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N-M-R Newsletter

No. 201

June, 1975

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Deadline Dates: No. 202: 7 July 1975
No. 203: 4 August 1975

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.

A U T H O R I N D E X - TAMU NMR NEWSLETTER NO. 201

IWAN N. STRANSKI-INSTITUT
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Dr. L.Pogliani

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

^{13}C-T_1 of Carboxyl Carbon in L-Proline

Dear Prof. Shapiro,

in a recent work (1a, b) it has been shown that the proton chemical shifts of L-Proline and L-HydroxyProline depend on the position of the Carboxyl plane. Preliminary T_1 measurements, in undegassed solutions, of the Carboxyl group in L-Proline gave the following results at different pH values:

pH =	1.0	2.0	5.0	7.5	9.2	10.0	11.0
T_1 =	3.1	4.6	6.8	5.7	4.1	8.5	6.2 (sec.)

A similar trend of values is observed in other amino acids (2), in acidic and neutral solutions. Although these values must be handled with care (see, e.g. TAMU NMR Newsletter 195-9 (1974)), we would like to put forward some suggestions. At $pH < 10.0$, where L-Proline assumes prevalently acidic and zwitterionic structures, our data are in accord with the behaviour of the other amino acids. However we note at $pH \geqslant 10.0$ a consistent increase in T_1 values not observed in other cases. We suggest that this fact may be due to a relative lowering in the hindered intramolecular rotation around the C_α-C_o bond, due to the influence of the lone pair electrons at the N atom interacting with the negatively charged COO^- group, being the internal rotation around the C_α-Co bond responsible for the variations in ^{13}C-T_1 values of the Carboxyl Carbon in amino acids (2). The consequent change in direction of the magnetically anisotropic COO^- planar group causes a corresponding change in direction of the magnetic contribution of this group, detected by the proton chemical shifts of the molecule.

I would like to thank my friend M.Ellenberger from C.E.N. de Saclay Dr. J.Y.Lallemand from Ecole Normale Supérieure de Paris and Dr. D. Ziessow from this institut for their assistance and help.

Best Wishes

Yours sincerely

L.Pogliani

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2- R.Deslauriers, I.C.P.Smith, "Topics in ^{13}C-nmr Spectroscopy" 2, ch.1, (1975), ed. by G.C.Levy, John Wiley Interscience, N.Y., to be published

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DEPARTMENT OF CHEMISTRY

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

6th May, 1975.

Dear Barry,

Effects of Relaxation Reagents on the Relative Width of Lines in Spin Multiplets. ^{15}N Puzzle

Since our issues of TAMU come by sea I have only recently seen Charlie Reilly's letter and queries on the above topic in number 197. Today, I received copies of the letters and answers of Gitte and Bob Vold, Jerry Heeschen and Zeef Luz in issues 198 and 199. The copies were made and sent to me by Rosanna Mondelli since she, Giovanni Fronza and I asked ourselves Charlie's questions some time ago. The results were published in J. Chem. Soc., Chem. Comm., 1974, 195 under the title above (reference 1).

Question 1. Charlie's first question (Why?) has been reasonably answered by all the above. Our first statements were in terms of a "generalized random field model" which included the scalar possibility.[1] That has been excluded now by a discussion "Differential and Non-differential Line Broadening Effects of Relaxation Reagents on Spin Multiplets in Liquids" concocted by Durgu Rao and I and accepted for Chemical Physics Letters (reference 2). The main point here was to explain the fact[1] that although broadening occurs for $-CD_2$ and $-CD_3$ fragments there is no differential effect between the lines in the multiplets as for -CD fragments. The explanation is done in terms of a random field, uncorrelated at the ^2D sites. This lack of correlation suggests that the mechanism is in fact dipolar rather than scalar. Incidentally, I persuaded Durgu to become interested at the Rayleigh ENC Meeting at which I conducted an interesting experiment related to Charlie's question 2 (How general is the phenomenon?).

Question 2. The generalisation in terms of the spin $\frac{1}{2}$ nucleus and the quadrupolar nucleus (except for more than one quadrupolar nucleus in the spin system) is reported in reference 1. The generalisation in terms of the paramagnetic was achieved in Rayleigh. I accepted free samples of gadolinium fod, and $CDCl_3$ from the Norell Chemical Company outside the lecture theatre. These were mixed in a Wilmad n.m.r. tube obtained at cocktails and the ^{13}C spectra were run on the Bruker demonstration instrument. The result was the same as for $Cr(acac)_3$! This was the zenith of my research entrepreneurship.

Question 3. Preliminary measurements in Milan by Giovanni Fronza show a lack of differential T_1 effects at the three ^{13}C lines of $CDCl_3$. You will have gathered that the investigation is a well travelled one. It also has an even earlier history. The effect first came to my attention (accidentally, of course) in a spectrum which Ed Rosenberg took here in 1972. The spectrum was published but we made no comment at all on the effect (J. Chem. Soc., Dalton, 1973, 1674). I hoarded the observation until it could become useful (the spectrum shows large effects on the ^{13}C resonance of C_6F_6 too, incidentally). In fact, the 'something or other' for which Gitte and Bob Vold suggest the effect is useful has in my case been to occasion visits to Milan. Once we also went to Bologna (for a T_1 measurement on Dr. Boicelli's instrument) where I can recommend the food.

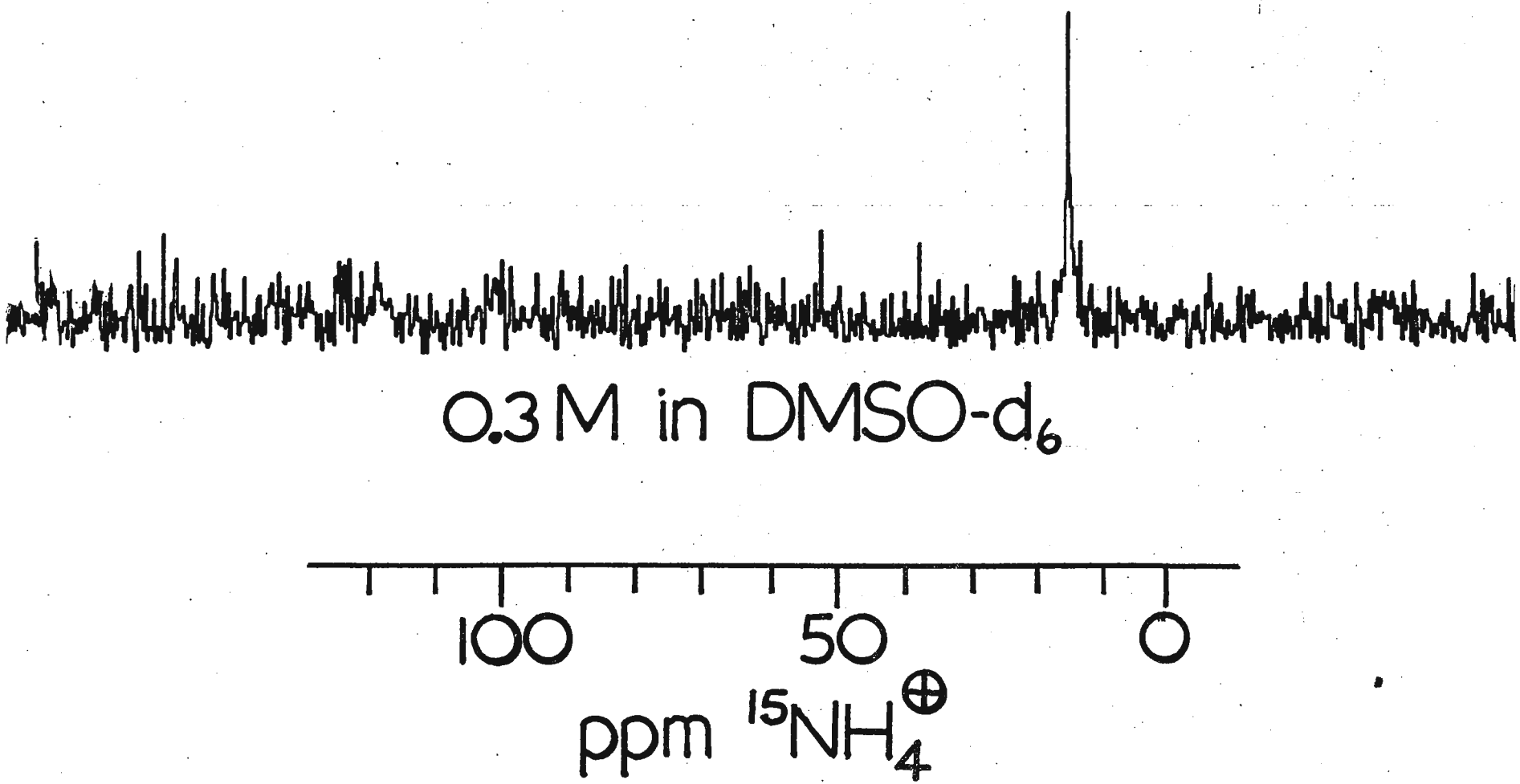
^{15}N Puzzle. Let me now bring your attention to another interesting spectrum due to Geoff Hawkes. It is a proton noise decoupled ^{15}N spectrum (at natural abundance) of Gramicidin-S in DMSO (N.B., no relaxation or other reagent has been used). The question is how to explain the absence of ^{15}N signals in the amido region (they can be observed under other conditions). An additional question is: how many ways are there of nulling ^{15}N resonances? Geoff and I have delineated about five ways, all contained in a note submitted to, but not yet accepted by, J. Mag. Res. "Had we but world enough and time" I would suggest a competition (with an entrance fee to swell your funds) based on these questions. Unfortunately the note may (if accepted) be out too soon for you to mount such a venture but, if you wish to proceed please do. The idea might appeal to you as a general fund raising technique! Should the note not have appeared by the time of the St. Andrews Meeting (July 6-11th) (see issue No. 194), any participant there with a valid solution may claim a prize. Its nature will depend upon the gender of the winner.

Rosanna Mondelli asks that you credit this contribution to her group!

Yours sincerely,

Ed.

Professor E.W. Randall.



Natural Abundance ^{15}N spectrum (9.12 MHz) of Gramicidin S:- cyclo-(-D-Phe-L-Pro-L-Val-L-Orn-L-Leu)$_2$; ^{1}H Noise decoupled, 15 mm o.d. tube, 120,000 scans in ca. 14 hours.

Department of Chemistry

YORK UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

May 7th 1975.

Dr. Barry Shapiro,
Dept. of Chemistry,
Texas A & M University,
College Station, Texas.
77843.

Dear Dr. Shapiro,

Teaching Postdoctoral Position.

We are looking for suitable applicants for a teaching postdoctoral position which will be open this september (1975) for one year at a salary equivalent to the NRC scale.

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Enquiries should be addressed in the first instance to one of us (below). The names of two referees willing to support an application are required, and it would be appreciated if the applicant would ask at least one of these to send a letter of reference to arrive near the same time as the application.

Yours sincerely,

for C. E. Holloway,
D. V. Stynes,
I. M. Walker.

Department of Chemistry.

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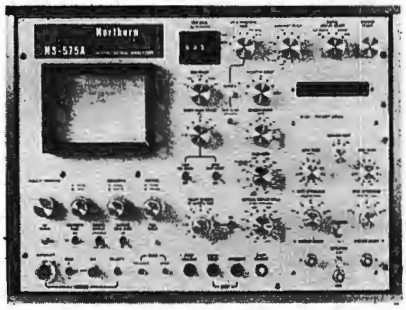

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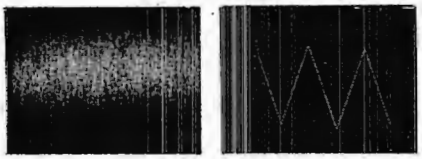

Left: NS-575A with Biomation plug-in module examines severe noise situation. Right: 100KHz triangular waveform is detected after 1024 sweeps (real time = 8 sec.).

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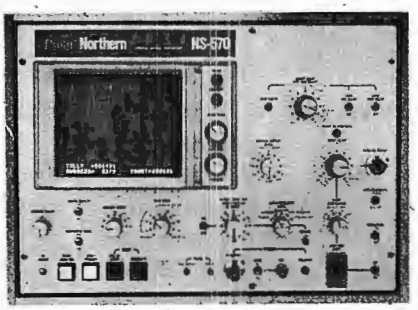

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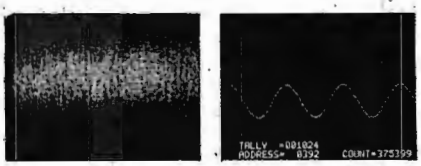

Left: NS-570 in a direct averaging application examines a severe noise environment. Right: Sine wave is detected after 1024 sweeps (real time = 20 sec.).

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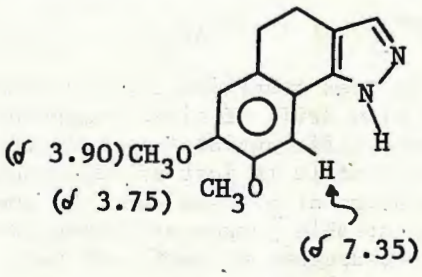
May 11, 1975

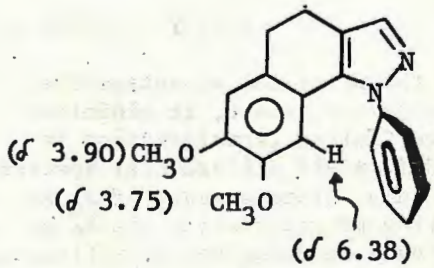
Professor B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, TEXAS 77843

Title: Non Planarity in N-Substituted Pyrazoles

Dear Dr. Shapiro:

We wish to report as our contribution to NMR Newsletter part of a study on certain N-substituted (aryl) pyrazoles in which evidence is presented that aryl groups can be orientated in a specific manner. Our best case is that shown below:





Note the observed shielding of the ring proton nearest to the phenyl ring attached to the nitrogen atom. This suggests that the phenyl ring is turned nearly perpendicular to the lone proton. There is some perturbation of the protons on the nearest methoxy group as well although the methoxy group furthest removed is unaffected. These molecules exhibit some biological activity and work is continuing in the area.

Sincerely yours,

Darrell

K. D. Berlin
Regents Professor

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8th May, 1975

RF/EP

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

Dear Barry,

Differential-Mode T_1 on CFT-20

Some years ago we suggested a mode of operation for inversion-recovery spin-lattice relaxation measurements, in which the spectra were plotted in a difference mode ($S_\infty - S_t$) as a function of the pulse interval. (J. Chem. Phys. 54, 3367 (1971)). The pulse sequence used,

$$[\ \ldots T \ldots\ 90^\circ(S_\infty)\ \ldots\ T\ \ldots\ 180^\circ\ \ldots\ t\ \ldots 90^\circ(S_t)\ \ldots.]_n$$

had the principal advantage that, by subtracting free induction signals obtained only seconds apart, it minimized errors due to slow drift of field homogeneity. Since Fourier transformation is a linear process, differential free induction signals yield differential spectra. We believe that it is just as important to get an accurate measure of S_∞ as an accurate measure of S_t, and that the computer-fitting programs which use S_∞ as an additional variable parameter (alongside T_1) are only reducing the significance of each S_t measurement by half, and hence have no net advantage.

There are some further conveniences which result from measuring T_1 by the differential mode. The T_1 program on the Varian CFT-20 for example, enters pulse intervals in terms of the initial pulse interval LT and the additive increment LI. (The multiplicative mode has steps that are too coarse.) With this system, it is not really possible to choose pulse intervals that are at the same time well matched to the sensitive part of the exponential recovery curve, and yet include a final interval sufficiently long to measure S_∞. The differential mode avoids this problem; relaxation times can be obtained even for experiments which failed for some reason before all the traces were obtained.

Another feature of differential-mode spectra is that the signals are always positive and they decay exponentially to zero. They thus avoid the problem of conventional inversion-recovery spectra when a signal near the null condition gets lost in the noise. Positive-going spectra may be more economically stacked on the recorder chart in the usual "three-dimensional" display, and following an individual line in very complicated spectra may be easier in this mode. It also allows the existing subroutine for peak-height print-out to be extended to T_1 studies (the program only detects maxima). This is particularly important in overnight runs where cassette or disc storage is not available, and where the

recorder pen may fail to write. It also relieves the tedium of measuring peaks with a ruler, and simplifies the process of feeding T_1 data into a least-squares fitting routine. (We also use this option as a method of interrupting and resuming an inversion-recovery run, since the program will stop if the printer is switched off. Modifications to the parameter list can be made and the program will then resume if the printer is switched on and the command LS is entered.)

We have written patches for the 16K version of the CFT-20 program part number 994114-07 revision E, and will be glad to provide details to any newsletter readers on request.* It requires the use of the computer front panel since we use the three sense switches to call in the three modifications, or to switch back to normal operation. The first patch (sense switch 1) modifies the pulse sequence to the one shown above. An even number of transients must be used. The second patch (sense switch 2) subtracts memory contents from the incoming signal where previously they were added. This has the effect of alternating the sign of the incoming free induction signal. The option can be used independently for many kinds of difference spectroscopy, for example double resonance/single resonance. (In this patch we also take care of a little problem with the d.c. correction of the free induction signal.) The third patch (sense switch 3) automatically prints out the peak heights. It can be used in the differential mode inversion recovery sequence or anywhere else that automatic listing could be useful.

Yours sincerely,

Geoffrey Bodenhausen
David Turner
Ray

Geoffrey Bodenhausen
David Turner
Ray Freeman *

ORGANISCH CHEMISCH LABORATORIUM
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CROESESTRAAT 79
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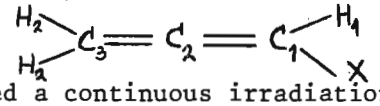
UTRECHT, may 13, 1975

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

Dear Professor Shapiro,

Deceptive Intensities in Selective Population Transfer experiments.

Recently some authors[1,2] have shown that the selective population transfer (SPT) technique is a very useful method for sign determination of long-range $^{13}C-^{1}H$ coupling constants. We used this method in order to determine the signs of $^{2}J(^{13}C\text{-}2,{}^{1}H\text{-}1)$ and $^{2}J(^{13}C\text{-}2,{}^{1}H\text{-}2)$ in some monosubstituted allenes (1) :



In our experiments we applied a continuous irradiation field H_2 ($\gamma H_2/2\pi = 0.2$ Hz) to one of the ^{13}C-2 satellites in the proton spectrum and recorded the ^{13}C spectrum of C-2 in the FT-mode. The observed intensity changes for those ^{13}C transitions which are progressively and regressively connected to the irradiated proton transition are due to so-called "generalized Overhauser effects". However, in this kind of experiments the pulse spectroscopy is applied to a system in a nonequilibrium state as defined by Ernst[3,4]. Therefore the observed intensity changes may depend on the flip angle of the non-selective ^{13}C-pulse. We studied this effect by taking some spectra at various flip angles.
The single resonance ^{13}C spectrum of Fig. 1a represents the C-2 region of chloroallene: a doublet due to coupling with H-1 and a triplet due to coupling with H-2. For the spectrum of Fig. 1b the rf field H_2 was placed at the resonance position of the most low field ^{13}C-2 satellite of H-2. The flip angle of the ^{13}C-pulse was 20°. As can be seen from this figure the progressively connected C_1-transition had an intensity of $+2\frac{1}{2}$ times its normal value, whereas the regressively connected C_4 transition had an intensity of $-\frac{1}{2}$ times its normal value. For saturation of the proton line the theoretical intensity changes are: +3 for the C_1 transition and -1 for the C_4 transition. In Fig. 1c the experiment was repeated under the same conditions except for the flip angle, which was 80°. The intensity of the regressively connected transition (C_4) now was $-2\frac{1}{2}$ times its normal value, whereas no serious intensity changes were found for the other resonances, including the progressively connected one! From these results it should be clear that

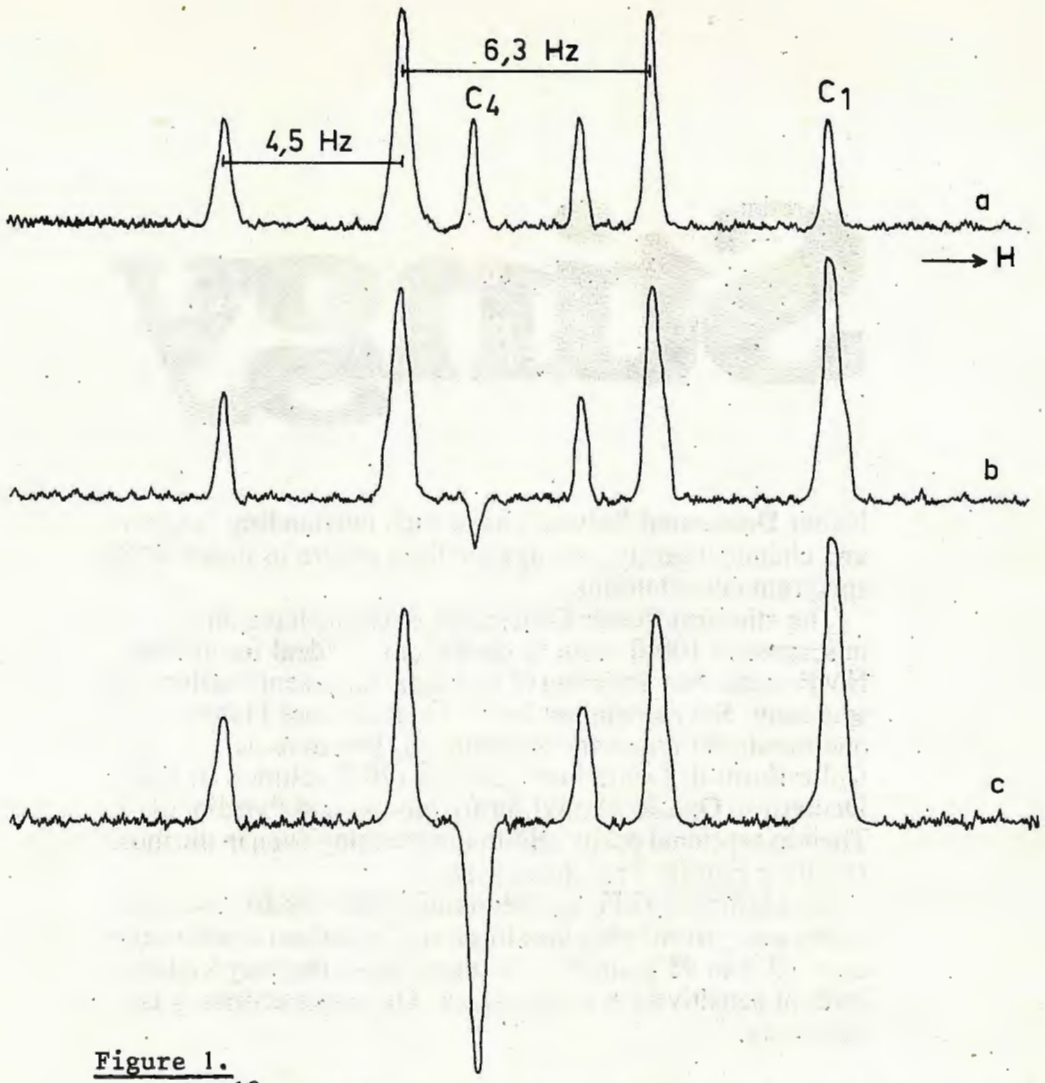


Figure 1.

25.2 MHz ^{13}C FT NMR spectra (Varian XL-100-15; 16k) of chloroallene (C-2).

a. Single resonance spectrum.

b. Continuous irradiation of the most low field ^{13}C-2 satellite of H-2; $\alpha = 20^{\circ}$.

c. Ibid. ; $\alpha = 80^{\circ}$.

Spectral parameters: acquisition time 4.0 s; pulse delay 0.0 s; number of transients 250.

care has to be taken in the quantitative interpretation of intensity changes in SPT experiments, especially at large flip angles.

References: 1. K.G.R. Pachler and P.L. Wessels, J. Magn. Resonance 12, 337, (1973).
2. S. Sørensen, R.S. Hansen and H.J. Jakobsen, J. Magn. Resonance, 14, 243, (1974).
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4. S. Schäublin, A. Höhener and R.R. Ernst, J. Magn. Resonance 13,196, (1974).

Please credit this contribution to the account of M.J.A. de Bie.

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N.J. Koole

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May 13, 1975.

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

Dear Dr. Shapiro:

Cyclobutane Rings in NMR and Biology

The cyclobutane ring system presents a challenging problem to NMR spectroscopists and is of considerable interest to scientists in the area of nucleic acid chemistry. Cyclobutane rings are generated by covalent linking of adjacent thymine bases upon u.v. irradiation of DNA. The formation of these thymine dimers causes local melting of double-helical DNA. We are attempting to evaluate some of the conformational consequences of thymine dimer formation with our PMR studies on the dinucleoside monophosphate d(TpT) and its u.v. - damaged counterpart d(T[p]T). Their 220 MHz (D_2O) spectra are shown in Figures 1 and 2. We were pleasantly surprised to find that the spectral bands were, for the most part, well separated and thus good spectral simulations could be obtained. The 6-hydrogen resonances of d(TpT) are located at 7.7-7.8 p.p.m. relative to TSP. In the photodimer they appear as an AB quartet centred near 4.30 p.p.m. ($J = 6.0$ Hz). This upfield shift and the mutual H_6-H_6 coupling constant is consistent with the presence of a cyclobutane ring in d(T[p]T).

There are some striking differences in the splitting patterns of the two molecules, particularly for the 4'-, 5'-, and 5"-hydrogens of their pT and [p]T fragments. These spectral changes can be translated into conformational changes and indicate that some distortion in the sugar-phosphate backbone is required to bring the thymine bases into an orientation suitable for covalent bond formation. Note, however, the similarity in the 5',5"-bands for the Tp and T[p] fragments (c.a. 3.7 p.p.m.). This indicates that the conformation of the hydroxymethyl group is essentially unaffected by the thymine dimer formation. We hope to extend the photodimer at the 3'-and 5'-positions in order to determine what influence, if any, dimer formation has on adjacent nucleoside fragments.

Please credit this effort to Ted Schaefer.

Sincerely,

Frank Hruska

F. E. Hruska,
Associate Professor.

Donald Wood

D. J. Wood

FEH/ud

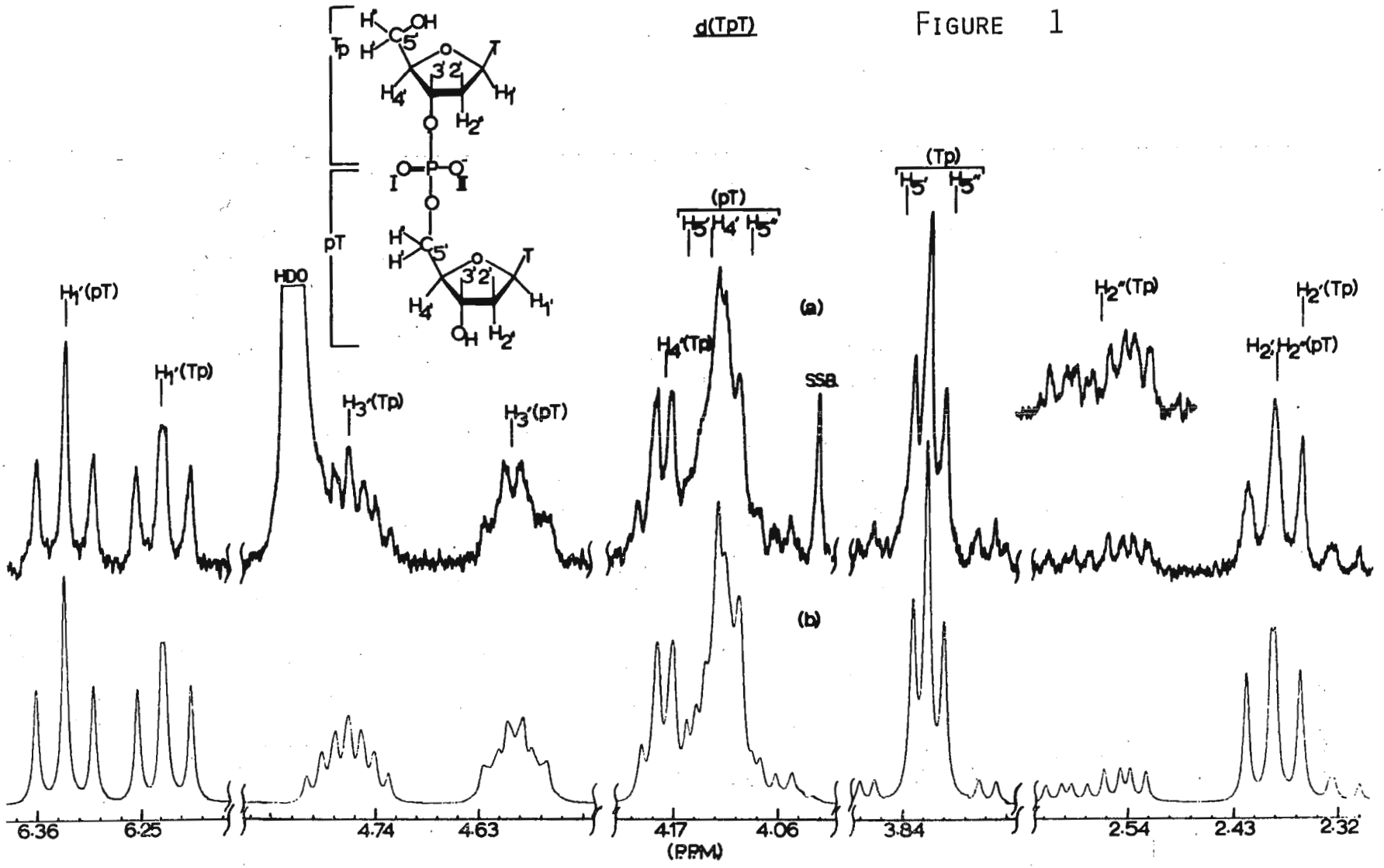
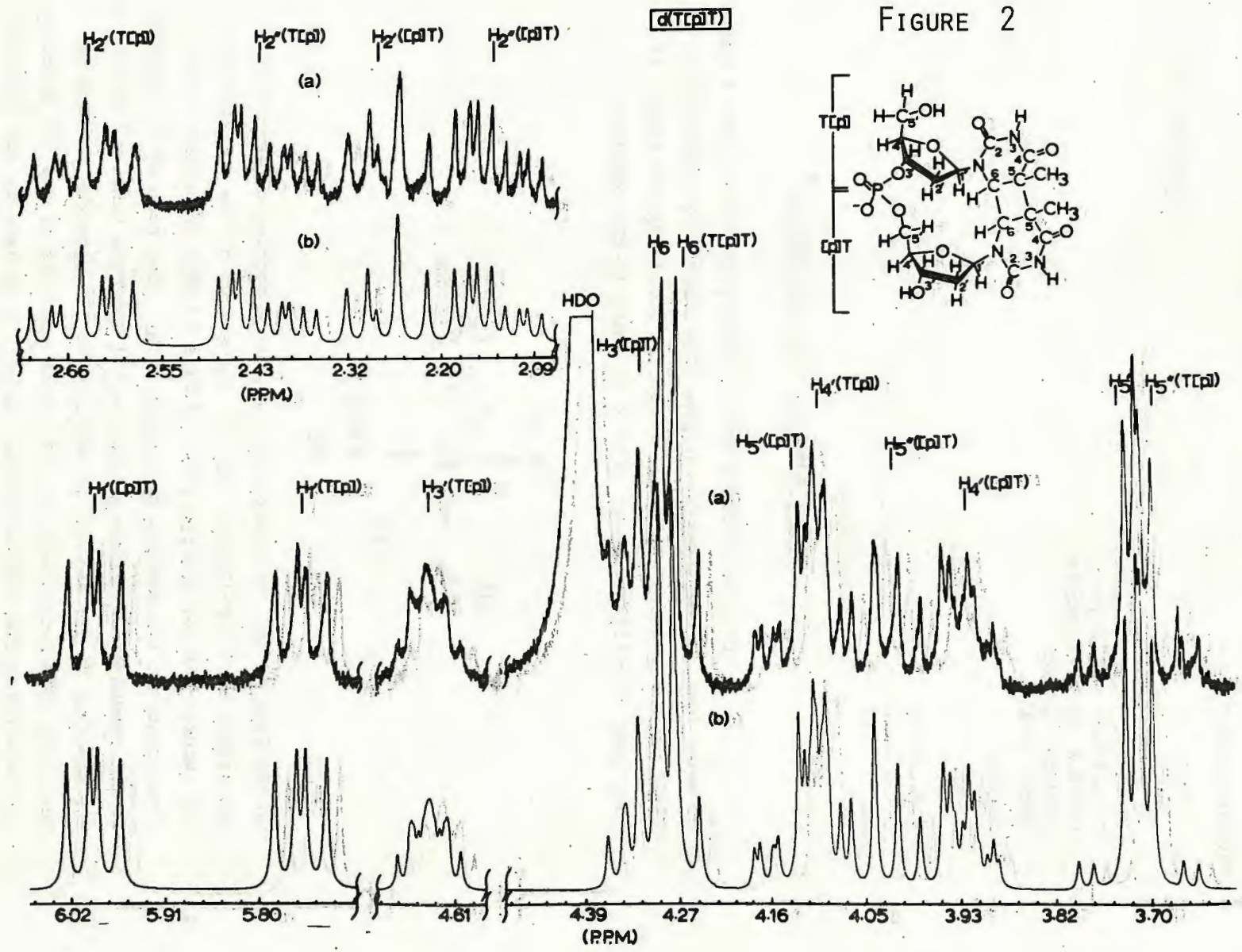

d(TpT)
Tp
pT
H1'(pT)
H1'(Tp)
HDO
H3'(Tp)
H3'(pT)
(pT)
H5'
H4'
H5''
H4'(Tp)
(a)
SSB
(Tp)
H5'
H5''
H2''(Tp)
H2'(Tp)
H2',H2''(pT)
(b)
6.36
6.25
4.74
4.63
4.17
4.06
3.84
2.54
2.43
2.32
(PPM)

FIGURE 1

FIGURE 2


d(T[p]T)
T[p]
[p]T
(a)
(b)
HDO
(PPM)
2·66
2·55
2·43
2·32
2·20
2·09
6·02
5·91
5·80
4·61
4·39
4·27
4·16
4·05
3·93
3·82
3·70

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DEPARTMENT OF CHEMISTRY

JMB/SC 13th May, 1975.

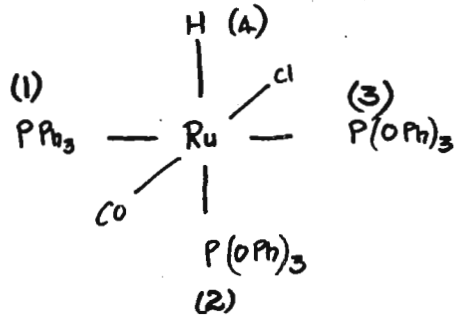
Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station,
Texas 77843,
U.S.A.

Dear Barry,

SUGGESTED TITLE

"FINGS AINT WOT THEY USED TO BE"*

Stephen Robinson has recently provided us with a number of metal hydride complexes which show some remarkably complex high field proton spectra; moreover things are not always as simple as they seem at a first glance. A case in point is the compound I.



I

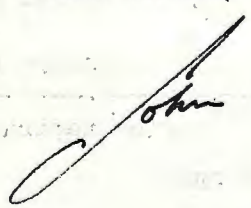
On the face of it, the hydride spectrum is a doublet of doublet of doublets due to ^{31}P-^{1}H coupling, but inspection of the computer print out (Bruker HFX-90, Nicolet 1084, ^{1}H FT @ 90 MHz) shows there to be no consistency in the doublet splittings (FIG). The root of the problem is the second order nature of the overall spectrum since $\nu_0\delta/J$ for the ^{31}P spectrum of (1) and (2) is small. The ^{31}P spectrum at 36.4 MHz bears out this hypothesis. An iterative analysis of the ^{31}P spectrum was made using the ITRCAL program (which can be used on the 1084 without either disc or cassette, and making use of the hardwired plot) regarding the ^{31}P spectrum as ABX under conditions of complete proton decoupling.

The analysis was then extended to a 4 spin system introducing (4) as an X nucleus (i.e. with a well separated chemical shift) and allowing all the hydride coupling constants to vary, but ignoring the presence of the phenyl groups in the system. Iteration was allowed on the proton transitions alone.

The ^{31}P spectrum was repeated with specific decoupling of the phenyl protons, but allowing the $H_{(4)}$ transitions to remain, hopefully unperturbed. The simulated spectrum using the ^{31}P parameters and ^{1}H parameters from the previous spectra have precious little resemblance to the observed spectrum, but allowing the ^{31}P-^{1}H couplings, then the ^{31}P-^{31}P couplings, and finally all parameters to vary, a good simulation was obtained. What transpired was that <u>all</u> the $J_{^{31}P-^{1}H}$ couplings had been reduced: obviously the power necessary to decouple the phenyl protons had effectively brought about an off-centre decoupling type of experiment as regards the hydride couplings, hence the title! In keeping with some other simulations we have performed $J^{trans}_{^{31}P-^{31}P}$ is of opposite sign to $J^{cis}_{^{31}P-^{31}P}$; $J^{trans}_{^{31}P-^{1}H}$ and $J^{cis}_{^{31}P-^{1}H}$ likewise, and $J^{trans}_{^{31}P-^{31}P}$ and $J^{trans}_{^{31}P-^{1}H}$ are of like sign (TABLE).

Please credit this contribution to Dennis Hall, and long may it keep the blue wolf from the door!

Best wishes,



J. M. BRIGGS.

---

*Including, perhaps, the Queen's English. What would Fowler say?!

B. L. Shapiro

TABLE

	SPECTRUM	SPECTRUM	SPECTRUM
	^{31}P ABX	^{1}H ABMX	^{31}P ABMX
J_{12}	34.4†	34.4	31.2 †
J_{13}	-463.0†	-463.0	-457.5 †
J_{14}		20.9 †	13.1 ††
J_{23}	36.8†	36.8	35.9 †
J_{24}		-194.6 †	-103.9 ††
J_{34}		18.1 †	8.7 ††
ν_1*	36.46†	36.46	36.45 †
ν_2*	122.48†	122.48	122.54 †
ν_3*	129.06†	129.06	129.16 †
ν_4**		-5.613†	-5.613
Assigned Trans	13	8	23
RMS Error	±0.843 Hz	±0.142 Hz	±1.85 Hz
Exptl. Error	±2.44 Hz	±0.610 Hz	±2.44 Hz

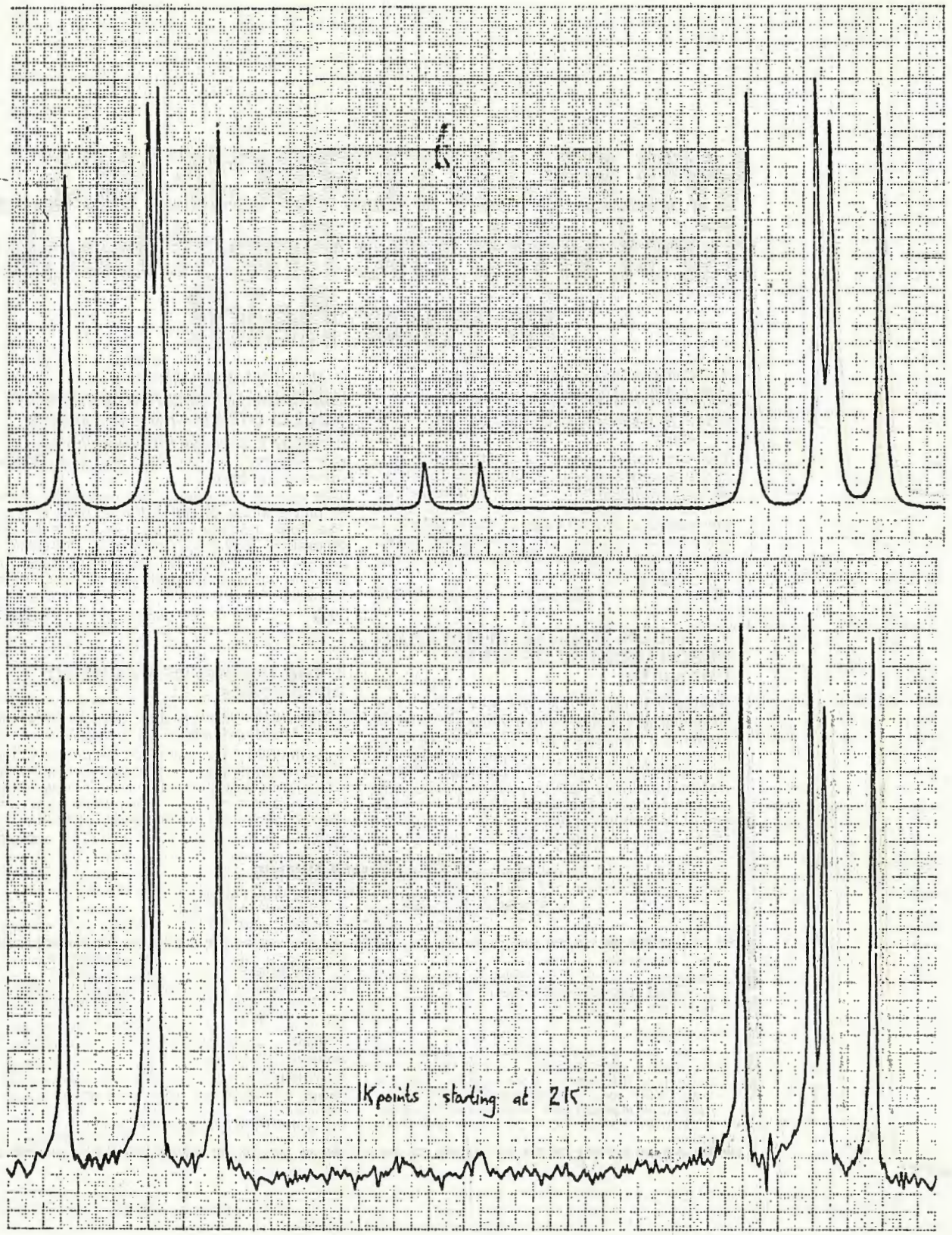
†Varied in iteration ††Varied separately in iteration

*w.r.t. ext. H_3PO_4 86% (δ ppm)

**w.r.t. int. TMS (δ ppm)

J_{x-y} in Hz

Parameters marked † agree to within exptl. error limits in ^{31}P spectra.



Observed (lower) and Calculated ^1H spectra of $Ru.PPh_3[P(OPh)_3]_2CO.Cl.H$ at 10·42 Hz/cm

F

Department of Chemistry

Colorado State University
Fort Collins, Colorado
80523

May 20, 1975

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

Dear Barry:

Bruker spectrometer owners might be interested in some relatively simple modifications we have made on the probe of our Bruker HFX-90 spectrometer to provide an external ^{19}F lock capability. As original equipment on our spectrometer, we have an internal ^{19}F lock, based on a double-tuned receiver coil (tuned for ^{19}F and for the nuclide being observed, e.g., ^{13}C). As internal locks are inconvenient to employ with some types of samples, even if a concentric capillary is employed, two of my graduate students, Jerry Dallas and Joe Ackerman, decided to modify the probe to incorporate the external lock capability. Two different configurations were explored. The basic layout is shown in the accompanying figure.

In both configurations the external ^{19}F tank circuitry was contained in a machined brass shielding compartment which fits snugly into a vacant region of the probe located at about 5 o'clock with respect to the active volume of the main (e.g., ^{13}C) receiver coil. Also in both configurations, the ^{19}F "magic T" and single coil tuning circuitry were contained in a second aluminum box that is attached to the probe; this box and its contents are identical to the original Bruker component used for the internal ^{19}F lock. Hence, both the internal and external lock circuitry are simultaneously intact in the probe, and the choice of which lock mode to use is implemented simply by attaching the appropriate cables from the spectrometer to the BNC connectors of the correct aluminum box.

The main differences between the two external lock configurations employed are the location and geometry of the ^{19}F receiver coil and the lock sample. In the first configuration, indicated by the heavy dotted lines in the figure, a neat sample of C_6F_6 in a 3 mm o.d. capillary was located within the brass compartment, with a 4 mm i.d. tuned receiver coil wound around the capillary (13 turns of 26 AWG magnet wire). In the second configuration, a neat sample of C_4F_8 in a 2 mm o.d. capillary was located closer to the main receiver coil. This was accomplished by inserting the lock sample and receiver coil (25 turns of 28AWG magnet wire)

Dr. Bernard L. Shapiro May 20, 1975

within a 5.4 mm x 39 mm tubular copper shield which is sealed at one end and with the open end inserted through the side and soldered to the machined brass shielding compartment. The tubular shield and its contents are located relative to the insert with their axes parallel approximately 2 mm away and directly alongside the main receiver coil, in the space which is normally occupied by the transmitter coil of the analytical channel. It was necessary to replace the ceramic transmitter coil housing with a duplicate made from machined plexiglass. A slot was drilled across the new plexiglass coil housing to accept the ^{19}F sample and copper shield. A replacement transmitter coil and a replacement coil for the second decoupler circuit were positioned on the plexiglass block directly alongside the tubular shield. Thus in the second configuration, the ^{19}F lock sample is positioned about 18 mm from the center of the main (e.g., ^{13}C) receiver coil in the 9 o'clock direction.

Excellent ^{19}F signal to noise ratios were observed in both configurations. The ^{19}F linewidths in the two arrangements are about 500 hz and 300 hz, the smaller linewidth corresponding to the configuration with the lock sample located nearest to the center of the main receiver coil.

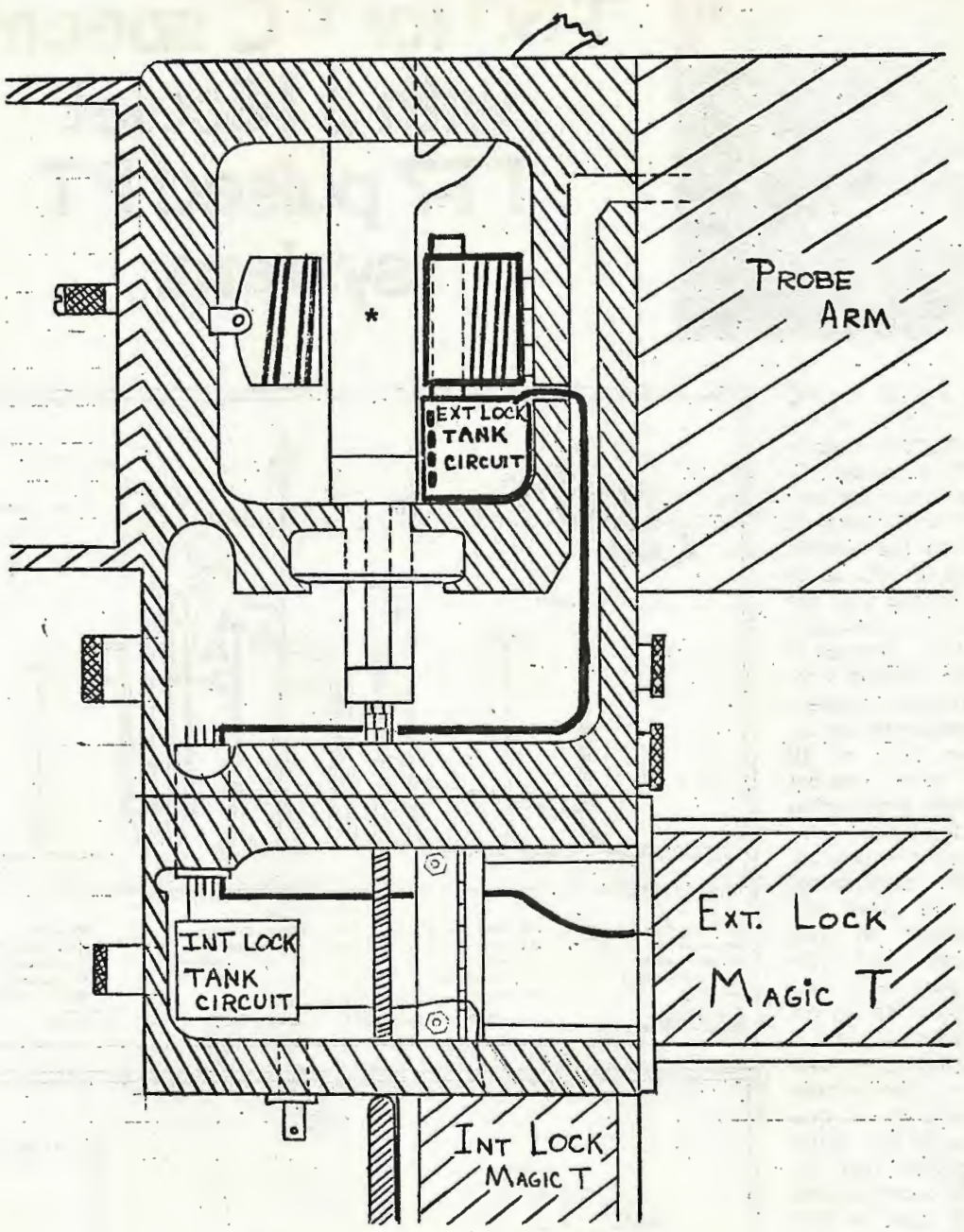
Satisfactory lock conditions were obtained with both arrangements. ^{13}C linewidths of less than 0.09 ppm are obtained for 8-hour, time-averaging FT experiments.

Sincerely,

Gary

Gary E. Maciel
Professor

GEM/md
Enclosure



Probe layout with external ^{19}F lock

* location of main receiver coil (e.g., ^{13}C)

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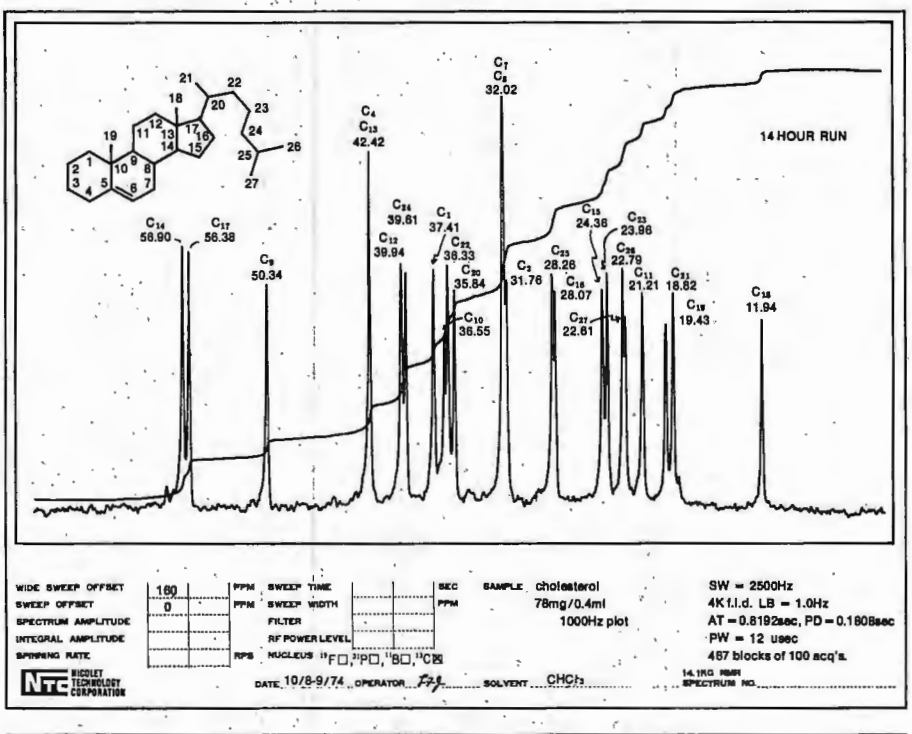

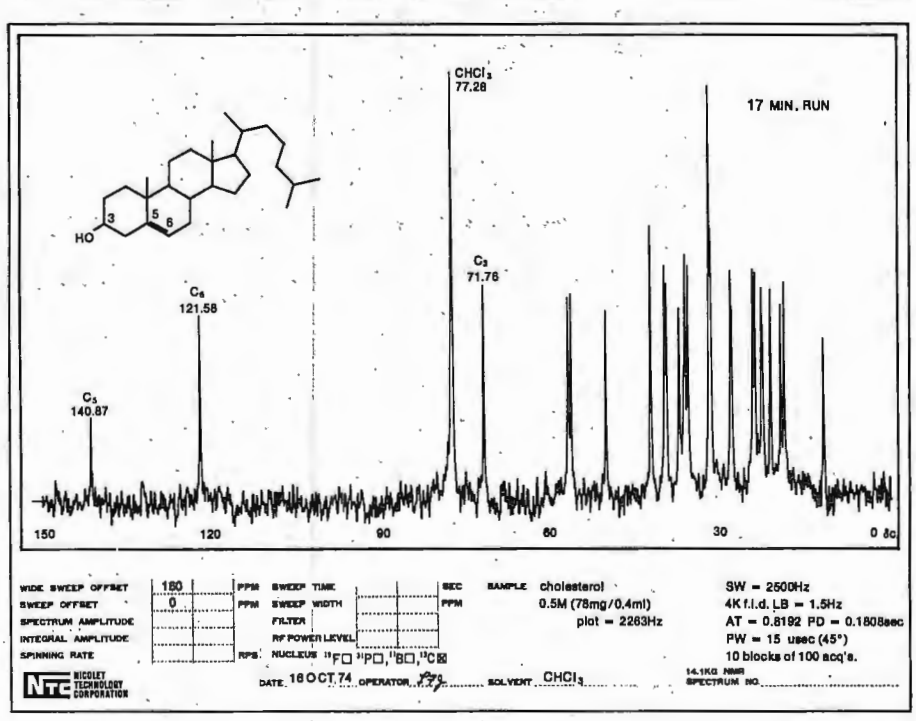

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DEPARTMENT OF CHEMISTRY

May 19, 1975

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

Dear Professor Shapiro:

Assignment of a ^{13}C Carbonyl Resonance in Oxytocin via Deuterium Substitution

The compound [6-hemi-[α-$^{2}H_1$]cystine]oxytocin has been synthesized in this laboratory in order to assign α-^{1}H and α-^{13}C resonances in oxytocin, as well as for use in ^{2}H NMR studies. We present results here showing how this compound can be used to assign the 6-half cystine carbonyl resonance in the ^{13}C spectrum of oxytocin.

The spectra in Figure 1 show the carbonyl region of oxytocin. The bottom spectrum is taken with complete decoupling (unlabeled oxytocin) while the top two spectra have no decoupling, the middle spectrum being unlabeled oxytocin and the top spectrum the specifically deuterated derivative. Though the interpretation of the undecoupled spectrum is complicated by the poor S/N ratio, it appears that the major change has occurred in the peak marked with an arrow. Deuteration of the α proton will effectively remove $J_{C-\alpha H}$, leaving only the smaller $J_{C-\beta H}$. Thus, the appearance of the spectrum changes from a doublet to a somewhat more closely spaced triplet. We therefore assign this resonance to the 6-half cystine carbonyl, in agreement with the assignment previously made by Deslauriers et al. (Biochem. Biophys. Res. Commun., 48, 854 (1972).

Please credit this contribution to the account of Mike Barfield.

Sincerely yours,

Jean-Paul Meraldi

Jean-Paul Meraldi

Donald A. Upson

Donald A. Upson

Michael Blumenstein

Michael Blumenstein

Victor J. Hruby

Victor J. Hruby

MB/VJH/JPM/DAU/mlt

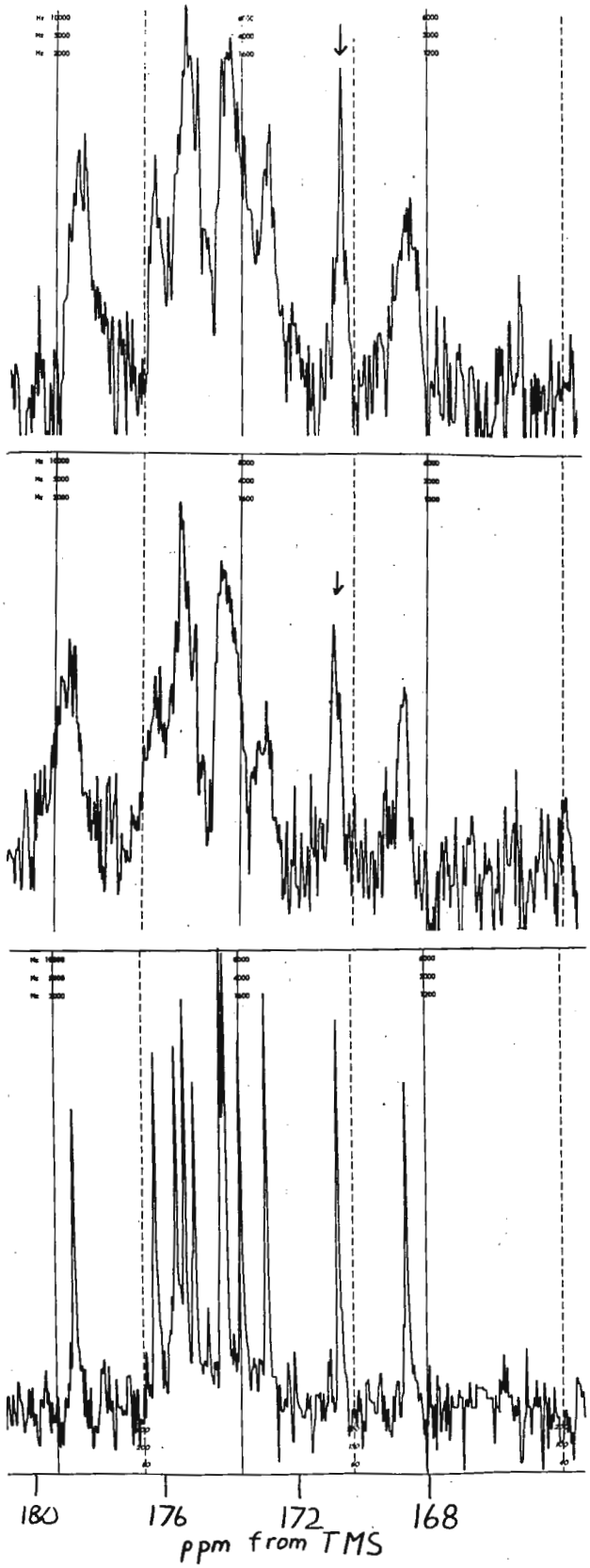

Figure 1. ^{13}C carbonyl region of oxytocin in D_2O, pH = 3.8 (direct meter reading). Bottom: unlabeled oxytocin, fully proton decoupled. Middle: unlabeled oxytocin, no decoupling. Top: [6-hemi-[α-$^{2}H_1$]cystine]-oxytocin, no decoupling. Spectra recorded at 22.6 MHz on WH-90 spectrometer; SW = 3000, 8K memory, 25,000 scans, repetition rate, 3.0 sec.

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PARIS, le 12 MAI 1975

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

Dear Professor Shapiro,

Title: THE USE OF THE FURFURAL CONFORMATIONAL EQUILIBRIUM AS A PRECISE TEMPERATURE PROBE IN ^{13}C NMR (+10°C;-70°C).

Accurate measurements of temperature during ^{13}C spectrum recording raise an embarrasing problem(1). Spectrometers are generaly provided with a temperature controler but there is always an appreciable difference between the temperature given by the controler and the real temperature of the solution, particulary when off-resonance experiments are performed. As it is not always possible to introduce directly in the solution neither a thermometer (capillary tube) nor a thermocouple (sealed samples), we found it was necessary to look for a compound which allow precise temperature calibrations in ^{13}C NMR, as methanol does in ^{1}H NMR. This sample must check the following conditions:

i)- Its concentration must allow the spectrum to be obtained with a small amount of pulses.

ii)- It must remain at liquid state at the lowest possible temperatures.

iii)- It must have one or several time-dependent parameters allowing significant measurements.

Formyl-2 furan seems liable to fulfil all these conditions. Indeed during the study of the cis trans conformational equilibrium of furfural(2), we noticed $\Delta\nu_{1/2}$ variations of carbon-3 signal on a wide range (-20°;-65°C) of temperature. So its measure can give a precise information about the temperature (fig. part A).

We used a sample of furfural (1ml)/$THFd_8$ (2ml) mixture. The ^{13}C spectrum is recorded in 80 s with a 50/1 sensitivity at normal temperature. For a 10 mm tube conditions are as following: spectral width: 5000 Hz, data points:8192, acquisition time: 0.8 s, pulse width: 20°. The spectrum is examined from 5000 to 2500 Hz with a ×2 expension in the course of C-4/C-3 measurements (fig. part C) and a ×10 expension for the $\Delta\nu_{1/2}$ determinations. Temperature recordings are performed before and after each run by introducing directly into the sample a previously carefully calibrated thermometer . We noticed for each change of the temperature read on the controler, and for a constant flow of nitrogen, a five minutes periode of stabilisation of the new temperature in the sample. The width of pulses has been choosen so that up to +10°C, the signals of protonated carbons might be largely relaxed during the acquisition time.

Averaged curves given fig. are obtained by solving a system of n non linear equations (n= number of data points = 45, part A):

$$\Delta\nu_{1/2} = f(a_1, \ldots, a_k, T);$$

T= temperature, a_k= coefficients of the theoretical function. The curves are run on a BENSON plotter connected to a UNIVAC-1108.

We have presently calibrated several spectrometers using this compound as external standard. The precision is about $\pm$ 1°C.

Please credit this letter to Bernard ROQUES account.

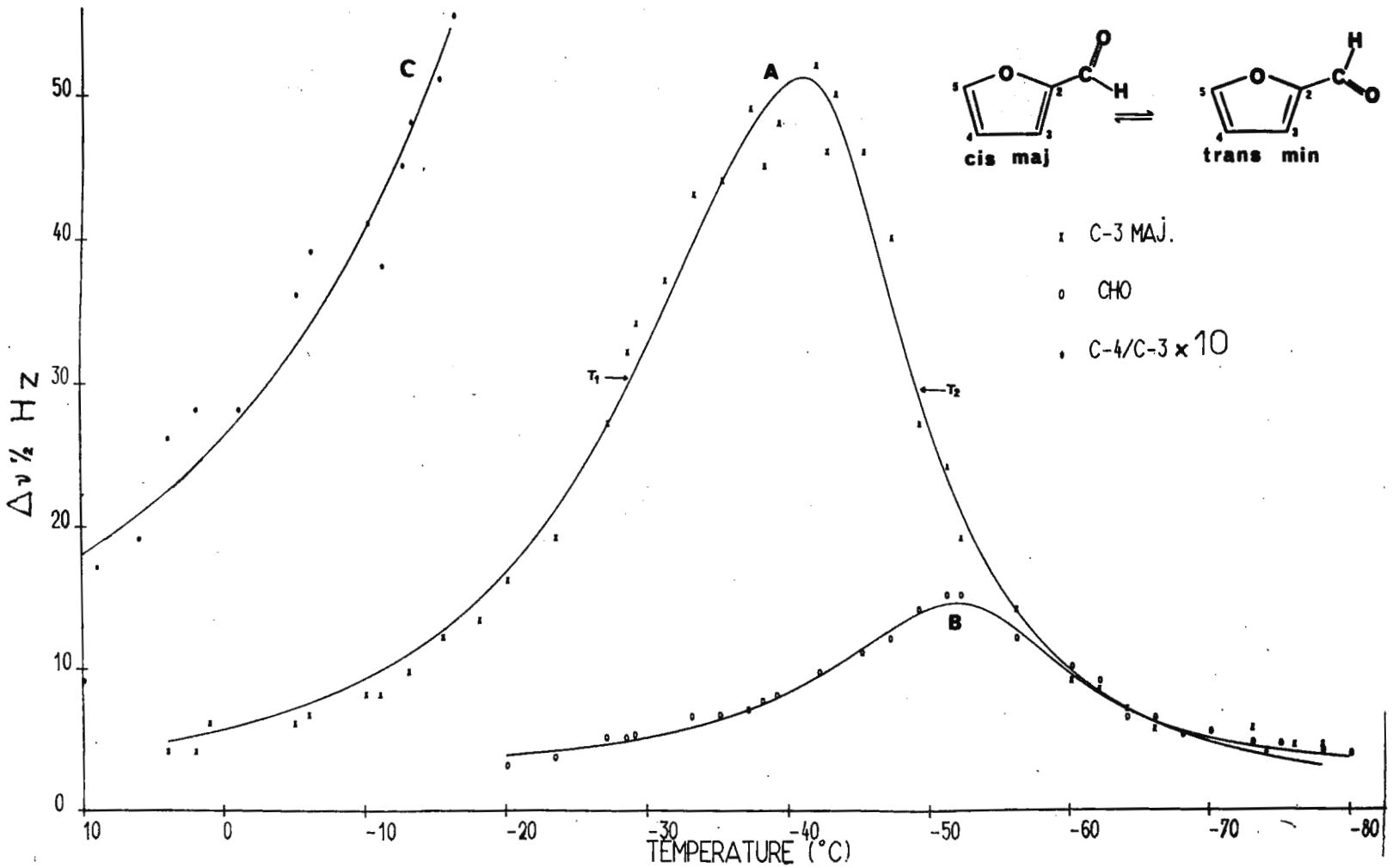
Sincerely,

Suzanne COMBRISSON

Thierry PRANGE

(1) see G.ZIMMERMANN, TAMU-192-41

(2) B.P. ROQUES, S.COMBRISSON, F.WEHRLI, Tetrahedron Lett., 12, 1047 (1975).


C
A
B
cis maj
trans min
C-3 MAJ.
CHO
C-4/C-3 x 10
T1
T2
Δν ½ Hz
TEMPERATURE (°C)
50
40
30
20
10
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80

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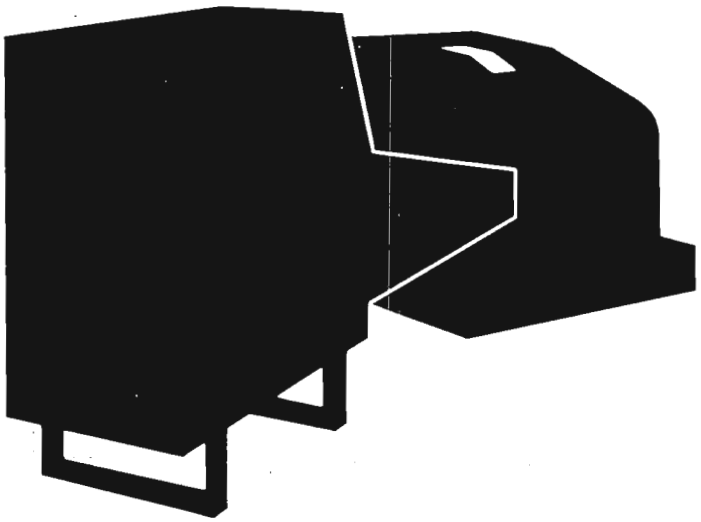

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Dr. V. Bystrov

USSR Academy of Sciences
Shemyakin Institute
of Bioorganic Chemistry

Ul. Vavilova 32
Moscow 117312 USSR

April 11, 1975

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

Title: On the Angular Dependence of the Vicinal $^{13}C'-NC^{\alpha}-^{1}H$ Coupling in Peptides.

Dear Barry,

Determination of the torsion angles ϕ and ψ of the peptide backbone is the basic operation for spatial structure elucidation of peptide and proteins. NMR spectroscopy provides data for the angle ϕ from the $H-NC^{\alpha}-H$ proton-proton coupling constant (1), but the Karplus-type nature of its angular dependence lends ambiguity to the results for certain ranges of values of the constant. Further progress in the NMR spectroscopy of peptide systems revolves about the problem of utilizing the spin-spin couplings with other nuclei, namely ^{13}C and ^{15}N, for the conformational analysis. First, such couplings aid in eliminating the ambiguity in the determination of ϕ angle and also of χ_1 angle of the side chain. Secondly, they can be used for determining the ψ angle and apparently ω angle in case of N-alkylated amide groups, inaccessible via the proton-proton coupling constants.

In this letter earlier calculated (2) angular dependence of the spin-spin coupling constant in the $^{13}C'-NC^{\alpha}-^{1}H$ fragments of the peptide backbone is compared with available experimental data, resulting in the proposal of tentative angular correlation of this vicinal couplings.

The theoretical calculation has demonstrated that the angular dependences in question obey a Karplus-type equation

$$^{3}J = A \cos^{2}\theta - B \cos^{2}\theta + C$$

Hence, for quantification of the angular dependence the experimental coupling constants for at least three different θ's are required.

For the $^{13}C'-NC^{\alpha}-^{1}H$ fragment the following constants are available: 1) The averaged coupling for N-methylacetamide as measured by

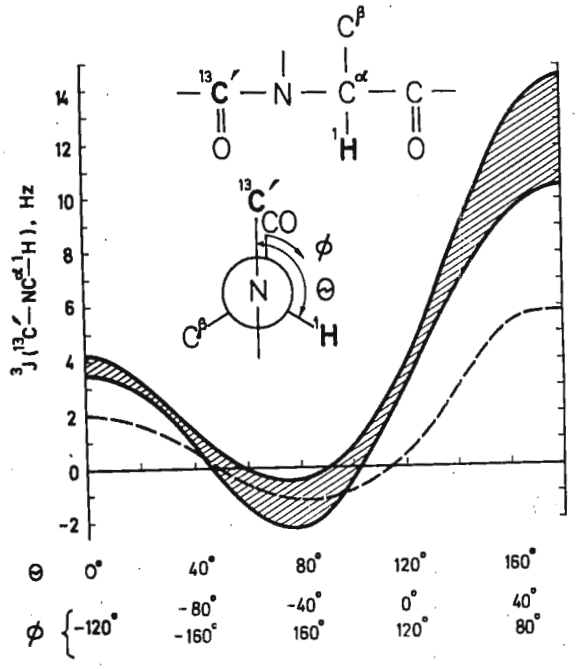

Fig. 1

Dorman and Bovey (2) for the pure liquid (3.7 Hz) and for the HD deuterated compound (3.5 Hz). We have measured a value of 3.9 Hz in our measurements of a solution of this compound in methanol-$\underline{d}_4$. The averaged coupling thus gives $\underline{A} + 2\underline{C} = 7.4 \pm 0.4$ Hz. 2) For a dihedral angle Θ of 90° one may take the value of -0.78 ± 0.8 Hz as evaluated by Rogers and Roberts (4) for N-acetyl-L-tryptophane bound to δ-chymotrypsin. 3) For the third necessary value a constant of 2.5 Hz was taken, we had determined for N-acetyl-L-alanyl-N--methylamide in methanol-$\underline{d}_4$. This is an averaged constant for the partitioned conformational state of the molecule. For this molecule the partition-averaged values of $\langle\cos^2\theta\rangle$ and $\langle\cos\theta\rangle$ have been calculated by Ramachandran et al. (5) from energy φ, ψ-map.

Simultaneously the above mentioned values give the angular dependence of the vicinal $^{13}C'-NC^{\alpha}-^{1}H$ coupling constant represented by hatched area in Fig. 1. Mean values for this area are approximated by the equation

$$^{3}\underline{J}(C'NC^{\alpha}H) = 9.0\cos^2\theta - 4.4\cos\theta - 0.8$$

For comparative purposes the theoretically calculated function (2) is also given in Fig. 1 in the form of a deshed curve.

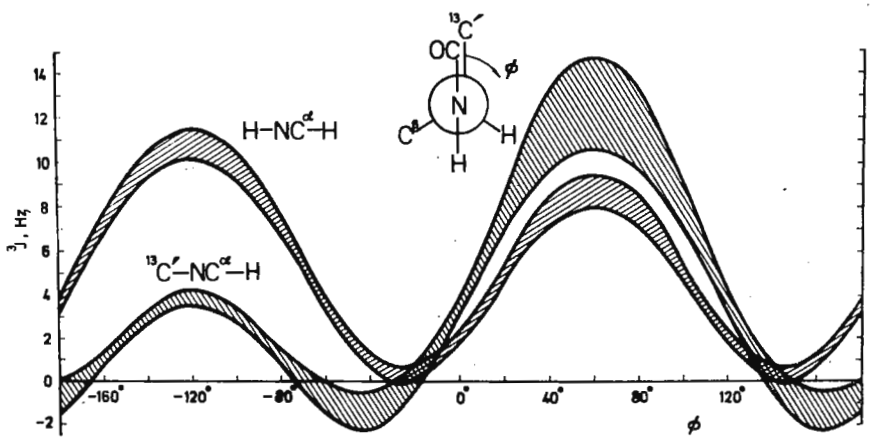

Fig. 2

Comparison of the angular dependences of the $^{13}C'-NC^{\alpha}-^{1}H$ and $H-NC^{\alpha}-H$ (1) couplings (Fig. 2) showed the relative maxima for both curves to be at the same angles (ϕ -120° and 60°), but their absolute maxima to be at reversed positions. Hence, by comparing the measured $H-NC^{\alpha}-H$ and $^{13}C'-NC^{\alpha}-^{1}H$ couplings, the conformational states of the peptide molecule can be determined more unequivocally. Application of this approach to the valinomycin depsipeptide antibiotic gives us a new information on the conformation in solution.

Sincerely yours,

Vladimir

References:

1. V.F.Bystrov et al., TAMU-NMR 175-21; Tetrahedron 29, 873 (1973).
2. V.F.Bystrov, V.N.Solkan, Izv. Akad. Nauk SSSR, Ser. khim. (Russian) 1308 (1974).
3. D.E.Dorman, F.A.Bovey, J. Org. Chem. 38, 1719 (1973).
4. P.Rodgers, G.C.K.Roberts, FEBS Letters 36, 330 (1973).
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ELASTOMER CHEMICALS DEPARTMENT
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May 27, 1975

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

Dear Barry:

^{1}H AND ^{19}F NMR ANALYSIS OF TETRAFLUOROETHYLENE-PROPYLENE COPOLYMERS

We have used both ^{1}H and ^{19}F NMR spectra to analyze the structure of a series of tetrafluoroethylene (TFE)-propylene (P) copolymers[1] prepared over a wide variation (2 X fold) in comonomer concentration by emulsion polymerization. The concentration range of the copolymers examined varied from 35 to 62 mole % propylene.

The ^{1}H NMR data were obtained at 220 MHz and the ^{19}F NMR data were obtained at 94.1 MHz. In the ^{1}H spectra the resonances of the different methyl groups of propylene were sufficiently resolved to use for determining the amount of alternating vs. non-alternating propylene sequences. In the ^{19}F spectra a more detailed determination of the large number of different resonances due to $\{CF_2CF_2\}_{n\geq 1}$ sequences was required to obtain the amount of alternating vs. nonalternating TFE sequences.

Figure 1 shows the results obtained from these determinations. From the plot we see that there is a symmetry in the relationship of the amount of nonalternating sequences with comonomer content. This symmetry of results supports the validity of the methods of determination which were entirely different for both spectra and shows that even though these copolymers are largely alternating, there is even ~10% nonalternating sequence structure at about 50 mole% comonomer content.

Sincerely yours,

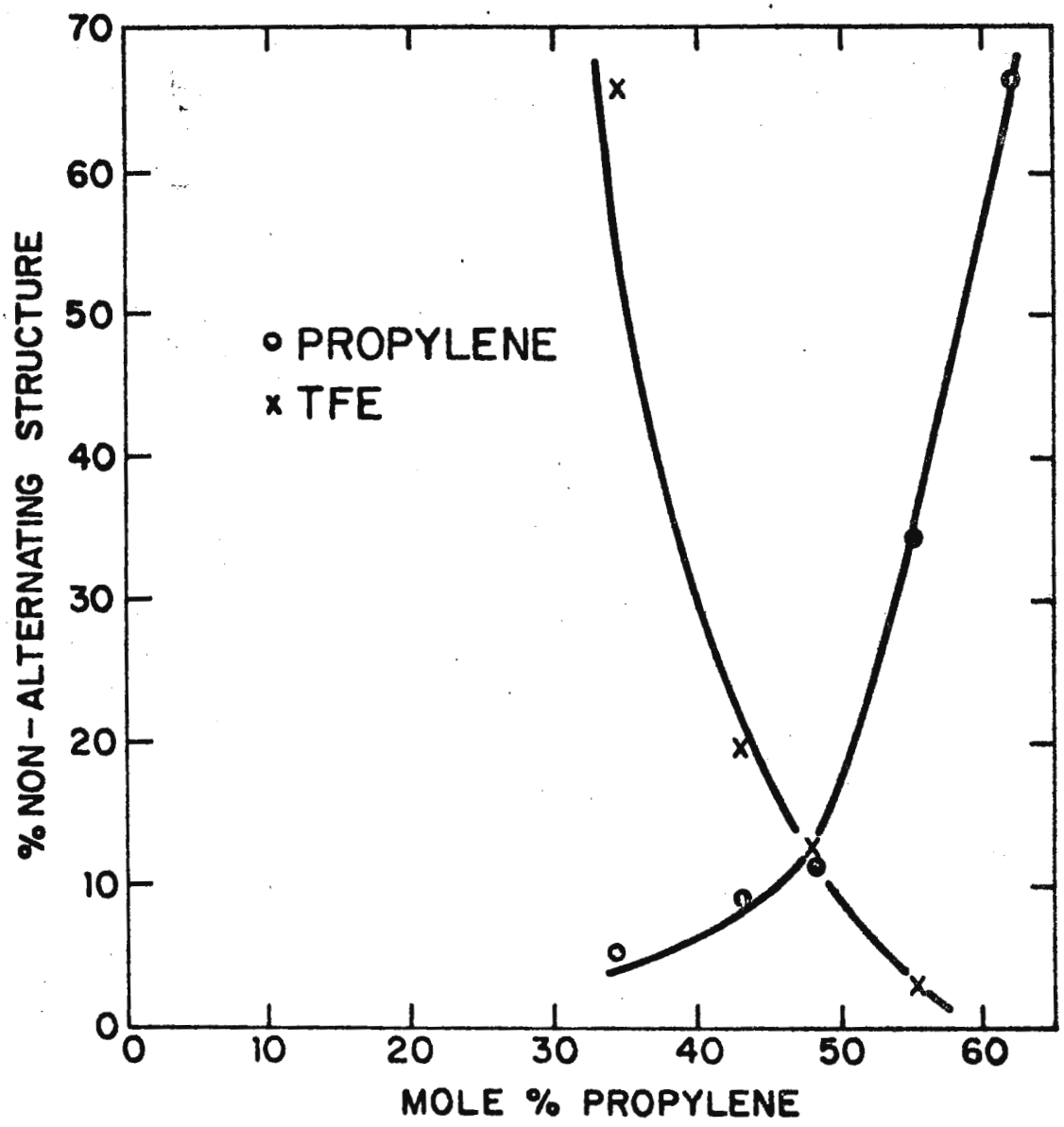
E. G. Brame, Jr. - Research Chemist
J. R. Harrell - Research Chemist
R. C. Ferguson - Research Chemist

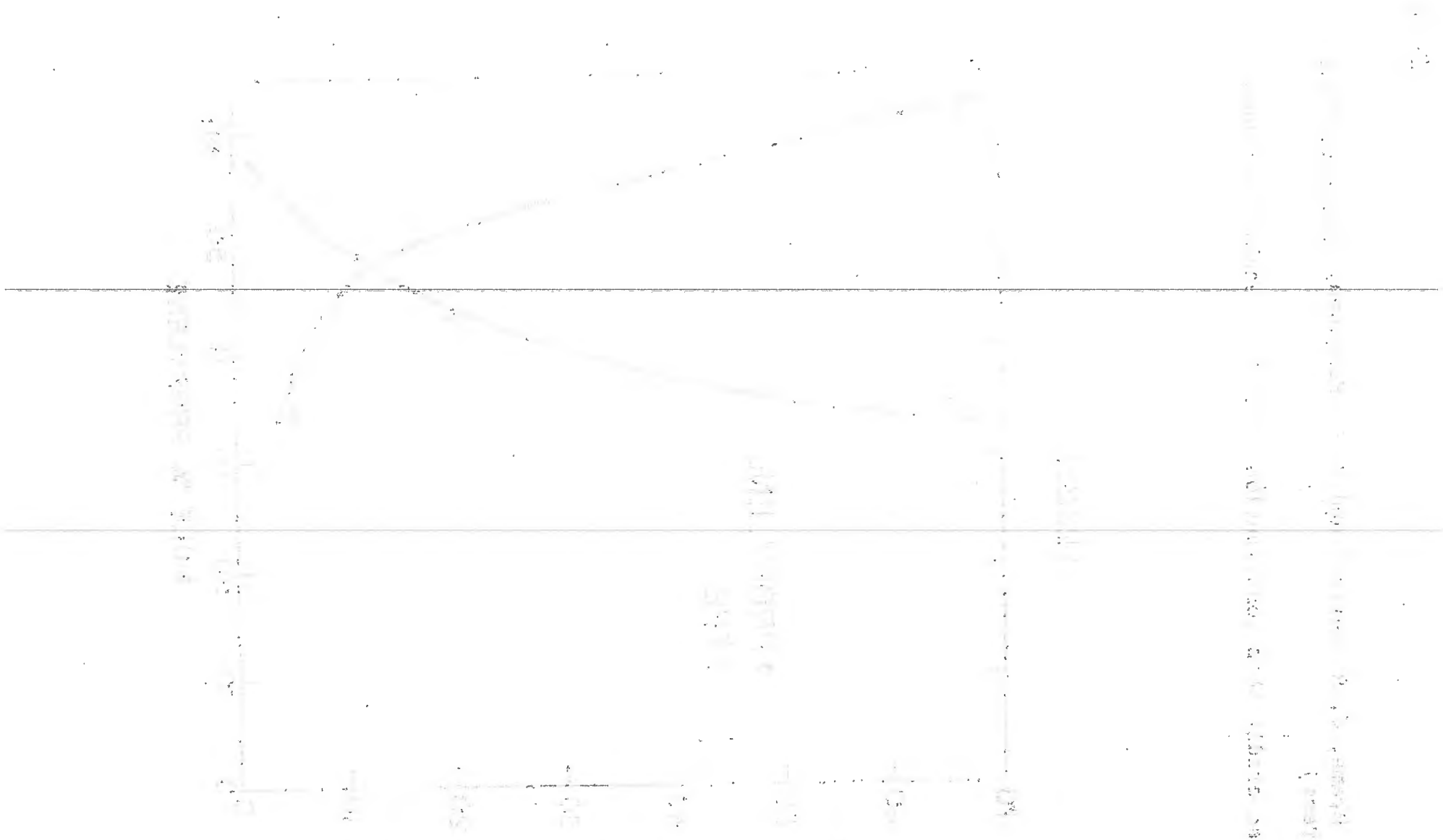
/gh
Attach.

1. E. G. Brame, J. R. Harrell and R. C. Ferguson, Macromolecules (in press)

P.S. Please credit this contribution to D. W. Ovenall's account.

Figure 1





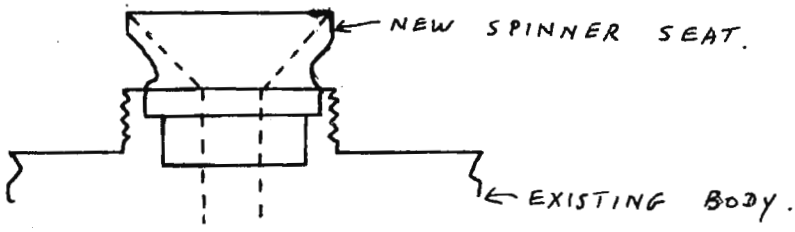
The machine shop time was about 8 hours and the T-60 was out of action for 1 1/2 days. Three spare spinner seats for future use were also provided.

Yours sincerely,

J.I.A. Thompson

J.I.A. Thompson
Senior Instrument Technician

JIAT/rg



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E. Breitmeier, G. Haas & W. Voelter
Chemisches Institut der Universität Tübingen

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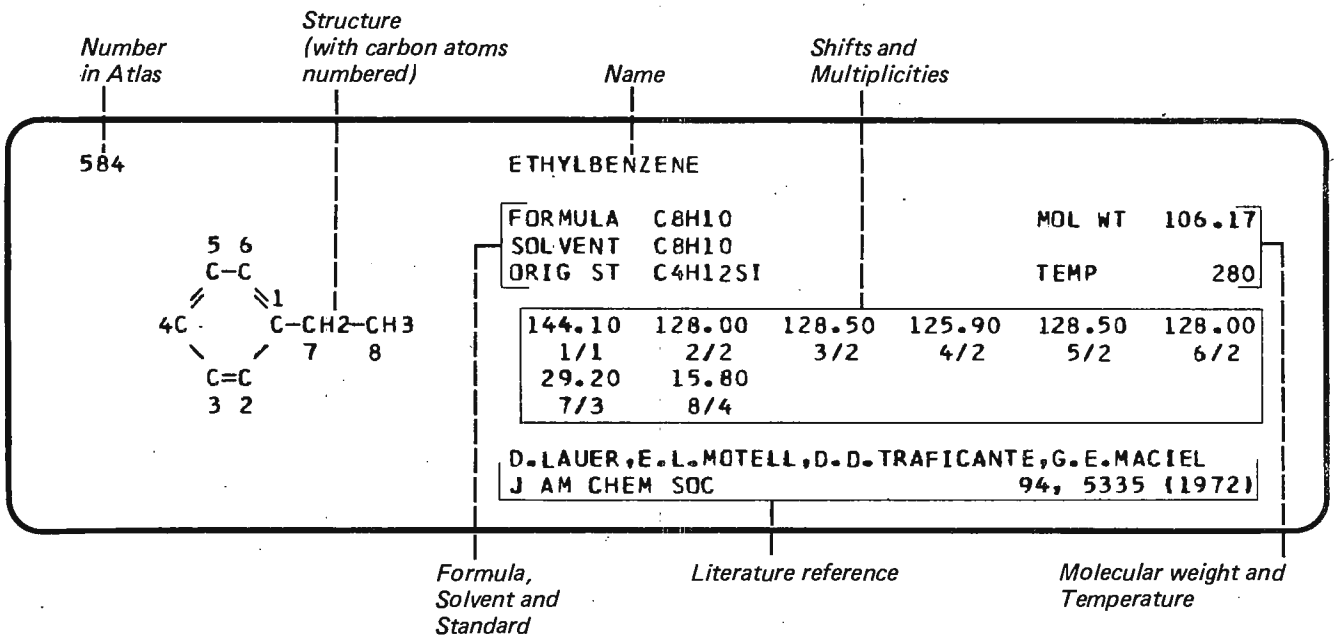
The extraordinary value of carbon-13 n.m.r. spectroscopy for conformational analysis makes this Atlas essential for everyone interested in organic molecules, natural and synthetic polymers and biological macromolecules.



To facilitate the fullest possible use of the Atlas there are FIVE indexes: Molecular Formula, Molecular Weight, Compound Name, Chemical Class and Chemical Shift.

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May 20, 1975

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

Dear Barry:

Frequency Dependent ^{31}P Relaxation Studies

In our studies of the structures of the binary Co-phosphoenolpyruvate (PEP) complex, and the ternary pyruvate kinase-Co-PEP complex in solution, we have found it useful to determine the paramagnetic contribution to $1/T_2$ of phosphorus at 3 frequencies.

The measurements at 25.1 MHz and at 40.5 MHz were made on the Varian XL-100-FT system locking on ^{23}Na (1) and ^{2}H respectively. The measurements at 101.5 MHz were made on the MPC HF-250 spectrometer at Carnegie Mellon University, with the generous help of A. Bothner-By, J. Dadok and R. Rowan.

In the binary Co-PEP complex $1/T_{2p}$ increases directly with increasing frequency while in the ternary complex $1/T_{2p}$ decreases slightly with increasing frequency. Computer analysis of the data in accord with Swift-Connick (2) and Solomon-Bloembergen (3,4) equations yields contact hyperfine coupling constants of 5×10^5 Hz and less than 1×10^3 Hz for the binary and ternary complexes respectively.

The 500-fold greater coupling constant in the binary complex is consistent with our independent Co-P distance calculations from $1/T_{1p}$ data of 2.7 ± 0.4 Å for Co-PEP and 5.0 ± 0.5 Å for pyruvate kinase-Co-PEP. The former distance indicates direct phosphoryl coordination while the latter indicates a second sphere complex.

Sincerely yours,

Elik Melamud

Elik Melamud

Albert S. Mildvan

Albert S. Mildvan

(1) Gupta, R.K. (1974) J. Mag. Res. 16, 185.
(2) Swift, T.J. and Connick, R.E. (1962) J. Chem. Phys. 37, 307.
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AMSTERDAM, May 20, 1975

Uw ref.:

Onze ref.: 75s45/GJDO/mvg

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

^{19}F chemical shift anisotropies from liquid crystal NMR.

Dear Professor Shapiro,

In this contribution we want to report about the determination of chemical shift anisotropies by the liquid crystal NMR method. This method is known to be hazardous for protons, but fluorine chemical shift anisotropies, which usually are much larger, can be studied conveniently. A serious limitation is that one experiment gives only one relation between the elements of the chemical shift tensor. Therefore, experiments have mainly been confined to highly symmetric molecules but even then additional assumptions are required unless the bond axis for the nucleus under investigation is along a three-fold or higher symmetry axis. It is customary to assume axial symmetry of the shift tensor around the bond axis, after which the quantity $(\sigma_{//} - \sigma_{\perp})$ can be determined from the chemical shift difference $\Delta\sigma$ between the molecules in the oriented nematic and the isotropic phase. We have tried to test this assumption by investigating molecules with C_{2v} symmetry for which $\Delta\sigma$ can be written as

$$\Delta\sigma = (2/3).5^{-\frac{1}{2}} C_{3z^2-r^2} \{\sigma_{zz} - 1/2\ (\sigma_{xx} + \sigma_{yy})\} + (15)^{-\frac{1}{2}} C_{x^2-y^2} \{\sigma_{xx} - \sigma_{yy}\}$$

If experiments with essentially different orientations can be performed, two combinations of tensor elements can be determined, giving two independent values of $\sigma_{//} - \sigma_{\perp}$. As an example we give the results for 2,4,6-trifluoronitrobenzene for which the shift anisotropy was investigated earlier in our

laboratory using an electric field to create the anisotropic liquid[1].

Fluorine spectra of a sample of 2,4,6-trifluoronitrobenzene and CF_4 (internal reference) dissolved in Merck's Phase V have been recorded on a XL-100 spectrometer at temperatures varying from -10 to 45° C in the nematic phase and from 45 to 70° C in the isotropic phase. The chemical shifts in the nematic phase vary over a range of about 1000 Hz with temperature, i.e. with orientation, whereas no significant temperature dependence of the isotropic shifts is detected.

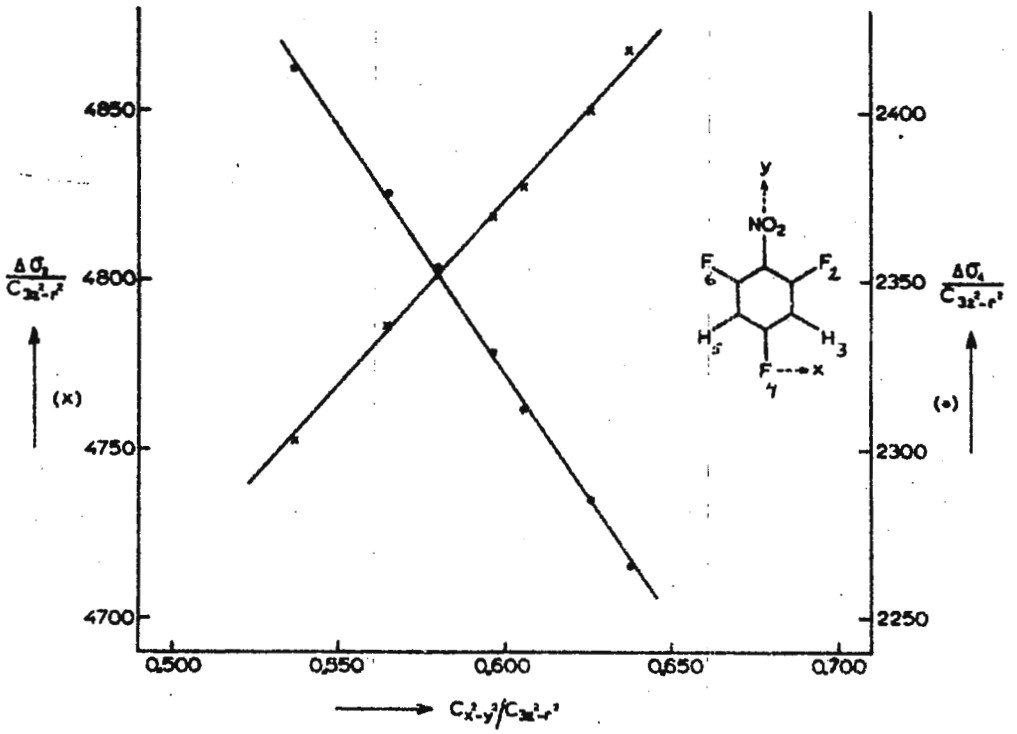
The anisotropic couplings and chemical shifts have been calculated with the LAOCOON 3 program using the indirect couplings from ref. 1. Neglecting the pseudo-dipolar couplings, the HF and FF couplings of all spectra are then fitted to one geometry, thus providing the values of $C_{x^2-y^2}$ and $C_{3z^2-r^2}$ for each experiment (The HH couplings cannot be determined accurately from the fluorine spectra). By assuming equal FF distances (4.685 Å), values of 4.348 Å and 2.581 Å are obtained for the HH and the H_3-F_2 distance respectively. The figure gives a plot of $\Delta\sigma/C_{3z^2-r^2}$ versus $C_{x^2-y^2}/C_{3z^2-r^2}$ for both fluorine nuclei (2-ortho and 4-para). Slope and intercept then give $\{\sigma_{xx} - \sigma_{yy}\}$ and $\{\sigma_{zz} - 1/2(\sigma_{xx} + \sigma_{yy})\}$. If the shift tensors are axially symmetric, both quantities yield a value of $(\sigma_{//} - \sigma_{\perp})$. These values, calculated assuming an angle of 30° between C-F(2) and the x-axis, are given in the Table. Although the uncertainties in these numbers may be large, because only a small range of $C_{x^2-y^2}/C_{3z^2-r^2}$ is covered, it is obvious that neither of the shift tensors is axially symmetric around the bond axis.

Sincerely yours,

C. MacLean G.J. den Otter

Reference:

J. Biemond, J.B.M. Neyzen and C. MacLean, Chem. Phys. 1, 335 (1973)



$\Delta\sigma/C_{3z^2-r^2}$ versus $C_{x^2-y^2}$ for both fluorine nuclei in 2,4,6-trifluoronitrobenzene in Phase V at different temperatures.

Chemical Shift Anisotropies (in ppm) of 2,4,6-trifluoronitrobenzene.

	$\sigma_{zz} - 1/2(\sigma_{xx} + \sigma_{yy})$	$\sigma_{xx} - \sigma_{yy}$	$\sigma_{//} - \sigma_{\perp}$	
	(a)	(b)	from (a)	from (b)
F(2)	149	45	-298	+90
F(4)	114	-60	-228	+60

UNIVERSITÉ DE DROIT, D'ÉCONOMIE ET DE SCIENCES D'AIX-MARSEILLE
FACULTÉ DES SCIENCES ET TECHNIQUES DE SAINT-JÉROME

Laboratoire des Organométalliques
J. C. MAIRE, Professeur.

15 May 1975

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

Dear Barry,

Pseudo σ_R° and σ_I values and solvents effects in chlorofluorophenylstannanes

As a part of our contribution to TAMU N-M-R Newsletter we send you some results concerning ^{19}F NMR of 8 aromatic fluorophenyltin compounds.

According to Taft's results, we have calculated some pseudo $\sigma(p\sigma)$ values (so called because of the asymetry of the substituent G), in compounds such as

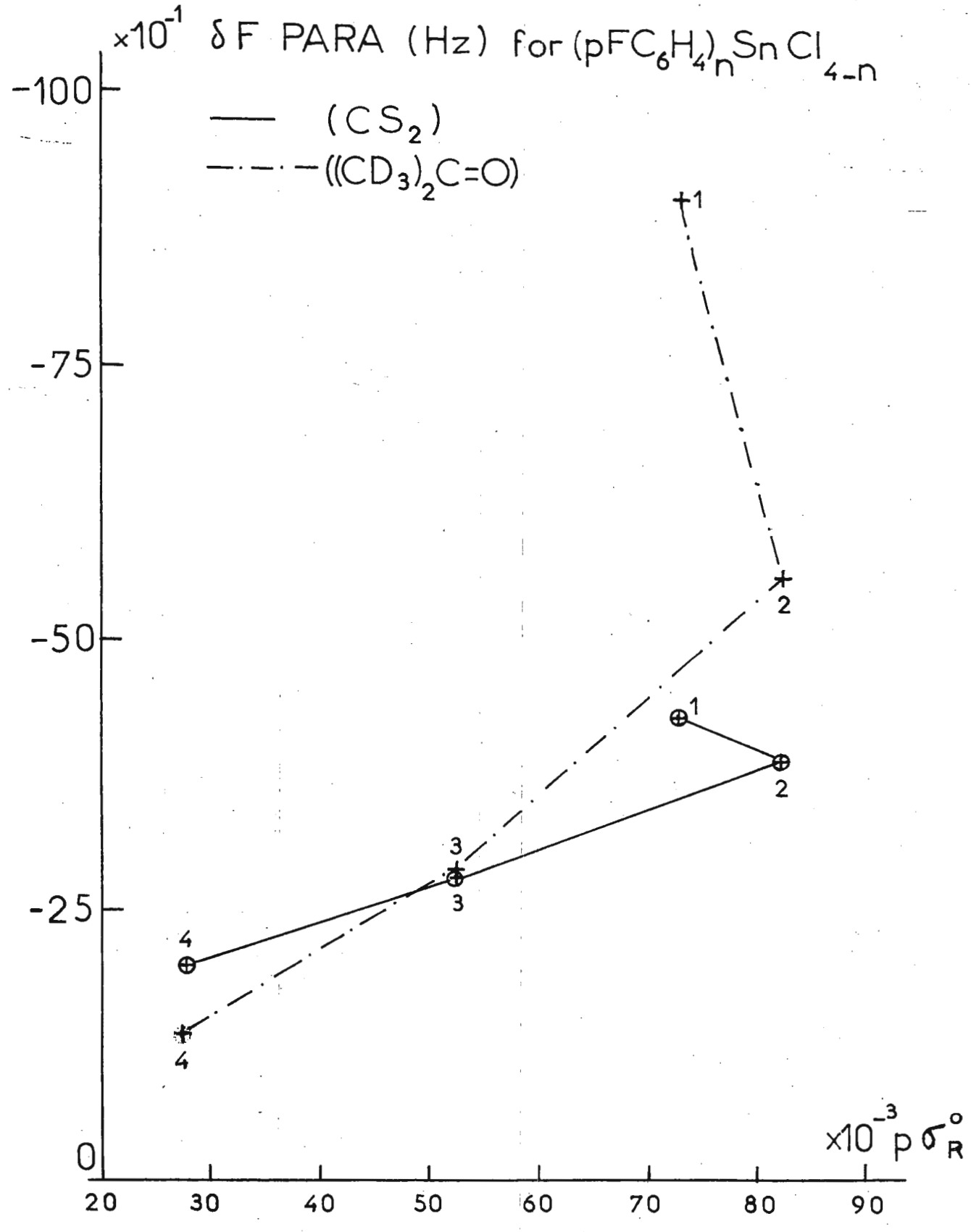
$pFC_6H_4G_1$ and $mFC_6H_4G_2$ $\begin{cases} G_1 = (pFC_6H_4)_{n-1}SnCl_{4-n} \\ G_2 = (mFC_6H_4)_{n-1}SnCl_{4-n} \end{cases}$

In a first approximation, we shall consider that the influence of the chlorine atom is more important than the perturbation due to the F atom position (para or meta) in the substituent, so to say that $G_1 \simeq G_2 = G$.

Compounds solvent	δ^aF PARA $(CD_3)_2C=O$	δ^aF META $(CD_3)_2C=O$	δ^aF PARA CS_2	$p\sigma_R^\circ$ [b]	$p\sigma_I$ [b]	G GROUP
$(FC_6H_4)_4Sn$	-196	-119	-136	+0,028	+0,262	$(FC_6H_4)_3Sn$
$(FC_6H_4)_3SnCl$	-282	-136	-288	+0,053	+0,279	$(FC_6H_4)_2SnCl$
$(FC_6H_4)_2SnCl_2$	-385	-156	-557	+0,082	+0,318	$(FC_6H_4)SnCl_2$
$(FC_6H_4)SnCl_3$	-427	-224	-909	+0,073	+0,419	$SnCl_3$

a chemical shifts in Hz measured with C_6H_5F as internal reference at 94,1 MHz (VARIAN XL100) negative value indicates deshielding.

b 29,5 p σ_R° = δF META (ppm) - δF PARA (ppm)
7,1 p σ_I = 0,60 - δF META (ppm).


×10⁻¹ δ F PARA (Hz) for (pFC6H4)nSnCl4-n
(CS2)
((CD3)2C=O)
-100
-75
-50
-25
0
20
30
40
50
60
70
80
90
×10⁻³ pσ°R
1
2
3
4

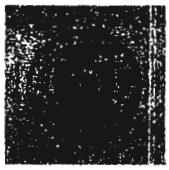
By plotting δF PARA in CS_2 against $p\sigma^{\circ}_R$ calculated in $(CD_3)_2CO$, we observe the same evolution of the phenomenon, so to say that $SnCl_3$ seems to be the less electron resonance acceptor (despite his high inductive attractive effect), and the highest electron resonance donor, due to chlorine back donation.

The chemical shifts in CS_2 are more important than in $(CD_3)_2CO$, perhaps due to the high polarisability of the sulphur-carbon bonds.

We are now investigating some other substituted fluorophenyltin compounds

Sincerely yours.

J.C.MAIRE J.M.ANGELELLI M.A.DELMAS J.P.ZAHRA



THE OHIO STATE UNIVERSITY

May 28, 1975

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

Bond Exchange in Methyllithium

Dear Barry:

Your dreaded pink sheet has finally caught up with me so I hereby describe some more of our organolithium research.

Some time ago Waake and colleagues reported how ^{7}Li nmr data for ^{13}C enriched methyllithium at reduced temperatures were consistent with three nearest neighbor lithiums coupling to ^{13}C within a tetrahedral $(CH_3Li)_4$ aggregate. In the course of other work we recently looked at a similar sample. With decreasing temperature the ^{13}C resonance broadens, reaching its maximum width by -70°. This absorption envelope is consistent with three equivalent lithiums coupling to each ^{13}C by ca 14 Hz.

Line-shape analysis of the exchange process responsible for the above effects should give rather accurate rate constants. One sticking point is that the components of the 10 line multiplet seem to continue broadening below -70°. Whether this comes from environment effects (including viscosity) or from ^{7}Li quadrupole relaxation, or ^{7}Li long range coupling is being checked with experiments on $(^{13}CH_3{}^{7}Li)_4$.

There is a position in my group for a post-doctoral to work with our multinuclear pulse spectrometer studying dynamic effects and structure in the field of organolithium chemistry. This person will also spend part-time looking after the instrument.

With best wishes.

Sincerely yours,

Gideon

Gideon Fraenkel
Professor of Chemistry

GF:bas

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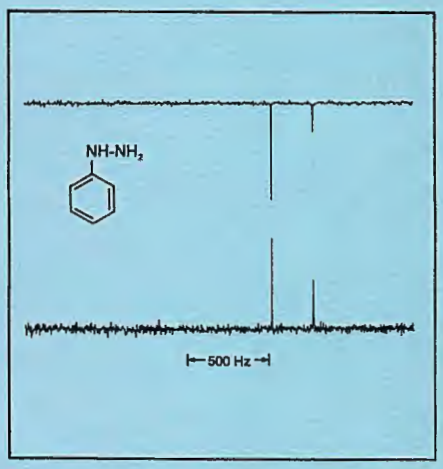
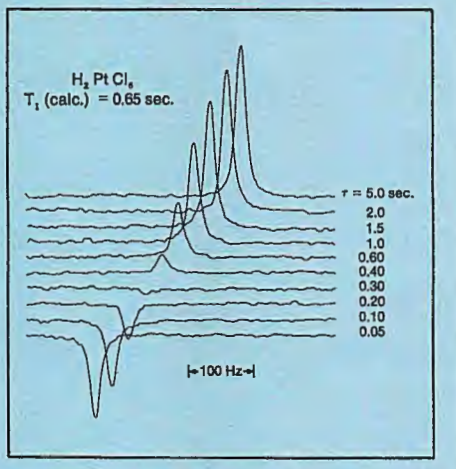


The nucleus observed for this spectrum is ^{15}N, at 10.1 MHz. The upper trace shows 500 transients ($\alpha = 90°$) of a proton noise-decoupled spectrum of phenylhydrazine in C_6D_6. The negative magnetogyric ratio of ^{15}N produces negative NOE, hence the inverted lines in the trace. The lower trace shows 2000 transients of phenylhydrazine ($\alpha = 90°$); the decoupler was on during acquisition and off during the pulse delay. This technique makes it possible to measure NOE while retaining the advantages of a ^{1}H noise-decoupled spectrum.



In this spectrum, the new accessory allows the observation of ^{195}Pt at 21.5 MHz; the sample was aqueous hexachloroplatinic acid. An inversion recovery ($180°$-τ-$90°$) pulse sequence was used in the automatic measurement of the spin-lattice relaxation time (T_1) for the ^{195}Pt nucleide.

We wish to acknowledge the cooperation of Professor Paul Ellis, of the University of South Carolina, whose early experimental work contributed to development of this capability of the XL-100.

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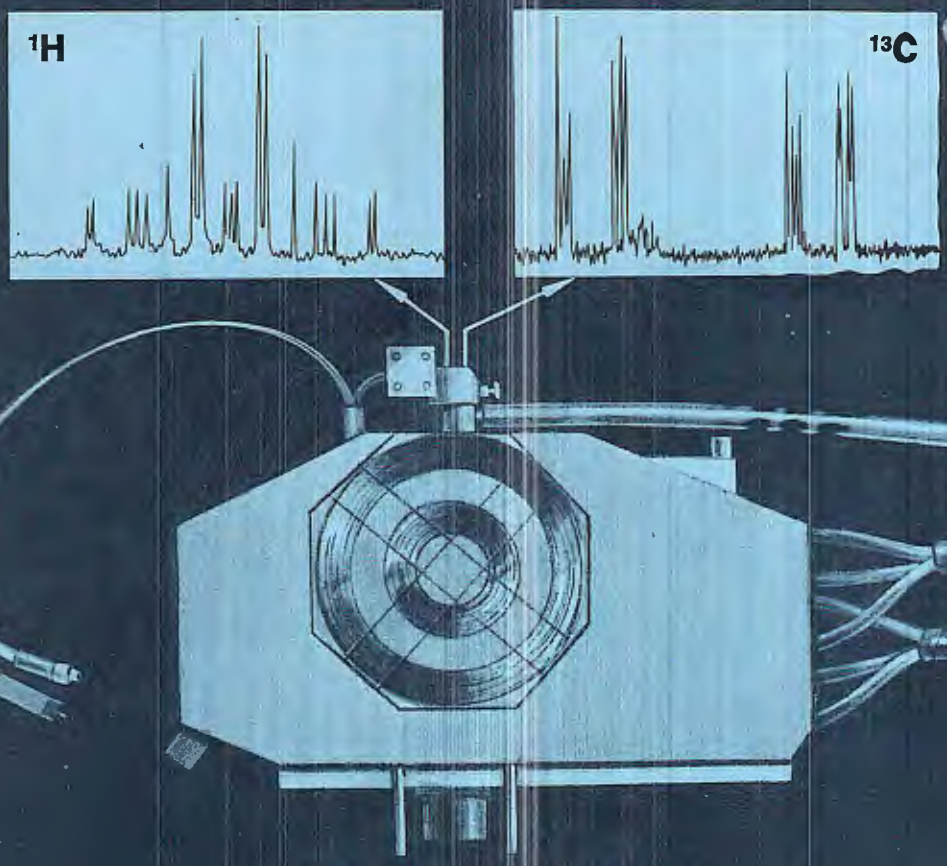

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Spectra: ^{1}H of ODCB; ^{13}C of ODCB with proton spin-coupling.