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Newsletter

No. 150
MARCH, 1971

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│ Deadline Dates: No. 151: 5 April 1971   │
│   No. 152: 3 May 1971   │
└───┘

All Newsletter correspondence, etc., should be addressed to:

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

ircha

**Direction générale
Services de Paris**

12, quai Henri-IV, Paris-4e
téléphone : 272 82 70

Pr. B.L. SHAPIRO
Texas A & M University
College of Science,
College Station, TEXAS, 77843

Paris, le   1er Février 1971

"Variable Temperature Study of Molecular Mobility
in Styrene-methyl Methacrylate Block Copolymers"

Dear Barry,

A number of papers have been devoted to structural studies of methyl methacrylate – styrene copolymers, mainly for elucidating the fine structure (monomer sequence, tacticity, a.s.o.) obtained in various conditions (1-5). Less attention has been paid (to our knowledge) to molecular mobility, except recently by Russian authors (6) who investigated PMMA-PS surface layers on Aerosil and Teflon by measuring the relevant T_1's. Having at hand such block copolymers, we considered proton mobility of PMMA-PS-PMMA trisequences (M_v: ca. 90.000; monomer ratio: 57 % PS; 43 % PMMA)[*] as observed at varying temperature in different media, one solvent of both polymers (CCl_4), one dissolving preferentially PMMA (CCl_4 + 10 % CD_3CN),

the last dissolving preferentially PS (CCl_4 + 10 % cyclohexane). The temperature range we covered was roughly from -30 to +120° C. Linewidth changes of the acetoxy group of PMMA and, to a lesser extent, of the phenyl of PS were easily used for characterizing the average mobility of the relevant sequences. Observations are roughly depicted in the following page. For the PMMA moiety, going from CCl_4 to C_6H_{12} reduces systematically the mobility;

the PMMA chains are retracted in a less efficient solvent; simultaneously, the PS chain moves more freely as shown by its reduced linewidth; dissolution occurs without solvation. Conversely, from CCl_4 to CD_3CN, the mobility of PMMA is reduced

. . . .

[*] Obtained from Drs. Riess and Periard, Ecole Supérieure de Chimie, 68. Mulhouse, whom we thank for their kindness.

at high temperatures, the PMMA chains being solvated by aceto-
nitrile and attached to a colloidal particle of PS behave as
homopolymers of much higher M_w; at low temperatures, the de-
pletion of melting point is big enough to maintain the whole
polymer in a dissolved state. For the PS moiety, the same sol-
vent is a bad one and throughout the covered temperature range,
it behaves as frozen, due to the retraction of its chains. The
investigation of other effects (especially chelating agents on
this behavior) is now planned. Very best regards.

G. MAVEL

(1) F.A. BOVEY, J. Polym. Sci., 62, 197 (1962).

(2) A. NISHIOKA, Y. KATO, and N. ASHIKARI, ibid., 62, S 10
(1962).

(3) Y. KATO, N. ASHIKARI, and A. NISHIOKA, Bull. Chem. Soc.
Japan, 37, 1630 (1964).

(4) K. ITO and Y. YAMASHITA, J. Polym. Sci. B, 3, 625 (1965).

(5) S. YABUMOTO, K. ISHII, and K. ARITA, J. Polym. Sci. A-1,
8, 295 (1970).

(6) Yu. S. Lipatov and F.G. FABULYAK, Polym. Sc., 11, 800
(1969).

CH₃COO linewidth in Hz

CCl₄ + C₆H₁₂ (10%)

CCl₄ + CD₃CN (10%)

CCl₄

High-field peak of φ group

CCl₄ + CD₃CN

CCl₄

CCl₄ + C₆H₁₂
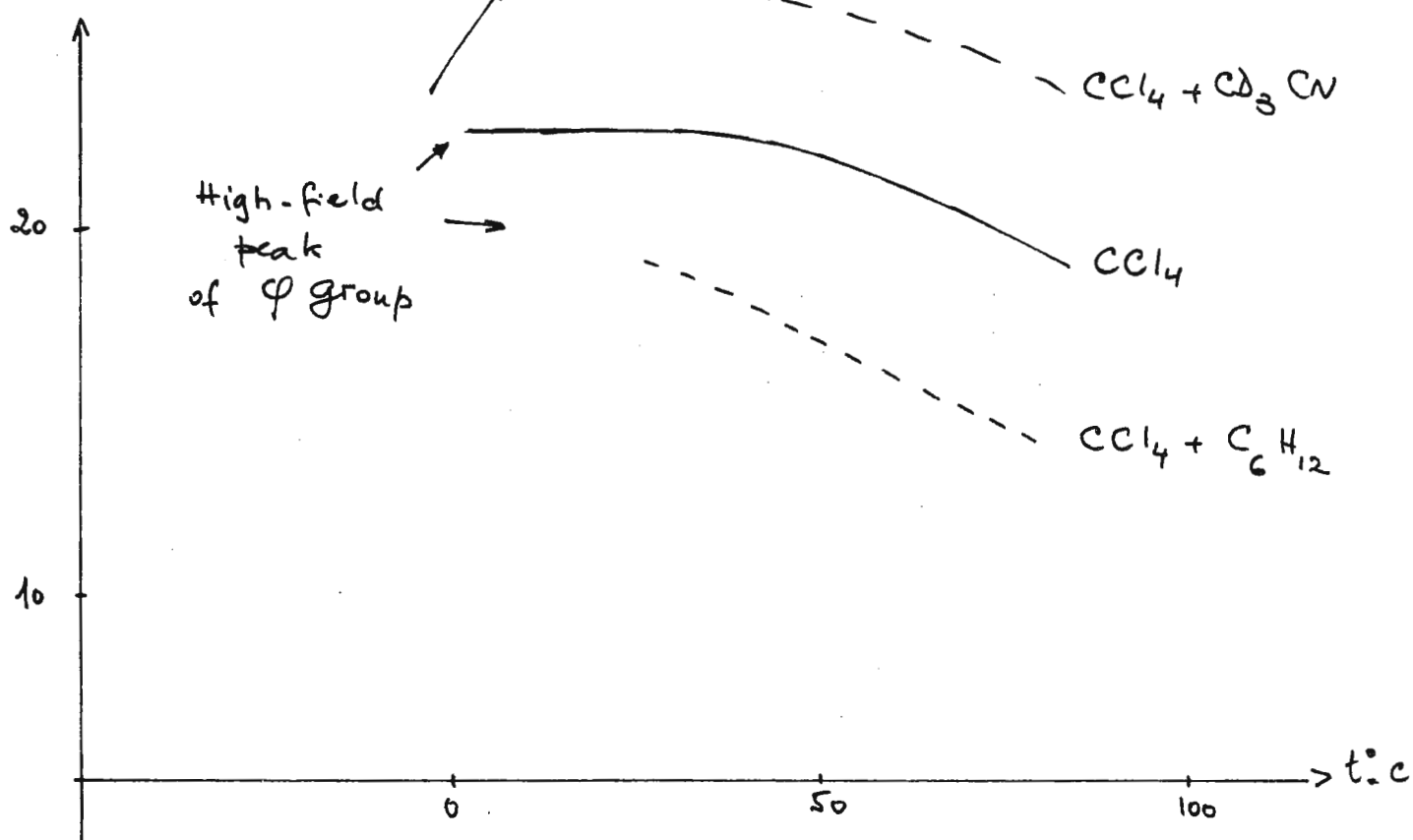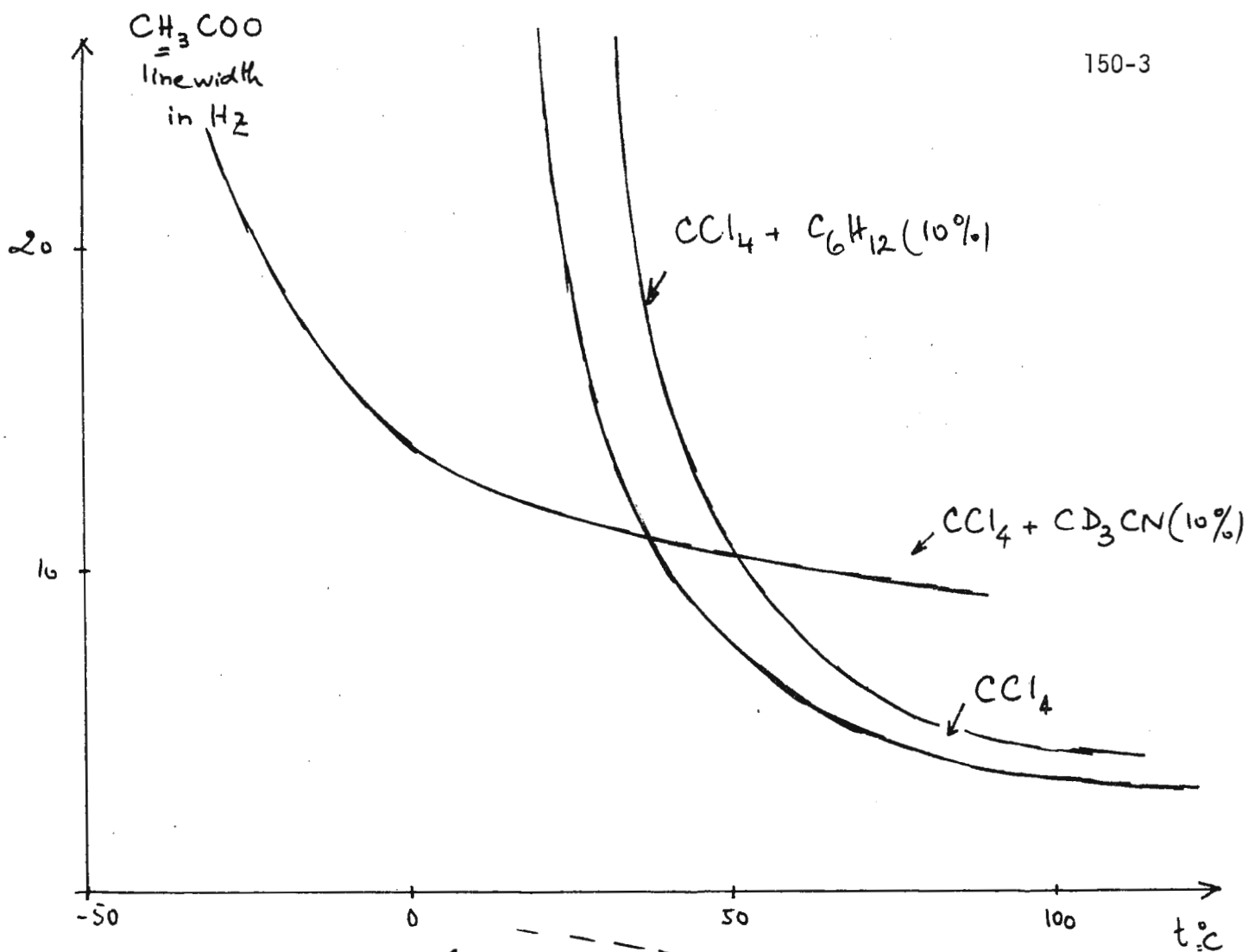
UNIVERSITY OF CALIFORNIA, SANTA BARBARA

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106

February 2, 1971

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas   77943

"The Interaction of p-Fluorocinnamate with α-Chymotrypsin"

Dear Barry:

As part of our studies of the interaction of carboxylic acids with the
proteolytic enzyme, α-chymotrypsin, we have determined the chemical shifts
of the hydrogen and fluorine nuclei of p-fluorocinnamate ion in its com-
plexed form with this enzyme.   The same experimental techniques that were
used in a comparable study with cinnamate were employed;[1] the chemical
shift differences (in p.p.m.) observed in these two systems are summarized
in the diagrams below.
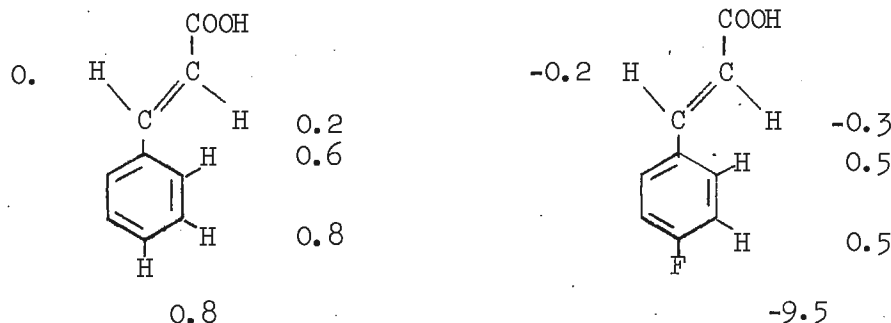
Although we had naively hoped that both of these molecules would bind in the
same manner to the protein, it is clear that this is not the case.   Most
striking is the very large <u>downfield</u> shift of the p-fluorine but a substantial
<u>upfield</u> shift of the corresponding p-hydrogen nucleus.   It has been previously
suggested that an aromatic ring current effect, likely from a tyrosine residue,
is responsible for the shift of the hydrogen atom[1,2] but this effect cannot be
the sole one operating in the case of the fluorine compound.   Professor Jack
Richards has suggested that possibly a hydrogen bond to this fluorine atom is
formed in the enzyme-anion complex.   Regardless of the sources of the effects

2

observed with these systems, these results suggest that care must be taken in interpreting fluorinated small molecule-enzyme interactions solely in terms of the behavior of the all-hydrogen analogs.

Sincerely yours,

J. T. Gerig
Assistant Professor

C. E. Ortiz

1. J. T. Gerig and J. D. Reinheimer, J. Amer. Chem. Soc. 92, 3146 (1970).

2. J. T. Gerig and R. A. Rimerman, Biochem. Biophys. Res. Commun. 40, 1149 (1970).

JTG:rt

**PHYSIKALISCHES INSTITUT
DER UNIVERSITÄT BASEL**
KLINGELBERGSTRASSE 82 — TEL. 43 04 22
VORSTEHER: PROF. DR. P. HUBER

NEUE NR.
061-44 22 80

Basel, February 2, 1971/ho
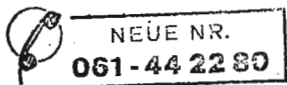
Prof. Dr. P. Diehl

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

U.S.A.

Postdoctoral Position Available

Dear Barry,

I will have funds available for a postdoctoral position for one year, beginning July 1st, 1971 (or later). The work will involve NMR exclusively (spectra of oriented molecules). The salary amounts to Swiss Francs 21'000.- to 24'000.- per year. There is no travel allowance. Any person interested should write to me as soon as possible.

Sincerely yours,

Peter

Prof. Dr. P. Diehl

February 5, 1971

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

Title: Studies of Sodium O,O-dimethylphosphorodithioate
        and Its Isomers

Dear Barry:

   We have observed that on heating, an aqueous solution
of sodium O,O-dimethylphosphorodithioate (I) isomerized to
sodium O,S-dimethylphosphorodithioate (II) and sodium S,S-
dimethylphosphorodithioate (III). At room temperature, only
I and II reacted with methyl iodide or ethyl iodide. The
reaction of II with ethyl iodide gave only the corresponding
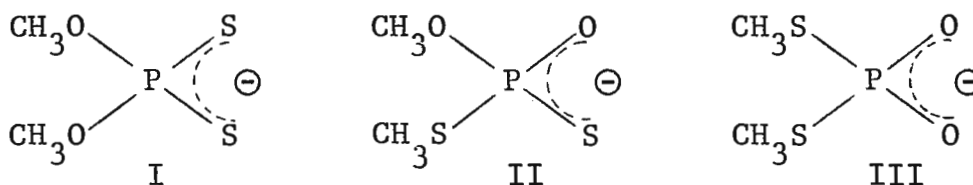
S-ethyl but no O-ethyl product. The relative rate of reaction
of I and II with methyl iodide-d_3 was determined by NMR to be
6.4 $\pm$ 0.3.

                              Sincerely yours,

                              C. K. Tseng

                              J. H. Chan

CKT/JHC/lh

Oregon Graduate Center

for Study and Research

February 8, 1971

Professor Barry Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas   97843

Re: Tape Cassettes for Minicomputers/$^1J_{CP}$'s in Organophosphonates

Dear Barry:

For several months we have had our Sykes Tape Cassette unit installed and functioning as a peripheral for our Varian 620-i which controls our HA-100. As the number of laboratories using mini-computers grows the number of people interested in this type of peripheral will increase. We have found it to be of tremendous help in time saving. Basically, the cassette unit is under 620-i control and can operate in read/write modes on tapes which possess both data and address tracks. A small program is used to read or write and perform corrective functions. This is normally stored in the data area of the HA-100 program so it is wiped out when the HA-100 program is entered. However, a small bootstrap program is stored outside the area occupied by the HA-100 program and can be used to recall the cassette program into core from its location on tape. All of our programs are stored in cassettes which can hold about 20,000 16-bit words each with a word transfer rate of 250 words/sec. This compares with a 5 word/second rate for the ASR 33 teletype normally used for reading paper tape. As you can see the time required for loading the bootstrap, binary load-dump, and HA-100 programs drops from about 45 minutes on the teletype to seconds with the cassette unit. This ignores the frequent troubles arising using paper tape which invariably mades one start all over again. Since our 620-i is interfaced to our E-3 switching over-and-back time is now on the order of a minute rather than the 1-1/2 to 2 hours previously spent. A number of cassettes can be purchased so that programs can be stored in duplicate to prevent loss. Spectral data can be stored directly and retained on tape rather than paper if desired. What we hope to do is modularize our program so we can separate our data collection, data processing (integration, smoothing, etc.) and data output functions so that only the programs being used are in core. This can free a great deal of memory for data points.

For those who are in the position of having a minicomputer which is not in constant use the cassette unit allows the minicomputer to be a general computer in seconds so that Fortran programs can be used   (Basic in some computers). Thus, the computer can serve needs normally taken care of by expensive programmable calculators or computation done at a central computer center. For some people

Prof. Barry Shapiro
Page 2
February 18, 1971

the latter reasons themselves might have enough economic weight to justify purchase of a cassette unit. We would be happy to share what we know with anyone interested.

As a preview to a paper coming out in JACS in May, I will list below some of the data obtained in ^{13}C nmr work on a series of diethyl phosphonates. Of primary interest are the $^1J_{CP}$'s available in the $(C_2H_5O)_2P(O)CH_2X$ compounds. By putting X on the carbon instead of the phosphorus we can hopefully use some of our understanding of coupling involving only first-row elements while introducing some second-row character into the problem.

X	$^1J_{CP}(\pm 0.2$ Hz)	X	$^1J_{CP}(\pm 0.2$ Hz)
OCH_3	163.9	$CH=CH_2$	138.7
Cl*	156.9	C_6H_5	137.0
I	152.7	CH_2Br	133.9
SCH_2CH_3	148.5	$CONH_2$	132.9
H	143.2	CH_3	131.7
CN	141.0	$CO_2C_2H_5$	131.3
$CH(OC_2H_5)_2$	139.0	CHO	126.5
$C_6H_4NH_2$	138.9		

* $(CH_3CH_2CH_2O)_2P(O)CH_2Cl$ used

The range of $^1J_{CP}$ is almost 30 percent while the phosphonate carbon chemical shifts range over 79 ppm and correlate very well with analogous $^{13}CH_3X$ shifts. Changes in effective nuclear charge do not appear to be the controlling factor in variations of the $^1J_{CP}$. Approximate SCF-MO calculations do much better in accounting for the magnitude and range for a number of model cases. There is a linear relationship between the calculated $P^2_{S_CS_P}$ (the notorious "s-character") and $^1J_{CP}$. However, the coupling constant changes almost twice as fast as the bond order.

Sincerely,

George

George A. Gray
Assistant Professor of Chemistry

GAG:nw

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PLEASE ADDRESS REPLY TO
RESEARCH LABORATORIES

Professor Bernard L. Shapiro   February 9, 1971
Department of Chemistry
Texas A and M University
College Station, Texas   77843

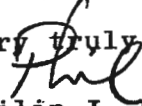Dear Barry: RE: Vacillating SHIMitis

We have had several months experience now with use of a Varian
Spectrosystem (8K) interfaced to an HA-100 spectrometer. The system,
on the whole, has met our expectations once the usual initial "shake-
down" period eliminated troublesome components and miswirings. We have
also had good results in interfacing with our Fourier pulse set-up.

However, we wish to point out to those who own or are interested in
the Spectrosystem a software deficiency (in our opinion) which can limit
the apparent versatility of the system. While there will always be a
number of software idiosyncrasies (the plotting routines are at times
annoying), we have diagnosed a problem with the SHIM routine which can
be a terminal disease for a multi-scan averaging. We purchased the Shim
option so that the computer is able to optimize both y and curvature.
Really excellent homogeneity optimization is observed after only a few
SHIM iterations. But applied to a situation in which long-term signal
averaging is required (perhaps the primary reason for buying the option)
we find the Spectrosystem SHIM control becomes inherently less capable
(under our conditions) of providing significant corrections. In this
regard we find that after overnight signal-averaging under computer SHIM
control the homogeneity is often severely degraded. This results whether
we have used a parameter of one or several shim iterations per scan.
Switching to manual shim allows homogeneity optimization using very modest
y or curvature corrections at this point. Alternatively, if the run
string is cleared, then the computer SHIM will re-optimize after only
a few iterations.

It appears that the SHIM routine, as the total number of iterations
increases, makes smaller and smaller corrections in a given SHIM iteration.
After as few as 50 iterations (only one iteration per scan for 50 scans)
the routine is completely unable to make noticeable correction for a
modest homogeneity loss (say ~20%). Thus if homogeneity changes only in
a very slow fashion (compared perhaps to a 1/2-hour sweep) the computer
SHIM ought to be adequate, but then one may expect to end up with as
little as 0 to 20% of the original lock voltage if the rate of change
of the homogeneity becomes large.

One may forestall the inevitable by specifying a minimum (one) number
of iterations/scan. Things might be improved if the operator specifies
even less than one iteration/scan. Probably more fundamental changes in
the routine should be made. Since we have been unable to obtain a listing
of the Teletype Control routine from Varian Associates, we have not made
any changes ourselves. We would be pleased to hear from anyone who has
some thoughts on the subject (Varian perhaps?)

Very truly yours,

Philip I. Rose   S. Gross   Cont.

PIR/SG/mg

Cont. from Page 10

"Vacillating Shimitis", post-script

    R. Graves of this laboratory has just found from studying the machine language listing of the program that much of the aforementioned difficulty could be removed by changing a single instruction in the program. The program tests at instruction 3437_8 to see whether it is continuing a shim or starting over again. Since the program tests this point only once in a shim operation, it is possible, by replacing this instruction with a jump (JMP) instruction, to get the program to always assume that it is starting its shim from a cold start. The appropriate portion of the program is shown below along with the change:

$Address_8$	Mnemonic	$Instruction_8$	$Change_8$
3434	T1B	5102	
3435	LDA	10174	
3436	STB	60174	
3437	JAZ	1010	1000 (JMP)
3440	3521	3524	

P.I.R.

THE UNIVERSITY OF GEORGIA

Department of Chemistry

ATHENS, GEORGIA 30601

February 10, 1971

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

Dear Barry:

Comments on: The use of ^{7}Li nmr in the investigation of Aromatic Ion Pairs.

The relatively large upfield shift ($\sim$6 ppm) observed for the ^{7}Li resonance in fluorenyl lithium (I) was rationalized[1] by suggesting that the lithium cation was located directly above the plane of the fluorenyl carbanion. Subsequently, it was shown that the effect of solvent itself on the ^{7}Li chemical shifts of LiBr and LiClO$_4$ can be of the same magnitude ($\sim$6 ppm).[2] Since a change in the ^{7}Li shift of 3.2 ppm was observed for I on changing the solvent from ether to benzene, there remains the question of whether this change in chemical shift observed for I is a result of a solvent effect or a change in the structure of the ion pair. We report here some ^{7}Li data on aromatic carbanion systems which shows that the Li cation in certain of these systems is located in the π-cloud of the anion and that the ^{7}Li shifts are determined largely by the distance separating the anion and cation.

The data obtained from four carbanion systems are given in Table 1. All shifts are upfield from external aqueous 1.0 M LiCl. Since III-IV form contact ion pairs[3,4] in solution and their relative shifts are approximately the same for a given solvent, the range of shifts observed for II-IV are probably due to structural differences of the ion pairs. Since the cation is known to be coordinated with the allyl part[3] of II, the large upfield shifts for III and IV are most likely due to the lithium cation being located in the π-cloud of these anions and hence experiencing a shielding due to the diamagnetic ring current in III and IV.

The data for I do not appear to support this view since the effect of solvent on the ^{7}Li shifts of I is as large as the range of shifts observed for II-IV. However, I is a unique system compared to II-IV in that I forms both contact and solvent separated ion pairs depending upon the solvent.[5] In ether, contact ion pairs are formed whereas solvent separated ion pairs are formed in THF, DME and HMPA. Therefore, it appeared that the ^{7}Li shifts of I could still be a result of the lithium cation being located above the π-cloud of the anion with

Dr. Bernard L. Shapiro
Page 2
February 10, 1971

solvent influencing the distance separating the anion and cation. The shielding of the lithium cation by the diamagnetic ring current in the anion is expected to decrease with increasing distance of separation. We have estimated the distance separating the two ions in the solvent separated ion pairs in THF, DME, and HMPA by assuming one solvent molecule between anion and cation. The distance in the contact ion pair in ether was taken to be the sum of the ionic radui of the two ions. There is an excellent linear correlation between the ^{7}Li shifts of I with solvent and the distance separating the two ions. Therefore, the large range of shifts observed for I is a result of solvent affecting the distance separating the two ions and the suggestion that the lithium cation is located above the π-cloud of the fluorenyl anion remains a valid description. The data do point out however, that a large upfield shift for the ^{7}Li resonance is not a requirement for a lithium cation being located in the π-cloud of an aromatic anion. The ^{7}Li shift depends directly upon the distance separating the two ions.

Sincerely yours,

Dick

Richard H. Cox
Assistant Professor

^{7}Li Shifts in Some Aromatic Anion Systems

Anion/Solvent[a]	δ, ^{7}Li
Fluorenyl/Ether	6.95
Fluorenyl/DME	3.04
Fluorenyl/THF	2.07
Fluorenyl/HMPA	0.73
II 1-Phenylallyl/DME	0.61
II 1-Phenylallyl/THF	0.96
III Cyclopentadienyl/DME	8.66
III Cyclopentadienyl/THF	8.37
IV Indenyl/DME	6.62
IV Indenyl/THF	6.17

a. 0.4 M solution

1. J. A. Dixon, P. A. Gwinner and D. C. Lini, J. Am. Chem. Soc., 87, 1379 (1965).
2. G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller and W. K. Musker, Inorg. Chem., 5, 554 (1966).
3. V. R. Sandel, S. V. McKinely and H. H. Freedman, J. Am. Chem. Soc., 90, 495 (1968).
4. J. B. Gruntzer, J. M. Lawlar and L. M. Jackman, private communication.
5. L. L. Chan and J. Smid, J. Am. Chem. Soc., 88, 307 (1966).

BRYN MAWR COLLEGE
BRYN MAWR, PENNSYLVANIA 19010, USA

DEPARTMENT OF CHEMISTRY   TEL: (215) LA 5-1000

10 February 1971

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

Dear Barry:

Calculation of Exchange-Broadened NMR Lineshapes

We have examined the application of Binsch's treatment
of chemical exchange [1969 JACS 91, 1304] to the nuclear
magnetic double resonance problem. The Liouville-space
representation of the problem developed by Binsch is especially
well-suited to treat the relaxation processes necessary in
understanding lineshapes and intensities in double
resonance.

For a simple two-spin-1/2 system, we find that the
populations of the four states respond, in a sense, to
competition between exchange and relaxation in the presence
of the strong (second) rf field. The result in terms of
lineshapes are a variety of nuclear Overhauser effects
brought upon by a combination of nuclear polarization by
the rf field, relaxation, and exchange.

Particularly useful may be a strong decoupling
experiment to measure exchange rates near the relaxation rate,
and a tickling experiment to more easily measure exchange
rates below coalescence.

The work will be reported in a future issue of J. Mag.
Res., and at the DNMR symposium, ACS meeting in Los Angeles.

Sincerely yours,

Jay Martin Anderson
Associate Professor

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

Metal Complexes of 1-(2-Aminoethyl)aziridine

Dear Professor Shapiro!

In the course of our studies of metal complexes of aziridine
as potential alkylating cytostatics we run the proton n.m.r.
spectra of such compounds. When checking the spectrum of an
aqueous solution of the paramagnetic complex $[Co^{II}(aziridine)_4]Cl_2$
we obtained the time-dependent contact shift spectra of fig. 1.

Fig. 1
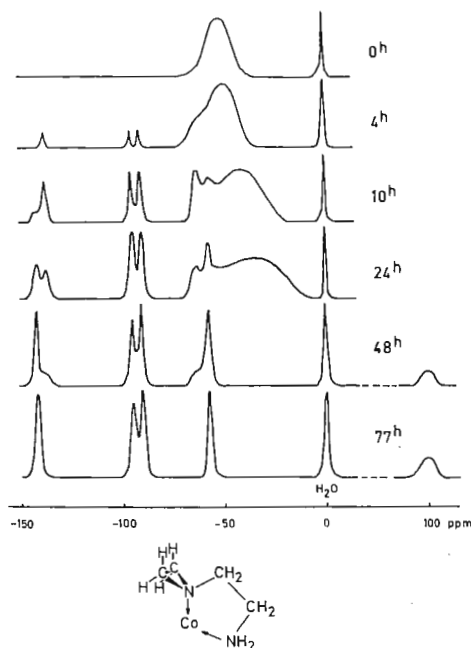
On decomposition of the finally present complex the amine ligand
proved to be dimerized, namely to be l-(2-aminoethyl)aziridine
with the proton n.m.r. spectrum of fig.2.

Fig. 2

This compound is normally the first step in the polymerisation
of aziridine. In the table the n.m.r. data of some other com-
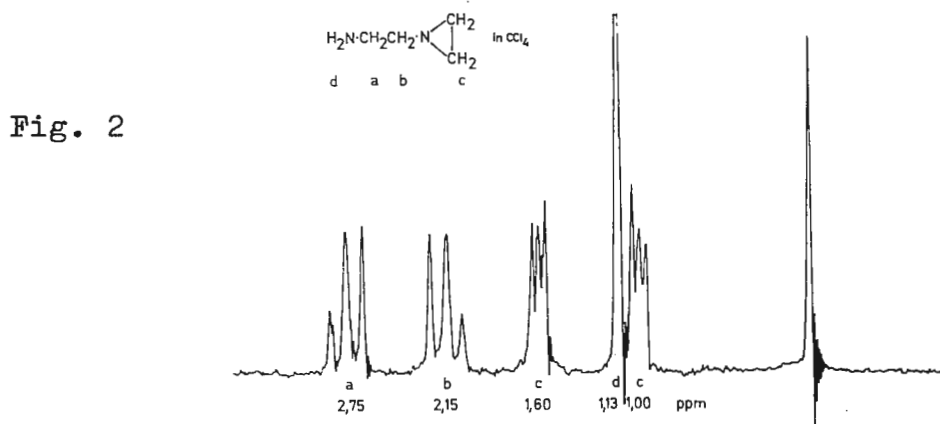plexes of that chelate ligand are listed. By comparison with
the spectrum of the free amine it seems plausible, to assume
a mono-dentate coordination of the ligand in the silver complex.

Since there seems to be a growing interest in the aziridine
system and its complexes, the data might be of some use to
other complex chemists.

Yours sincerely

(Heinz P. Fritz)   (G. Hierl)

^{1}H-n.m.r. spectra of 1-(2-aminoethyl)aziridine and some of its complexes.

Substance	solv.	a	b	c	d	e
1-(2-aminoethyl)aziridine = diin	--	-1,04;	-1,59	-2,14	-2,72	-1,42
	CCl$_4$	-1,02;	-1,60	-2,15	-2,75	-1,26 [b)
	D$_2$O	-1,32;	-1,73	-2,32	-2,77	b)
[Ag(diin)$_2$]NO$_3$	D$_2$O	-1,43;	-1,85	-2,38	-2,94	b)
[Zn(diin)$_2$]SO$_4$·H$_2$O c) [Zn(diin)$_2$]J$_2$ c)	D$_2$O	-1,73;	-2,04	-2,50	-2,91	b)
[Zn(diin)$_3$](ClO$_4$)$_2$	D$_2$O	-1,63;	-1,93	-2,42	-2,86	b)
[Cd(diin)$_2$]SO$_4$·H$_2$O c) [Cd(diin)$_2$](NO$_3$)$_2$ c)	D$_2$O	-1,72;	-2,04	-2,42	-2,88	b)
trans-[Co(diin)$_2$(NO$_2$)$_2$]NO$_3$	D$_2$O	-2,18;	-2,27	-2,52	-2,80	b)
		a	b	c1,2 or c1d1	d1,2 or c2d2	e
[Co(diin)$_2$(H$_2$O)$_2$]Cl$_2$·2H$_2$O d)	H$_2$O	-142	-58	-89	-94	+100

Header: Assignment, δ-values [ppm] at 37°,a)

a) Center of signals rel. int. DSS (in D$_2$O) or int. TMS (in CCl$_4$); negative values at low fields.

b) Due to exchange in CCl$_4$ concentration dependent, in D$_2$O not observable.

c) For both pairs of substances there are within experimental error identical δ-values.

d) Contact shifts rel. H$_2$O-signal.

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA, CALIFORNIA 91109

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
GATES AND CRELLIN LABORATORIES OF CHEMISTRY

February 11, 1971

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

EARTHQUAKES AND NMR

Dear Barry,

Some of your readers located in earthquake-prone areas may wonder what to expect if their nmr equipment is shaken up by an earthquake. The recent quake here at 6 a.m. on February 9, of intensity 6.5 Richters, at an epicenter some 30 miles away, can supply one experimental point. Perhaps others can supply more points.

Our ^{13}C - ^{15}N digital-frequency-sweep spectrometer is located on the third floor of the Church Laboratory and, in the course of the earthquake, the 12" Varian magnet mounted on a wooden pallet with its long axis east and west, made a permanent move 5" due south. The Varian super-stabilizer, mounted in the usual way on top of the magnet, at some time in the 30-sec duration of the quake, moved north rapidly enough to leave the top of the magnet and crash into a wall 3' from the magnet. A possible morale is that super-stabilizers should be fastened to the top of the magnet. No further reports of damage to the several other nmr machines at Caltech have been received, so that some of the problems with the DFS spectrometer magnet may have been due to a special building resonance.

It boggles one's mind a bit to contemplate the prognostications of the Caltech geologists who say that a "great" quake is possible - indeed some years overdue - on the basis of an average of one per 100 years, involving the San Andreas fault (the world's largest) running from about 50 air miles from here up all the way north to practically underneath Varian Associates. Such a quake along the San Andreas fault could be up to 8.5 Richters - 100 times the magnitude we experienced the other day. In such a quake, I think we can expect magnets on upper floors to go right through the walls (if not the floors), and maybe one should consider this in selecting sites for future nmr installations, especially of 15" magnets.

With all good wishes,

Very truly yours,

Jack

John D. Roberts

Sodium binding as an adaptation mechanism to extreme saline conditions in Halophilic bacteria.

The state of sodium in a Halophilic bacterium taken from the Dead Sea has been studied by ^{23}Na nmr. The first side band of the sodium resonance taken at a modulation frequency of 400 Hz, which is larger than the linewidth, has been measured. The observed line in the preparation is broader than that of an aqueous 2.0M or 0.2M NaCl solution. The total area of the resonance measures the total concentration of "observable" sodium, (i.e. sodium which is not bound so firmly that its linewdith would be extremely broad). The bacteria have been cultured under two conditions: (1) in a low NaCl medium (0.2M) and (2) in a high NaCl medium (2M).

When the calculated inter-cellular sodium is subtracted, the percentage of the total bacterial sodium observable by nmr has been found to be: (1) 60% in low salt; (2) nill in high salt. The intracellular concentrations of sodium have been found to be 0.08M and 1.3M for preparations (1) and (2) respectively.

The change in the nature of the sodium binding between low and high salt cells has been studied by measuring the decrease in the "observable" sodium as a function of time when low salt cells are transferred to high salt medium.

B. Schachar-Hill   H. Gilboa
Lab. of Biochemistry   Lab. of Phys. Chemistry

Technion-Israel Institute of Technology
Haifa, Israel

LABORATORIUM VOOR ORGANISCHE
SCHEIKUNDE DER UNIVERSITEIT VAN
AMSTERDAM
NIEUWE ACHTERGRACHT 129
TELEFOON 947174 (5 LIJNEN)

AMSTERDAM, February 22nd, 1971

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

SIMEQ, an NMR program for the Varian 620-i

Dear Professor Shapiro,

We found the spin simulation program, issued with the
Varian SpectroSystem 100, very useful, especially for
teaching purposes. The Varian software however, has several
limitations, some of which are overcome in our new program
"SIMEQ".
SIMEQ computes NMR spectra from chemical shifts and
coupling constants. It uses magnetic equivalence factoring
(R.C.Ferguson and D.W.Marquardt, J.Chem.Phys. $\underline{41}$, 2087
(1964)).to reduce the size of the Hamiltonian matrix.
Output: 1. energy levels and assigned transitions
         2. list of frequencies and intensities
         3. plot
            (contrary to the Varian program, SIMEQ allows
             variation of the plot width).
Limitations:
The maximum size of a sub-matrix of the Hamiltonian is
35 x 35. Some limiting systems are: ABCDEFG, $A_6B_5C_2D$,
$A_8B_6C_5$. In addition, one group X (up to X_6) is accepted,
for which the X-approximation is used.
The maximum number of transitions that can be stored
to be used for outputs 2 and 3 is 449.
Timing: ABCDE   90 s
         ABCDEFG   7 min
         $X_6A_6B_6C_5$ many hours (21,504 levels)
The program is written in Assembler Language and uses
8 k core store.

Object tape and operating instructions are available
upon request.

Sincerely Yours,

C.W.F.Kort

P.C.van der Haak

LABORATORIUM VOOR FYSISCHE CHEMIE

Toernooiveld
Driehuizerweg 200, Nijmegen
Telefoon (08800) 5 83 33

FACULTEIT DER WISKUNDE
EN NATUURWETENSCHAPPEN
KATHOLIEKE UNIVERSITEIT
NIJMEGEN, NEDERLAND

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

U.S.A.

Uw kenmerk   Uw brief van   Ons kenmerk

Datum February 24, 1971.

Onderwerp Spin relaxation between two aromatic hydrocarbon anions.

Dear Professor Shapiro,

In a recent publication [1,2] we pointed out that paramagnetic aromatic anions might act as suitable spin relaxers in solutions of other aromatic anions, in this way increasing the nuclear relaxation times of the latter so that the NMR signals can be more easily detected [3,4].
To test this idea we have carried out ^{1}H and ^{2}D NMR experiments on a mixture of the anions of naphthalene-d8 (Nl-d8), 0.5 M, and biphenyl-h10 (Bp-h10), 1.2 M, dissolved in 1,2-dimethoxyethane (DME) with Na$^+$ as counter ion.
The results of our measurements are summarized in table 1 and 2, and clearly demonstrate the effect.

	1.2 M Na$^+$.Bp-h10$^-$ }DME +0.5 M Na$^+$.Nl-d8$^-$	1.2 M Na$^+$.Bp-h10$^-$/DME	1.7 M Na$^+$.Bp-h10$^-$/DME
$T_{2,H_{meta}}^{-1}$ (rd/s)	420	700	400
$T_{2,H_{ortho}}^{-1}$ (rd/s)	9800	17200	9600

Table 1 Proton linewidths of Na$^+$.Bp-h10$^-$/DME

The accuracy of the linewidth measurements is $\pm$ 7%.

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KATHOLIEKE UNIVERSITEIT
NIJMEGEN

| Geadresseerde | Prof. Shapiro | Ons kenmerk | Datum | Blad No 2 |

	1.2 M $Na^+.Bp-h10^-$ $\big\}$DME $+ 0.5$ M $Na^+.Nl-d8^-$	0.5 M $Na^+.Nl-d8^-$/DME	1.7 M $Na^+.Nl-d8^-$/DME
$T_{2,D\beta}^{-1}$ (rd/s)	200	1400	280
$T_{2,D\alpha}^{-1}$ (rd/s)	1200	7200	1700

Table 2 Deuterium linewidths of $Na^+.Nl-d8^-$ /DME

The accuracy of the linewidth measurements is $\pm$ 7%.

Table 1 shows that the linewidths of the ortho and meta protons of $Bp-h10^-$ in the mixed sample (total radical concentration of anions equal to 1.7 M, but the Bp^- concentration only 1.2 M) are almost equal to the proton linewidths measured on a solution containing only $Bp.h10^-$ in a concentration of 1.7 M and considerably smaller than the linewidths measured on a sample containing only Bp^-, in a concentration of 1.2 M. The ^2D linewidths of $Nl.d8^-$ show the same behaviour (table 2), except that the ^2D linewidths observed for $Nl-d8^-$ in the mixed sample are still smaller than those observed for the 1.7 M solution containing only $Nl-d8^-$.

Approximately the linewidths vary   linearly with the reciprocal of the radical concentration, indicating that the Fermi-contact interaction is the dominating relaxation mechanism [2].

From the measurements one may draw the conclusion that

$$J_{Bp^-, Bp} \simeq J_{Bp^-, Nl^-} \rangle J_{Nl^-, Nl^-}$$

where J represents the exchange interaction between the electron spins. This means that the exchange interaction between Bp^- and Nl^- or between two Bp^- anions is more effective than the exchange interaction between two Nl^- anions. Since Bp^- is a rather stable anion and well soluble in most ethers it is a convenient relaxing agent for the study of NMR spectra of other radical anions.

Model 154 500 4 69

Geadresseerde Prof. Shapiro   Ons kenmerk   Datum 24 – 2–1971   Blad No 3

[1] G.W. Canters, B.M.P. Hendriks and E. de Boer J. Chem. Phys. 53, 445 (1970).

[2] B.M.P. Hendriks, G.W. Canters, C. Corvaja, J.W.M. de Boer and E. de Boer Mol. Phys. in press (Febr. 1971).

[3] R.W. Kreilick, J. Am. Chem. Soc. 90, 2711 (1968).

[4] R.A. Zelonka and M.C. Baird, Chem. Comm. 1448 (1970).

(B.M.P. Hendriks)   (E. de Boer)

𝔇uke 𝔘niversity
DURHAM
NORTH CAROLINA
27706

DEPARTMENT OF CHEMISTRY
PAUL M. GROSS CHEMICAL LABORATORY

February 25, 1971

TELEPHONE 919—684—2414

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

Some NMR Properties of Phospholenes

Dear Dr. Shapiro:

Two TAMUNMR letters have recently appeared on organophosphorus compounds that prompt the present contribution.

First, G. Mavel has reported on his nmr work on 1-phenyl-3,4-dimethyl-phosphole (TAMUNMR 140.2). The coupling constant for P and the α-proton is 37.5 Hz, consistent with our assignment [Quin, Bryson and Moreland, J. Am. Chem. Soc., 91, 3308 (1969)] in 1-methyl phosphole of the large coupling (39.5 Hz) to the α-proton, and the small coupling (13.9 Hz) to the β-proton. This is the opposite of the assignment for trivinylphosphine. Mavel then made the suggestion that this effect may be attributed to the aromatic character of the phosphole system. We want to point out, however, that the α-proton in 2-phospholenes also has a very large coupling constant (see below), of the same size found for the phospholes. Aromatic character of the phosphole system, then, is not responsible for the large J_{PCH} value. Much of our work on the 2-phospholenes is described in a paper in press in J. Org. Chem. (Myers and Quin).
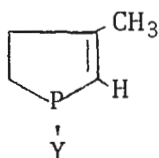
Y	J_{PCH}, Hz
CH_3	42
Cl	46.5
Br	46.5
$N(C_2H_5)_2$	40

Second, Dorothy Denney reports (TAMUNMR 148.17) some unusual ^{31}P chemical shifts for phosphetanes, finding that small changes in the substitution pattern around the ring caused substantial differences in the ^{31}P values. Of

interest to us are the values reproduced below.
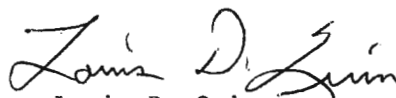

-1.5, -2.5   -8 ppm   -44
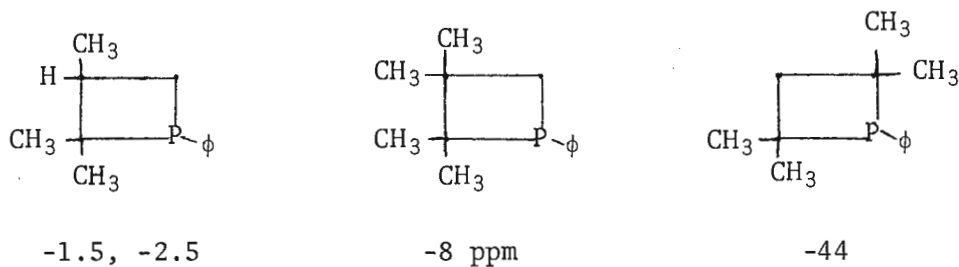
Thus, strong deshielding accompanies increased ring methylation, especially at the α-position to phosphorus. We have observed a similar effect in 3-phospholenes. The values below (relative to 85% H_3PO_4 as standard) show that the steric environment about phosphorus has a pronounced influence on the ^{31}P chemical shift, deshielding again accompanying an increase in substitution or in crowding.

δP^{31} = +33.5 ppm   +27.6   +16.7   +8.9
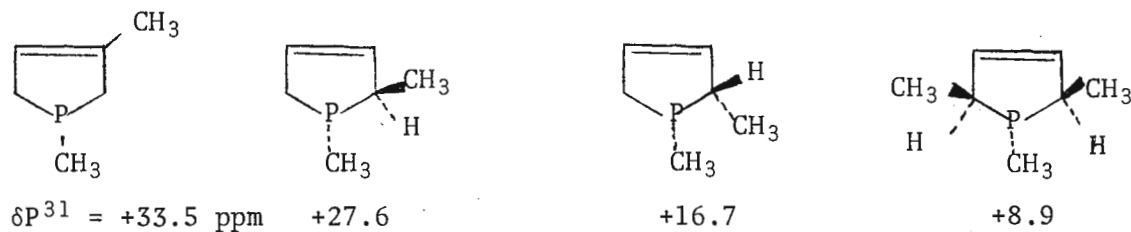
This submission is made on behalf of Peter W. Jeffs of this Department.

Very truly yours,

Louis D. Quin

Joseph J. Breen

John F. Engel

LDQ/cp

UNIVERSIDADE DE COIMBRA
LABORATÓRIO QUÍMICO DA FACULDADE DE CIÊNCIAS
COIMBRA--PORTUGAL--TELEF. 22826

CENTRO DE ESTUDOS DE QUIMICA NUCLEAR E RADIOQUIMICA

THE CHEMICAL LABORATORY

UNIVERSITY OF COIMBRA

PORTUGAL

26th February 1971

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

Dear Professor Shapiro,

FURTHER N.M.R. STUDIES OF THE CONFORMATION
OF BENZALANILINES

Our previous work on the conformation of benzalanilines based on
proton chemical shifts (to appear in Tetrahedron) is being extended to si-
milar imines that are expected to be effectively more planar, namely sali-
cylalanilines:
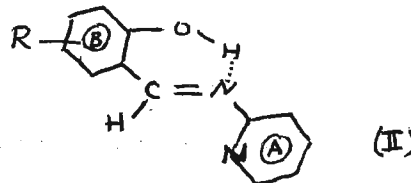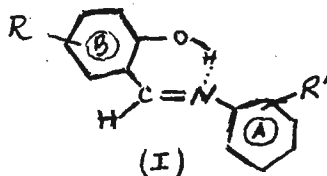
The proton N.M.R. spectra of (I) and (II) clearly reveal a decrease of the
averaged (effective) dihedral angles between the H-C=N nuclear plane and
the ring planes relative to benzalanilines. For the B-rings this is obviously
due to a very strong intramolecular hydrogen bond ($\tau_{OH} \approx$ — 2.4 — —2.7,
in C_6H_{12}); for the A-ring of (II) the decrease is due to an attractive in-
teraction between the pyridine N atom and the H atom in H-C=N.

Yours sincerely,

Victor M.S. Gil

M.E.L. Saraiva

Uppsala universitet
Fysiska institutionen

University of Uppsala
Institute of Physics

24.2.1971

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

Substituent effects on ^{19}F chemical shifts and spin
couplings in fluorothiophenes

Dear Professor Shapiro,

Professor S. Gronowitz and Dr. U. Rosén at Chemical Center,
University of Lund, Sweden and I have now completed an
extensive NMR investigation of substituted fluorothiophenes,
which was started some years ago by Professor Gronowitz
with the main interest to study substituent effects on ^{19}F
NMR chemical shifts, and if possible relate them to reacti-
vity parameters. One paper about synthesis of substituted
fluorothiophenes will be published in Chemica Scripta and
two papers about the NMR investigation will be published
in Acta Chem. Scand. but as it will be several months be-
fore they appear in the journals I want to report some of
the results obtained.

The ^{19}F chemical shifts and spin-spin coupling constants
of 5- and 4-substituted 2-fluorothiophenes (denoted I and
II) and of 5-substituted 3-fluorothiophenes (denoted III)
have been correlated with the reactivity parameters $\mathscr{F}$ and
$\mathscr{R}$ of Swain and Lupton[1] by means of linear two parameter
equations z= i+f$\mathscr{F}$ +r$\mathscr{R}$. The regression constants f and r
and the intercept i obtained are given in the Table. The
J_{2F-5} coupling in 4-substituted 2-fluorothiophenes was not
found to correlate significantly with $\mathscr{F}$ and $\mathscr{R}$, which in
part is due to the small substituent dependence of this
coupling, and is therefore not included in the Table. For
comparison with the results of the fluorothiophenes the
regression constants from analyses of the fluorine shifts
in para and meta substituted fluorobenzenes determined by
Taft et al.[2] are also included in the Table. It can be
noted that the fluorine shifts in 5-substituted 2-fluoro-
thiophenes and in para substituted fluorobenzenes are very
similarly affected by the resonance parameter, whereas the
fluorothiophene shift is 50% more sensitive to the induc-
tive effect.

For the "meta"-substituted fluorothiophenes the field effect is also of greater importance in the determination of the fluorine shifts than for the meta substituted fluorobenzenes. However, while the mesomeric contribution to the shifts is of importance in the two thiophene cases it is insignificant in the benzene case.

There exists an approximate linear relation between the fluorine shifts in the two "meta" substituted fluorothio-phenes:

$$\delta_F^{III} = -0.2 \pm 0.5 + (0.81 \pm 0.08)\delta_F^{II}$$

with a standard deviation of 0.8 ppm and a correlation constant of 0.93.

There is also a linear relation between the H-F couplings J_{2F-3}^{I} and J_{3F-2}^{III}:

$$J_{2F-3}^{I} = 0.61 \pm 0.07 + (1.02 \pm 0.05)J_{3F-2}^{III}$$

with a standard deviation of 0.08 Hz and a correlation constant of 0.98.

Yours sincerely,

Sören Rodmar

References

1. Swain, C.G. and Lupton, Jr., E.C.
    J. Amer. Chem. Soc. 90 (1968) 4328.

2. Taft, R.W., Price, E., Fox, I.R., Lewis, I.C.,
    Andersen, K.K. and Davies, G.T.
    J. Amer. Chem. Soc. 85 (1963) 709, 3146.

Table   Regression constants r and f and intercepts i for the ^{19}F chemical shifts[a] and the spin couplings (in Hz) of monosubstituted fluorothiophenes and for the ^{19}F chemical shifts[a] of fluorobenzenes[b].

z	i	f	r	σ^c	C^d	N^e
δ_F^I	-3.8 ± 1.1	-7.5 ± 1.8	-25.0 ± 3.1	2.2	0.96	12
δ_F^{II}	-1.3 ± 0.5	-8.0 ± 0.9	5.3 ± 1.6	0.9	0.94	10
δ_F^{III}	-1.6 ± 0.6	-6.4 ± 1.0	4.9 ± 1.6	1.1	0.89	11
J_{34}^I	3.91 ± 0.05	0.59 ± 0.09	-0.11 ± 0.16	0.11	0.90	13
J_{2F-3}^I	1.54 ± 0.04	0.99 ± 0.06	-3.17 ± 0.12	0.08	0.99	11
J_{2F-4}^I	3.26 ± 0.09	0.58 ± 0.15	0.72 ± 0.28	0.19	0.85	11
J_{35}^{II}	1.83 ± 0.06	0.27 ± 0.10	-0.69 ± 0.17	0.10	0.80	10
J_{2F-3}^{II}	1.64 ± 0.11	-0.57 ± 0.20	0.35 ± 0.37	0.18	0.69	8
J_{24}^{III}	1.52 ± 0.07	0.62 ± 0.11	-0.78 ± 0.22	0.12	0.87	11
J_{3F-2}^{III}	0.90 ± 0.06	0.98 ± 0.10	-3.30 ± 0.22	0.11	0.98	9
J_{3F-4}^{III}	-0.83 ± 0.10	0.07 ± 0.15	-0.82 ± 0.33	0.17	0.60	9
δ_F^p	1.0 ± 0.8	-5.0 ± 1.2	-22.5 ± 1.5	1.5	0.98	16
δ_F^m	0.9 ± 0.3	-4.2 ± 0.4	-0.6 ± 0.5	0.5	0.95	14

a)   In the regression analyses the shifts are given in ppm relative to that of the unsubstituted compounds, and a minus sign of a shift means a downfield shift.

b)   The experimental shifts of the para and meta substituted fluorobenzenes are taken from ref. 2.

c)   Standard deviation.

d)   Correlation coefficient.

e)   Number of substituents in the regression analysis.

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NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

OTTAWA 7.

February 16, 1971

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

Additional FT-100 Capabilities

Dear Barry,

       Some time ago we acquired a computer and associated box of tricks from "Varian Associates" for obtaining proton-Fourier Transform spectra at 100 MHz. To my surprise it was found that a continuous wave signal averaging capability was not included in this package. A short program was written to fit into the Fourier Transform program and to give signal averaging capabilities. It requires a voltage controlled audio oscillator, e.g. "Wavetek" 113 and uses the spare multiplex part in the "Varian" ADC. Further details are available to interested parties.
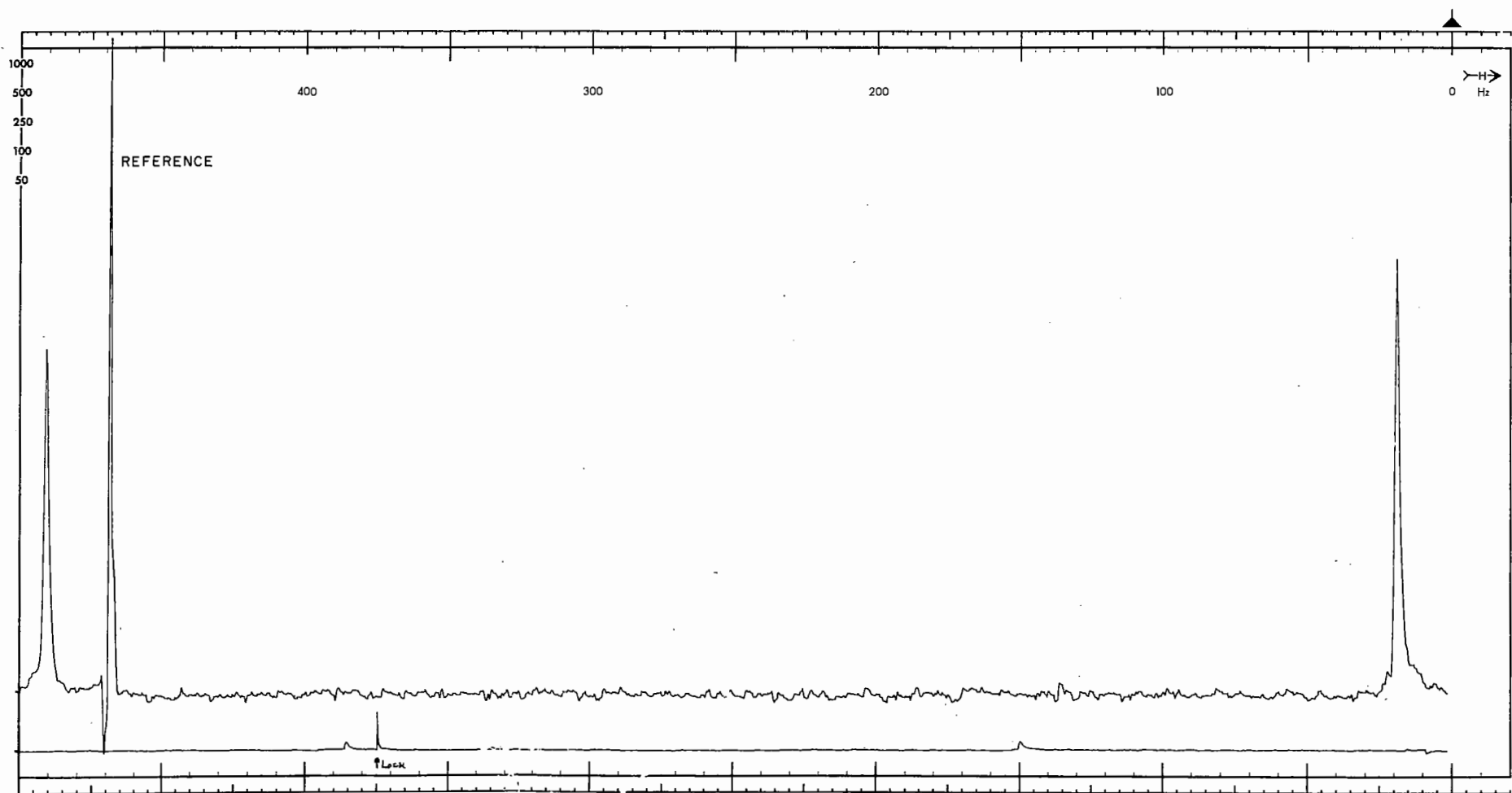
       It was found that when the HA-100 system is tuned for 94.1 MHz and looking at fluorine the bandwidth of the power amplifier in the FT-100 is sufficient to obtain fluorine Fourier Transform spectra without difficulty. The accompanying figure shows the spectrum of a 0.1 molar solution of PF_5 at -80°C. The reference is CF_4.

Yours truly,

S. Brownstein.

SB/dn
Enc.

REFERENCE

HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

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

February 19, 1971

Dear Barry,

"Fourier Transform T_1 Measurement"

We have recently been using the Vold et. al.[1] pulse sequence on our FT-100 spectrometer to determine T_1 nuclear spin relaxation times for complete spectra. The spectrometer is a Varian HA-100D with Varian Fourier Transform accessories. For T_1 determinations the pulse sequence used is T - 180° - t - 90°, where T is some long "wait" time to allow the magnitization to fully relax along the z-axis, and t is the variable time-delay between the 180° and 90° pulses. The transient is collected after the 90° pulse and transformed to give the spectrum.

The procedure described above was applied to a solution of 1.6 M ethyl iodide and 0.75 M benzene in deuterobenzene. The spectrometer was locked on internal benzene between pulse sequences but the lock was turned off during pulses to prevent distortion of the spectra.

Figure 1 shows the spectra obtained for t in the range 2.0 - 5.0 sec.: the chemical shift between the methyl triplet and methylene quartet is 128 Hz. It is clear from the spectrum at t = 3.5 sec. that the methyl triplet has a somewhat shorter T_1 than the quartet. The complete range of delay-times used was 0.02 - 60.0 sec., while the wait-time T was set at 50.0 sec.

For relaxation along the z-axis following a 180° pulse the peak heights should obey the equation

$$P(t) = P_\infty (1-2e^{-t/T_1}), \tag{1}$$

where t is the delay time, and P_∞ is the peak height at $t \Rightarrow \infty$. Rearranging (1) we have

$$\ln \left(\frac{P_\infty - P(t)}{2P_\infty} \right) = \frac{-t}{T_1} \tag{2}$$

so plots of LHS vs t have slopes of $-1/T_1$.

The value of P_{∞} for each peak in the ethyl iodide spectrum was determined from the average of five measurements at t = 60.0 sec. A computer program was written to perform a linear least-squares analysis of the data and plot the results. The data for each peak include 12-15 points in the time range 0.02 - 10.0 sec. The plot obtained for the central peak of the triplet is shown in Figure 2. The numbers at the bottom of the graph are the y and x coordinates of the point in the lower-right corner.

Table I gives the results for ethyl iodide with the peaks numbered from low to high field and the least-squares stand. dev. and y-intercept in natural log. units. The error estimate on T_1 is derived from the stand. dev. From (2) we expect the intercept to be zero and for all peaks except 2 and 3 it is less than or about equal to the stand. dev.

TABLE I

PEAK	STAND. DEV.	Y-INTERCEPT	T_1
1	0.041	−0.009	5.03 ± 0.20
2	0.023	−0.049	5.48 ± 0.14
3	0.020	−0.036	5.40 ± 0.11
4	0.020	+0.007	4.92 ± 0.10
5	0.033	−0.021	4.69 ± 0.15
6	0.018	−0.017	4.67 ± 0.10
7	0.021	−0.024	4.74 ± 0.09

It is interesting to note that the relaxation times fall into three groups: the triplet peaks all relax with T_1 = 4.7 sec. while the inner peaks of the quartet have T_1 = 5.4 - 5.5 and the outer peaks have T_1 = 4.9 - 5.0. We do not feel that intercept error is entirely responsible for the T_1 differences observed in the quartet.

1 Journal of Chemical Physics. 48, 3831 (1968).

Yours sincerely,

Steve Patt

Brian D. Sykes

Joel Cook

William Hull

BDS:krs

T=2.0

T=3.0

T=3.5

T=4.0

FIGURE 1

T=5.0

ETHYL IODIDE 2.18   6
TI PLOT
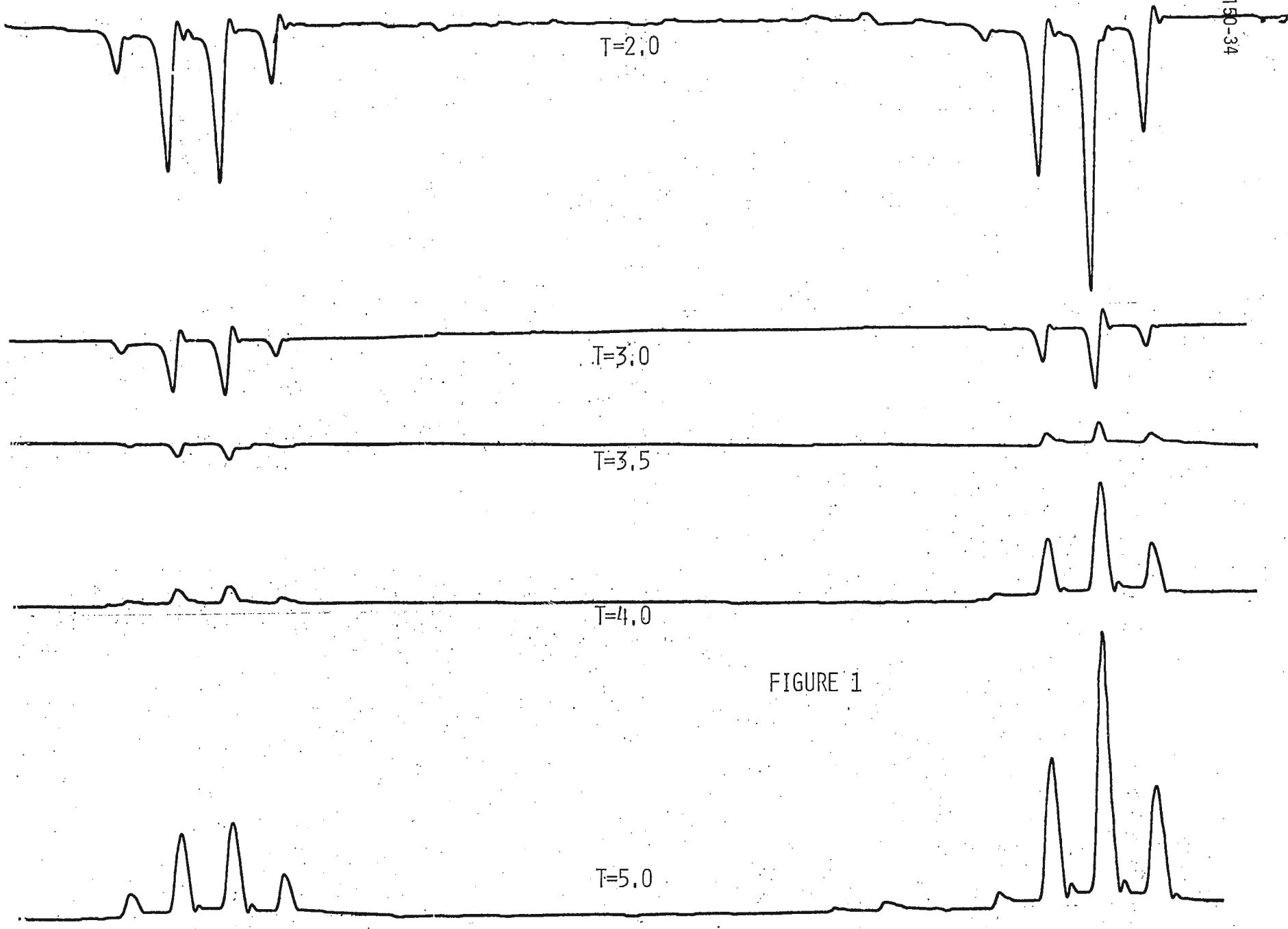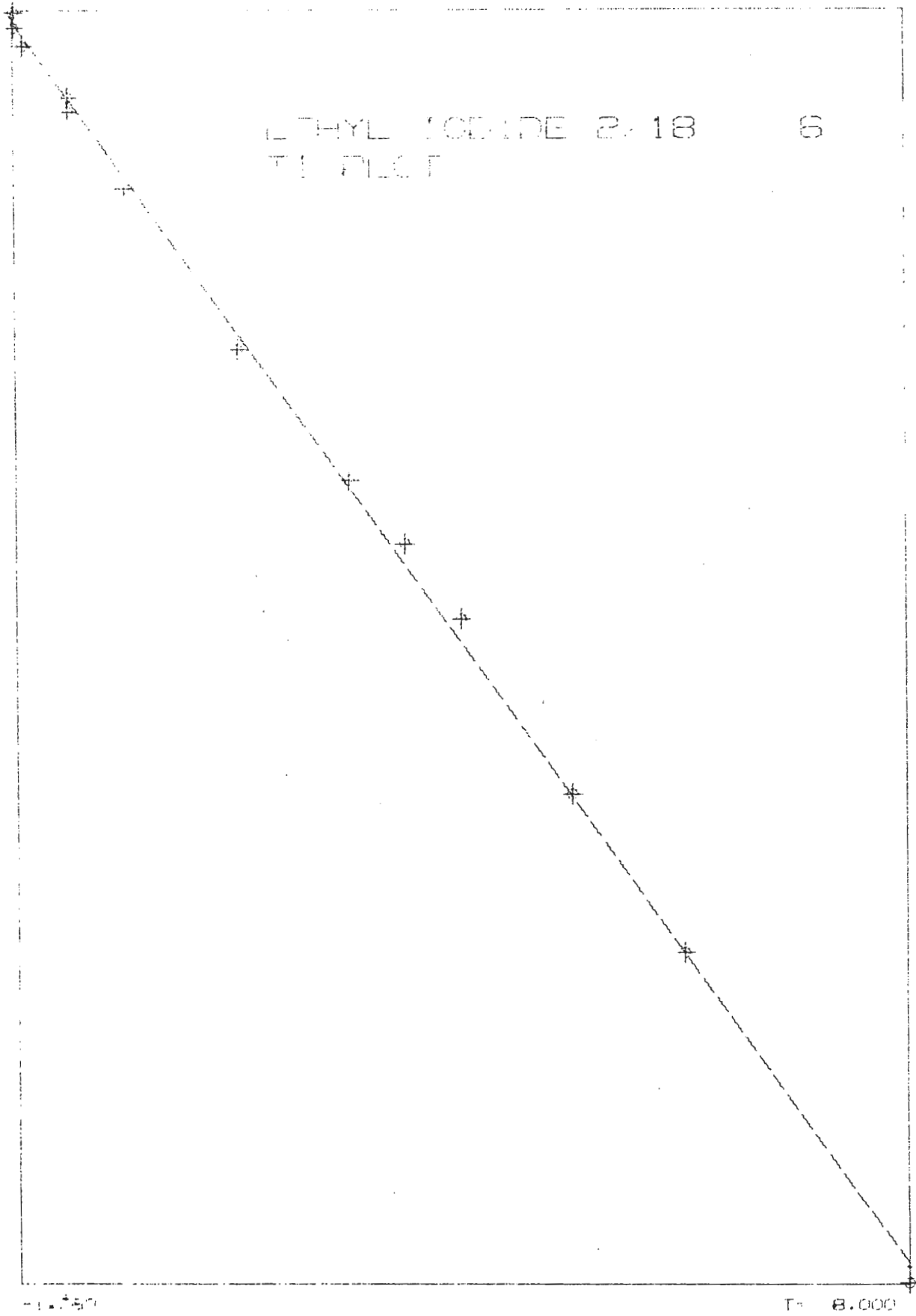
TEXAS CHRISTIAN UNIVERSITY

Fort Worth, Texas 76129

Department of Chemistry   March 2, 1971

Dr. B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas   77840

Conformations of α-Naphthaldehydes;
Another "Through Space" H-F Coupling

Dear Barry:

Recently we have examined the spectra of a number of unsymmetrically
substituted 1,4-di-X-naphthalenes with a view to learning yet more
about substituent effects on proton chemical shifts. In the series
1-formyl, 1-acetyl, 1-propionyl, 1-isobutyrl, 1-pivalyl-4-methoxy-
naphthalene there is a striking upfield march of H_8 from 0.78 $\underline{\tau}$ to
2.44 $\underline{\tau}$ as the bulk attached to the carbonyl group increases.

From our experiences with benzaldehydes and acetophenones we began
to suspect that the aldehyde group unexpectedly preferred conforma-
tion I to II. Without supplying all the data, the argument can be
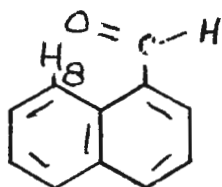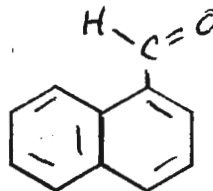
I   II

supported by several lines of fact. The behavior of H_2 for a series
of 1-X-4-methoxynaphthalenes follows a Q relation which requires the
Q characteristic of an aldehyde held so that the ortho proton is as
In I — not as in II. Secondly, there is no long range coupling of
the aldehyde to H_3. Thirdly, as H_8 marches upfield in the series
above there is a concomitant downfield swing of H_2. Finally, there
is a significant NOE for H_2 but none for H_8 on irradiating the acetyl
methyl. The effect decreases as one goes up the series.

Calculations based on the Pople-Jackman model for the carbonyl bond
anisotropy suggest that in going from I to a form with the carbonyl
at right angles to plane, H_8 should shift about 1.1 ppm upfield. The
experimental range above is 1.6 ppm.

Dr. B. L. Shapiro   2

Sterically II should be favored over I if the formyl group is to be planar with the ring. The conclusion that I is the more stable form suggests a hydrogen bonding interaction to H_8. To the best of our knowledge this is the first example of such to an aromatic proton.

We were interested in the recent report of Dahlquish and Hornfeldt, TAMUNMR 148-34 and recognize that our conclusions are contra to theirs regarding the C=O anisotropy. We feel compelled to stick with our case.

   Best regards,

                              Bill

                              W. B. Smith
                              Chairman
                              Department of Chemistry

WBS/dc

Given all this extra space, I'll pen you a note. While Art Ihrig was here, we noted in _ortho_ fluoro-acetophenone a large coupling (5.1 H_3) between the fluorine and the methyl. The value increased to 6.2 H_3 at -63° and decreased to 4.1 H_3 at 150°. Coupled with proton chemical shift data on _ortho_ substituted benzaldehydes and acetophenones one can make a good case for

More
Stable
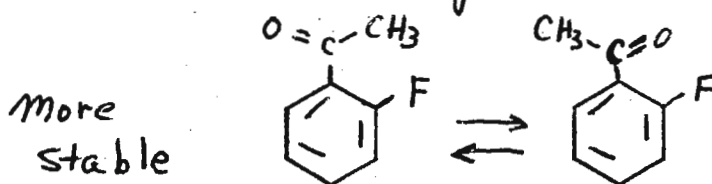
This work was rejected by J. Phys. Chem. on the grounds solely that it was physical organic chemistry. Chacun à son gout.

The H—F coupling seems to be another example of a "through-space" effect.

Zug, March 1, 1971

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

College Station, Texas 77843

Suggested title: "^{13}C satellites of ^{13}C satellites"
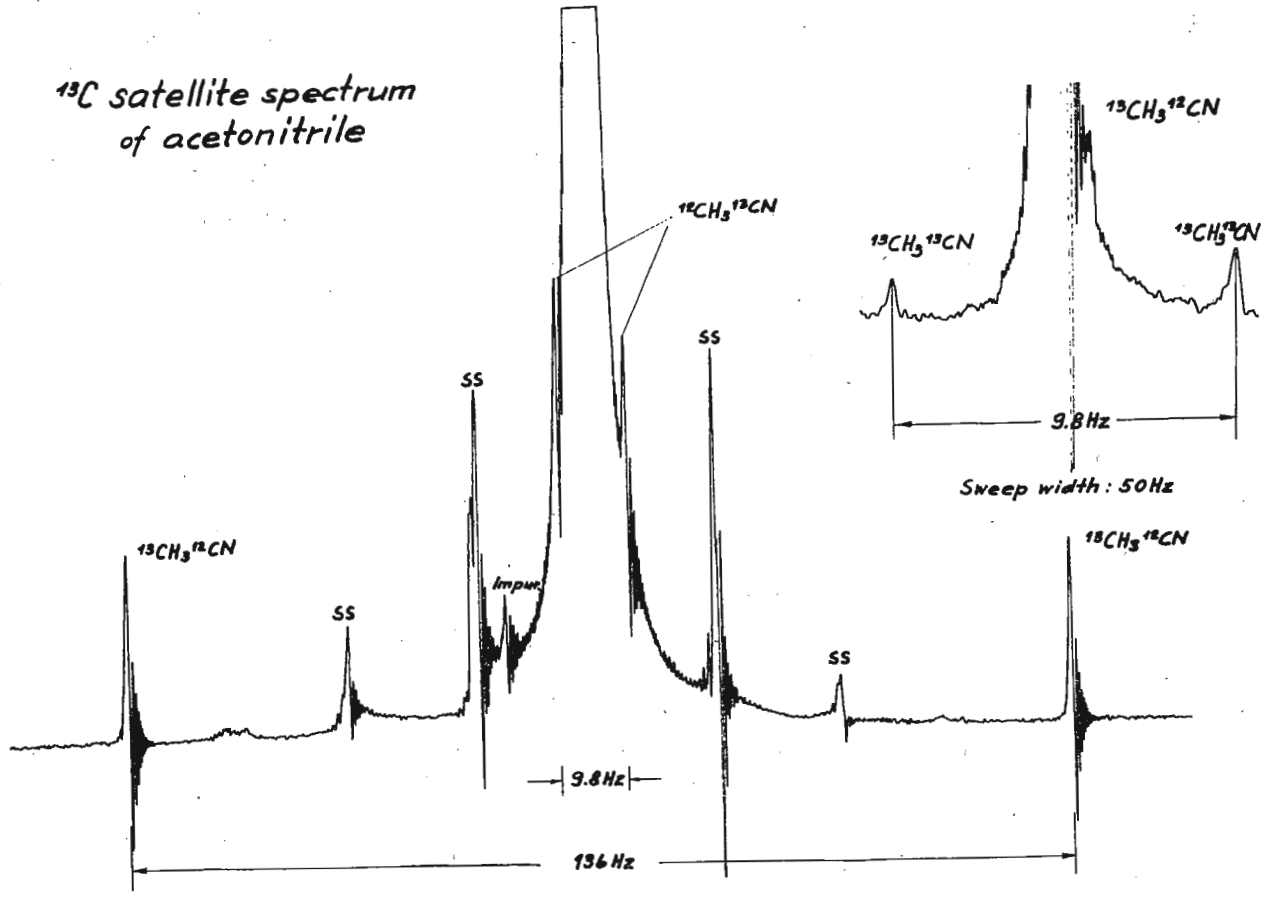
Dear Professor Shapiro,

In search of a new sensitivity standard in proton resonance we were
wondering whether it is possible to detect the ^{13}C satellites of a
molecule containing two ^{13}C atoms in natural abundance in one single
scan. For this purpose we chose acetonitrile, in which the isotopic
species $^{13}CH_3^{13}CN$ gives rise to a simple A_3MX system whose A part
consists of a doublet of doublets with known coupling constants. The
latter can easily be measured from the normal ^{13}C satellite spectrum
in which a pair of outer satellites ($J_{^{13}CH}$ = 136,0 Hz) and inner
satellites ($J_{^{13}C^{12}CH}$ = 9,8 Hz) appear, due to molecules $^{13}CH_3^{12}CN$
and $^{12}CH_3^{13}CN$ respectively. Assuming neglectable isotope effect on
the coupling constant $J_{^{13}C^{13}CH}$, two further subsatellites are to be
expected on both sides of the outer satellite lines, with a splitting of
9,8 Hz and a relative intensity of 3×10^{-5} with respect to the centre
line. The XL-100 proton spectrum below shows the two pairs of
^{13}C satellites in acetonitrile. The region of the upfield outer satellites
was extended at higher rf power and gain with the two "satellites of
satellites", due to doubly ^{13}C substituted molecules, being clearly
recognizable.

Yours sincerely,
VARIAN AG, Research Laboratory

Dr. F.W.Wehrli

Encl.

^{13}C satellite spectrum of acetonitrile

$^{12}CH_3{}^{13}CN$

$^{13}CH_3{}^{12}CN$

SS

SS

SS

Impur.

SS

SS

$^{13}CH_3{}^{12}CN$

9.8 Hz

136 Hz

$^{13}CH_3{}^{13}CN$

$^{13}CH_3{}^{12}CN$

$^{13}CH_3{}^{12}CN$

9.8 Hz

Sweep width : 50 Hz

Sample	: Acetonitrile
Solvent	: neat
Tube o.d.	: 12 mm
Sweep width	: 250 Hz
Sweep time	: 500 sec.
Filter	: 2 Hz
RF field	: 55/65 db
Spectrum amplitude	: 10/100
Sweep offset	: 83791 Hz

150-39

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