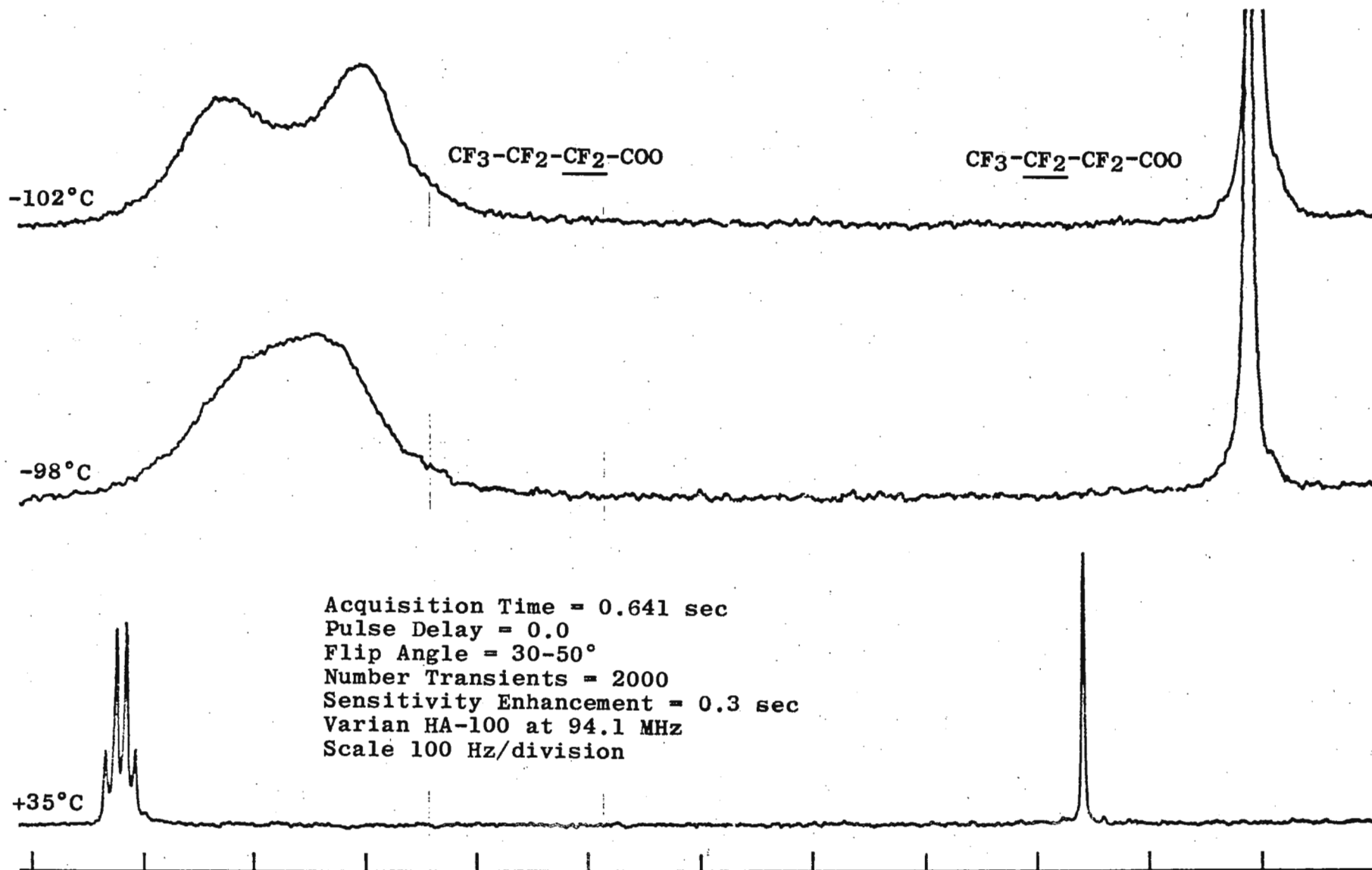
Paul Mark Henrichs *Stanley Gross*

PMH:nc
Enc.

Paul Mark Henrichs
Chemistry Division
Research Laboratories

Stanley Gross

¹G. A. Olah and A. M. White, J. Am. Chem. Soc., **89**, 3591 (1967).



THE ROYAL INSTITUTE OF TECHNOLOGY

DIVISION OF PHYSICAL CHEMISTRY

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SWEDEN

Stockholm, December 20. 1974

Cable address: Technology

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

Dear Barry,

Br-NMR in a gel system

Agarose is polysaccharide, which in hot water goes into solution. When cooled it forms a gel. Its melting and setting exhibits pronounced hysteresis¹.

The sol-gel transition may be monitored by measurements on the polysaccharide itself as well as on the water. This latter observation was earlier interpreted as a substantial modification of the state of water in the gel. Later investigations have, however, been rationalized in terms of rapid exchange between small amounts of bound water and essentially unperturbed liquid water in the bulk^{2,3}.

We have now shown that the sol-gel transition may also be followed by monitoring the line width of Br-NMR, when some alkali bromide is added to the agarose-water system (Figs. 1 and 2).

The line broadening of the bromide ion resonance is known to occur in a variety of aqueous solutions and are believed to arise from the presence of internal phase boundaries^{4,5}.

If our observed line broadening is due to the interaction of bromide ions with the agarose polymers, then this interaction is likely to take place by mediation of water molecules, since no ionic groups are contained in the polymer chains. The question now arises whether the small amount of bound water inferred from earlier investigations are capable of explaining

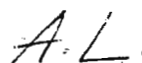
the bromide results or whether one has to consider either a different hydration number or several states of modified water. Three states of water in agarose gels have indeed been suggested by previous workers⁶.

Experiments aiming at a more quantitative description are now under way in this laboratory.

Sincerely yours,



Per Forslind

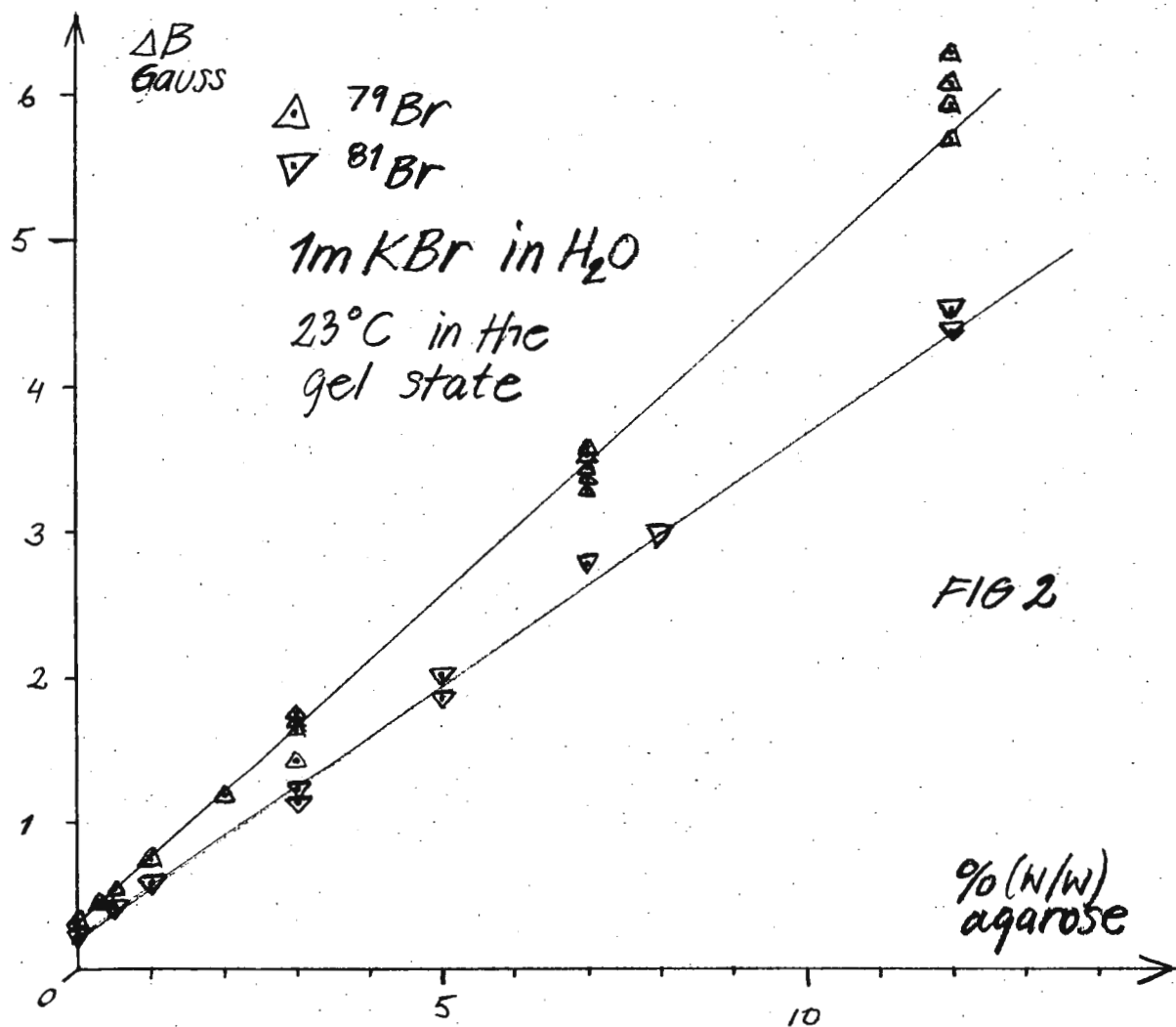
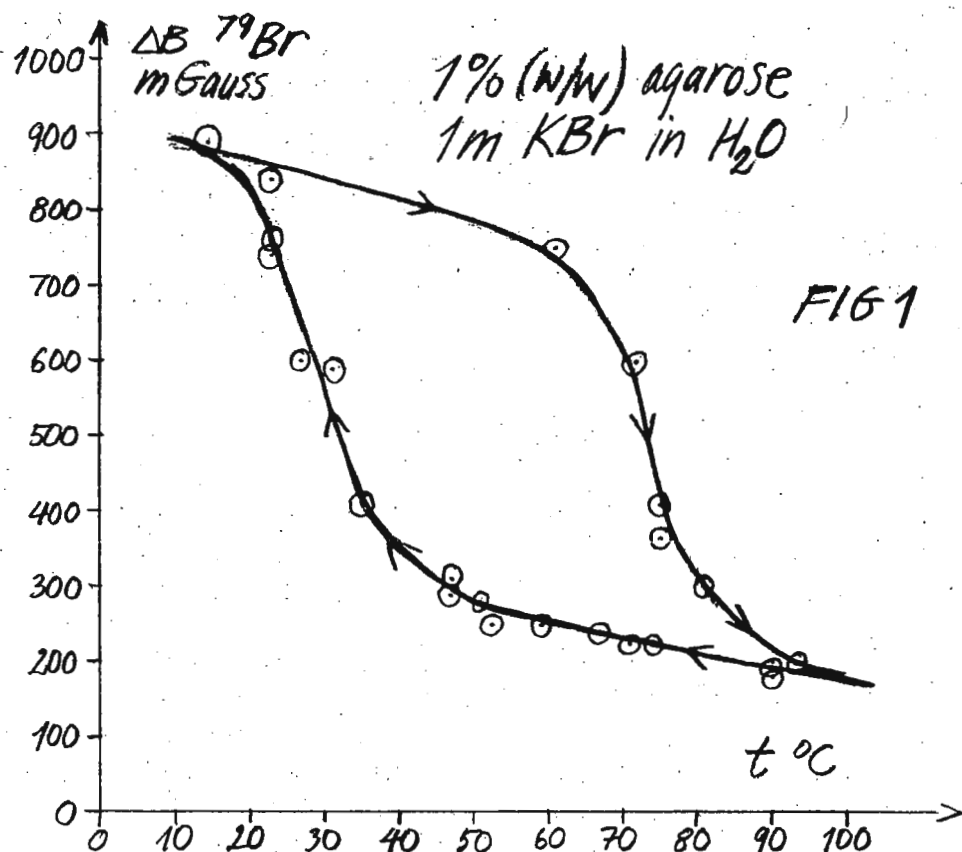


Anders Löfvenberg

P.S. Please credit this contribution to dr Ödberg's subscription.

References

1. D.A. Rees *et al*, J. Polymer Sci. Part C, 28, 261-76 (1969)
2. D.E. Woessner, B.S. Snowden Jr., J. Colloid and Interface Science, 34, (2), 290, (1970).
3. R.K. Outhred, E.P. George, Biophysical Journal, 13, 83 (1973).
4. B. Lindman, S. Forsén, E. Forslind, J. Phys. Chem. 72, 2805 (1968).
5. M. Zeppezauer *et al*, Biochem. Biophys. Res. Commun., 37, 137 (1969).
6. M. Aizawa *et al*, Bull. Chem. Soc. Jap. 45, 3031 (1972).



STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94035

STANFORD MAGNETIC RESONANCE LABORATORY

Professor Oleg Jardetzky

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

December 31, 1974

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

Dear Barry:

The Stanford Magnetic Resonance Laboratory is currently searching for an Operations Manager. Qualifications for the position include a Ph. D. in one of the exact sciences, expertise in High Resolution Nuclear Magnetic Resonance, facility with relevant instrumentation, including superconducting magnets, electronics and computer programming and familiarity with chemical and biophysical applications of the method. The level of expertise should be sufficient to qualify the successful candidate for an appointment as a Senior Research Associate or Adjunct Professor at Stanford University.

The primary duties consist of complete responsibility for the operation and maintenance of the 360 MHz spectrometer, consultation with qualified users, training and supervision of spectroscopists, development of new techniques and instrumental improvements. Some time for personal and collaborative research will also be available.

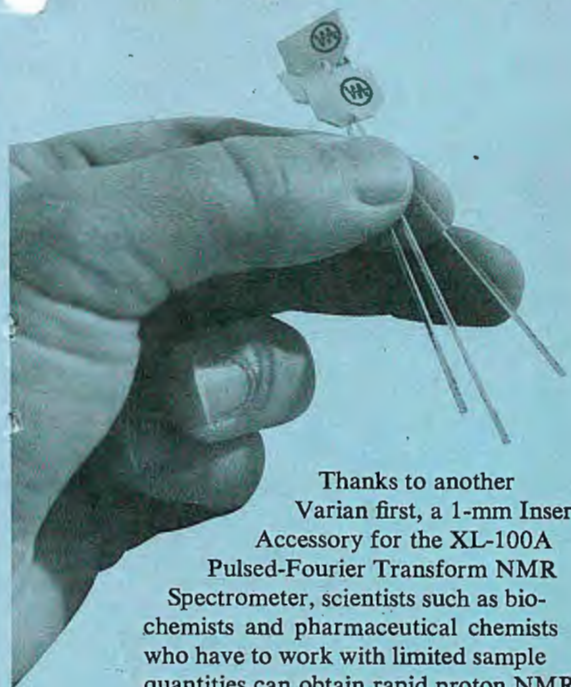
The position is currently advertised in accordance with University policy. The Administrative Committee for the Laboratory will be most grateful for your suggestions of suitable individuals. Nominations and applications from women and members of minority groups are especially welcome.

Yours sincerely,


Oleg Jardetzky

OJ:mv

Now the XL-100A NMR Spectrometer lets you think small.



Thanks to another Varian first, a 1-mm Insert Accessory for the XL-100A Pulsed-Fourier Transform NMR Spectrometer, scientists such as biochemists and pharmaceutical chemists who have to work with limited sample quantities can obtain rapid proton NMR analysis of microgram samples.

Using the insert, it's possible to run spectra of 50 μg or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of Δ^9 -tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 μg of sample in a 1-mm tube) and Spectrum C (20 μg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

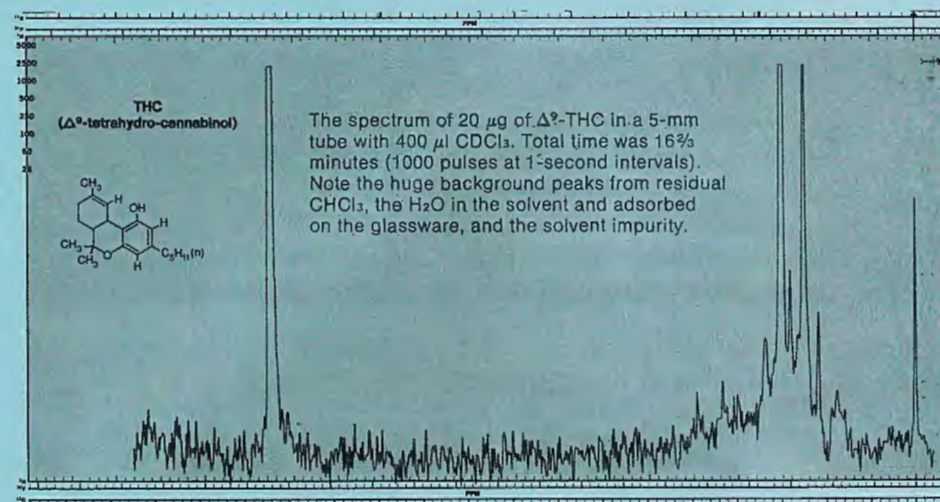
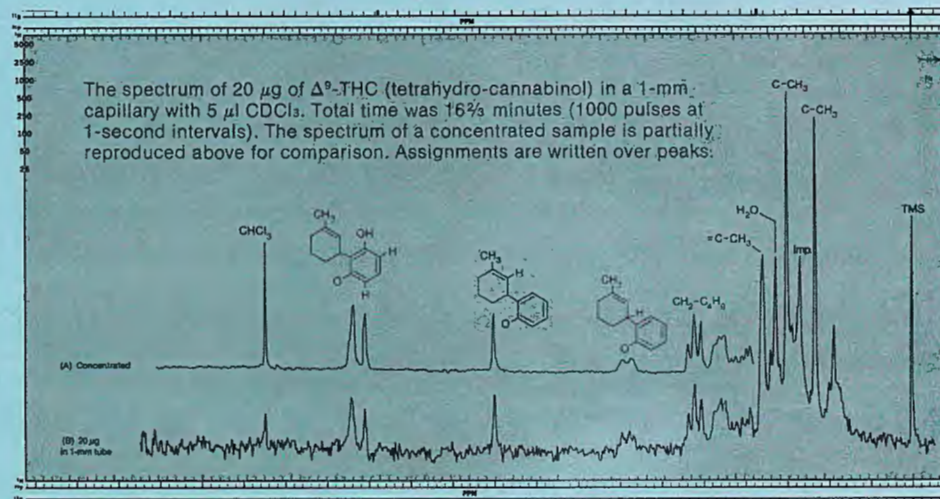
This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5 μl of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

The sample volume in the 1-mm Insert is so much less than the 400 μl required for 5-mm tubes that use of deuterated species becomes more economical.

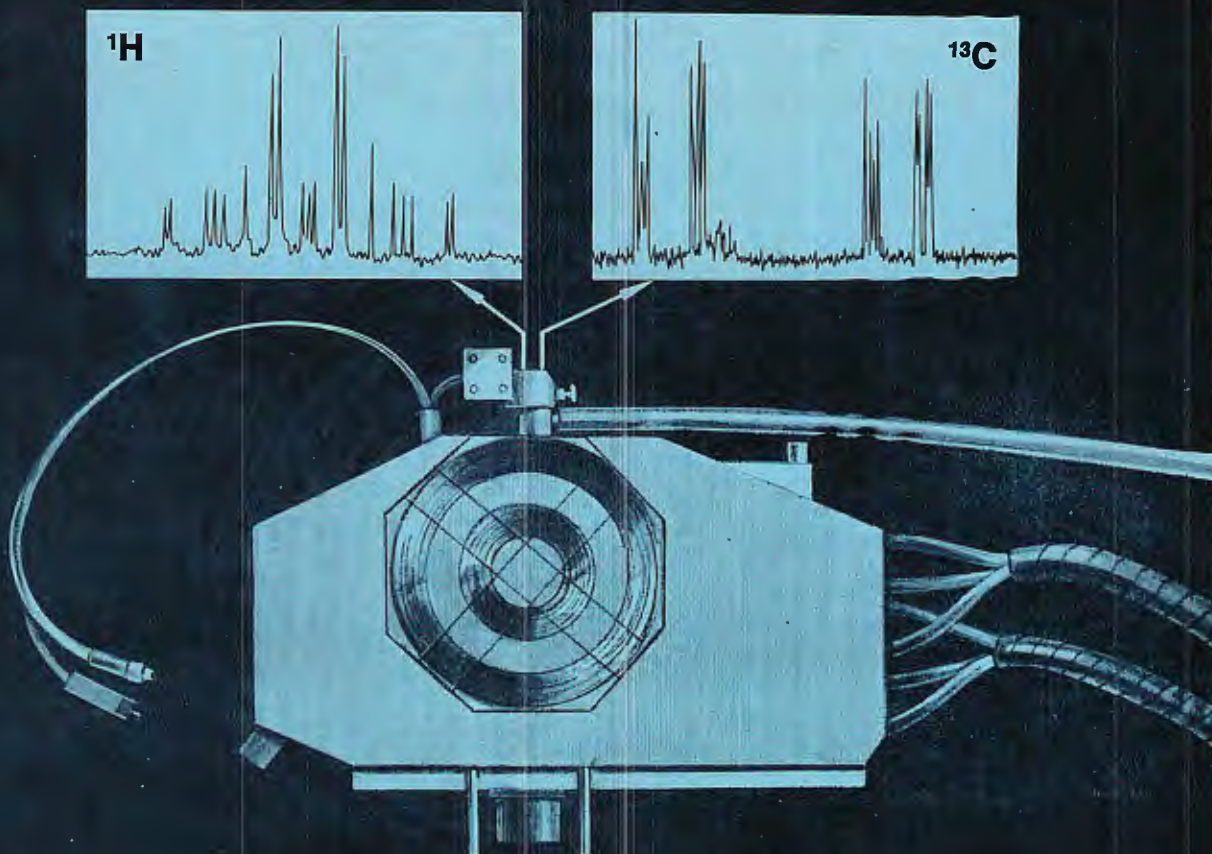
The 1-mm capillary has its own spinner turbine attached. Unlike other existing techniques designed to accommodate small quantities of samples, there are no plugs to adjust and no sample positioning is necessary. Proper positioning is automatic thereby assuring reproducible homogeneity.

Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.



Varian Associates
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Our FX60 $^1\text{H}/^{13}\text{C}$ Dual Probe makes even Lighter Work of FT NMR Spectroscopy

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