Texas A & M University N-M-R Newsletter

No. **230**

November, 1977

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DEADLINE DATES: No. 231:   1 December 1977
                  No. 232:   3 January 1977

All Newsletter Correspondence, Etc. Should Be Addressed To:

UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

September 30, 1977

313.01

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

Are Line Position Standards Needed?, Tin-119 NMR

Dear Barry:

The response to my letter of December (TAMUNMR 219-41) has been nil.
Nevertheless, I am sending you the results of the round-robin on a
tentative line position standard run in the National Capital Area.
Results are given at 30° C.; errors are rms errors from a least
squares fit of data from four to seven labs; spectra were run at
several fields from 14.1 to 63.4 kG. The most interesting point
in the whole exercise is not the actual numbers which are after all
dependent on both temperature and concentration, but the precision.
The first set of results included one proton and one carbon spectrum,
from two different labs, which reported chemical shifts substantially in error.
These were returned with the note that they were discordant, and in each
case an error was found in the commercial FT system which had been used
(from different manufacturers). The re-run spectra, after rectifying
the errors, were then in excellent agreement. These instruments were
run by experienced NMR spectroscopists whose only error may have been
that they believed a computer printout must be correct. There appears
to be a warning here: even though modern FT NMR systems produce results
of high precision, it is nevertheless a good idea to run some known
mixture to be sure that the accuracy is acceptable.

The accompanying chart is the Sn-119 spectrum of $(CH_3)_3SnSn(CH_3)_3$
obtained by FT of 4096 transients acquired in 2 hours on our homemade
multinuclear spectrometer at 22.372 MHz and 14.1 kG. The multiplet
splitting is about 17 Hz.

Do your blue and pink forms come under the Post Office' proscription
on threatening letters?

Yours very truly,

Rolf

Rolf B. Johannesen
Inorganic Chemistry Section

Dear Rolf:

In answer to your last question, no. Please construe the pink and
blue form letters as repeat notices of the conditions under which
you may choose to continue your subscription. It is my view that
people in Washington are the Threateners, not the Threatenees.

Not very seriously,

Barry

TABLE

Vol.	Compound	^{1}H Shift	^{13}C Shift
1.5cc	TMS	0.0 (defined)	0.0 (defined)
2.0cc	$CH_3COOC(\underline{CH_3})_3$	1.4050 ± .0023	28.066 ± .046
	$\underline{CH_3}COOC(CH_3)_3$	1.8688 ± .0020	22.109 ± .034
2.0cc	$(\underline{CD_3})_2CO$		29.604 ± .062
1.5cc	p-dioxane	3.5651 ± .0021	67.016 ± .060
3.0cc	CH_2Cl_2	5.2950 ± .0026	53.658 ± .015
	$CH_3COO\underline{C}(CH_3)_3$		79.462 ± .019
8.5cc	$C\ Cl_4$		96.298 ± .030
1.5cc	benzene	7.2834 ± .0020	128.371 ± .067
	$CH_3\underline{C}OOC(CH_3)_3$		169.380 ± .037
	$(CD_3)_2\underline{CO}$	$J_{CD} = 20.0$ Hz	204.358 ± .081
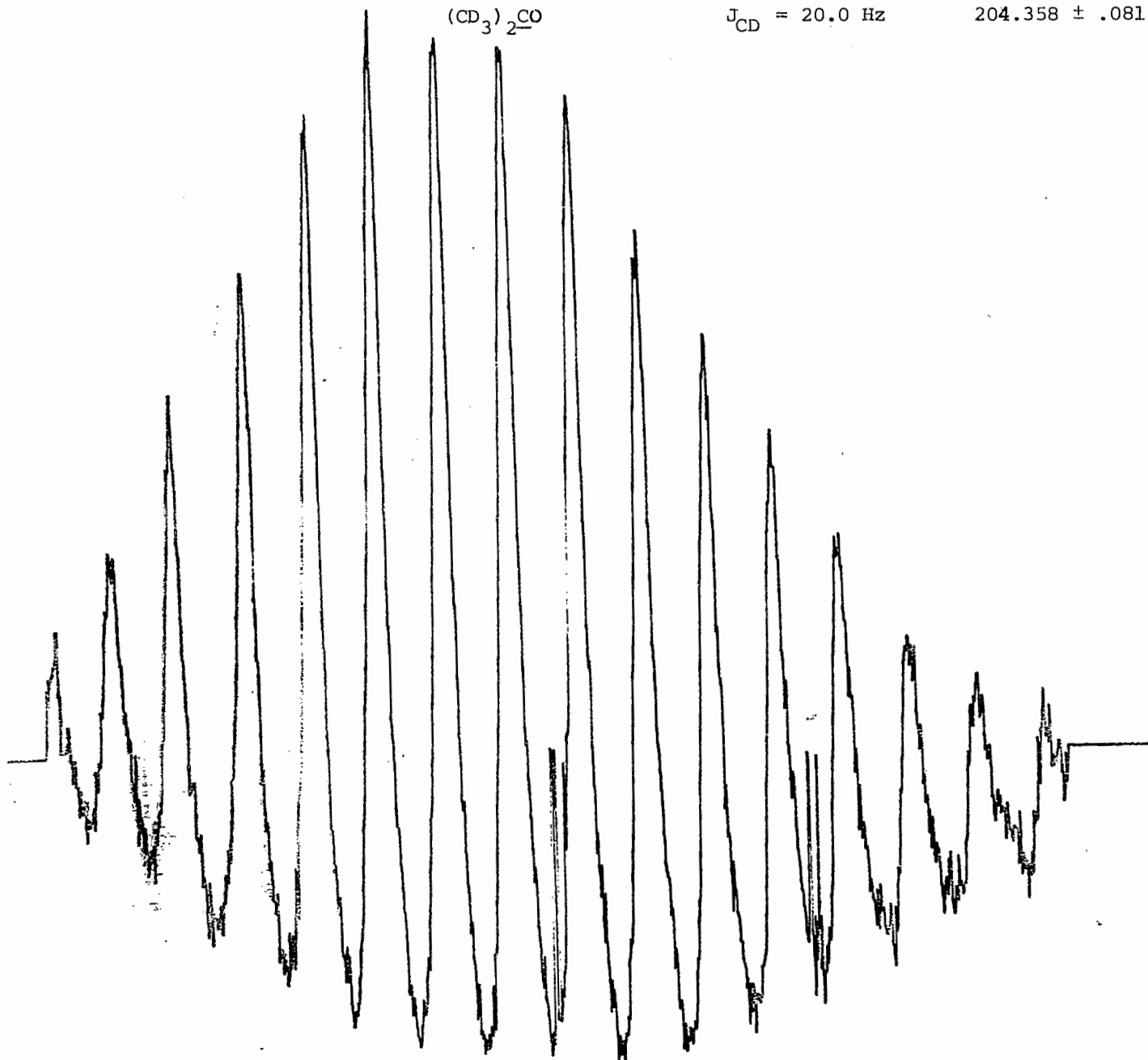
THE UNIVERSITY OF TEXAS AT AUSTIN

AUSTIN, TEXAS 78712

Department of Chemistry

September 22, 1977

Professor Barry Shapiro
TAMU NMR NEWSLETTER
College of Science
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Suggested Title: Computer Generated Scale for NMR

Dear Barry,

The chart paper supplied by all of the NMR spectrometer manufacturers is adequate for proton spectra but very unsatisfactory for other nuclei. We have solved this problem by using blank paper with a scale that is plotted by the computer. This gives us a scale that will expand and offset with the spectrum. An added extra is that the spectra are ready for publication without further art work.

This was done without a new program. We simply generated a scale with the debugging program and stored it on disk as if it were a spectrum. We then call this scale and plot it with the same sweep width as the spectrum it is to go with. We have used this same scale for C-13, P-31, F-19 and even H-1 spectra. We originally designed our scale for C-13 so that we must multiply the sweep by an appropriate constant for the other nuclei. This scale may be used to produce small spectra like the ones shown by calling a large sweep width.

Best regards,

Ben A. Shoulders
Research Scientist

P.S. Credit this to Professor Charles Wade's account of TAMU NMR.

^{13}C cholesterol

230-4
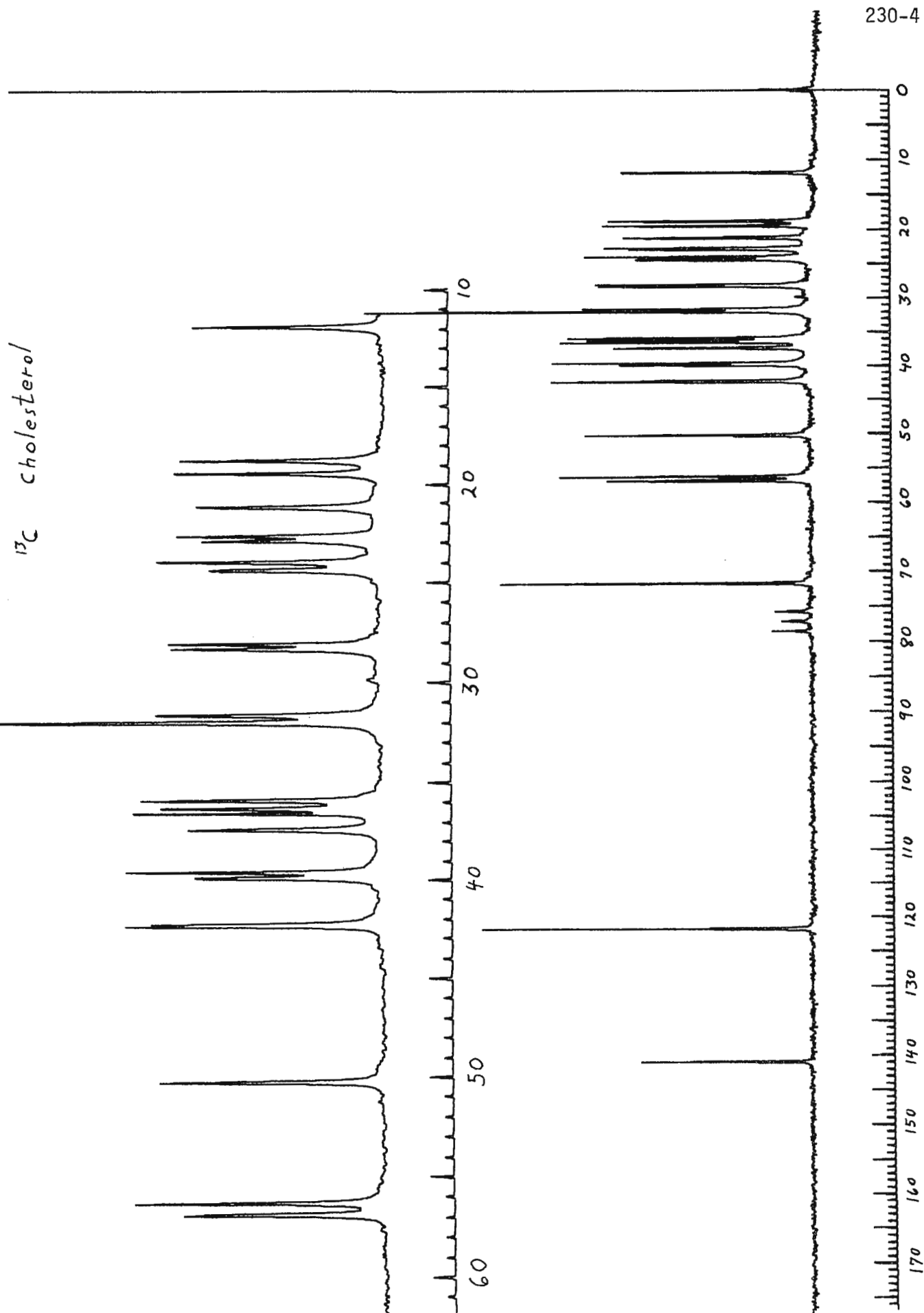
University of Nottingham

Department of Chemistry

UNIVERSITY PARK NOTTINGHAM NG7 2RD
TEL. NOTTINGHAM 56101

HB/MJS

26th September 1977

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

Apparent loss of signal in ^{15}N
pulsed Fourier transform ; phase
anomalies due to rapid pulsing.

Dear Professor Shapiro,

It is rather quiet here and I wish I could report
something more interesting than a freakish experiment in
which we apparently lost an ^{15}N signal in a p.F.t.
experiment (cf. ref. 1).

The sample was the sodium salt of penicillin G (which
contains two amide nitrogen atoms), with nitrate as internal
reference, dissolved in water and recorded in a coaxial tube,
with the ^{19}F lock provided by C_6F_6. The F.I.D. was trans-
formed and automatically given a phase correction identical
to that of the preceding experiment. To our suprise, there
was no sign of the signal due to the nitrate nitrogen.
However, we soon located the signal, which was entirely in
the imaginary part of the spectrum (see Figure).

In our greed, we had reduced the pulse repetition time
to 0.25 s. and whilst this appeared to improve sensitivity,
it had produced phase anomalies (ref. 2). Indeed, we were
quite unable to phase the spectrum correctly and had to be
content with a magnitude spectrum.

Yours sincerely,

Harold Booth.

Dr. H. Booth.

1. G.E. Hawkes, W.M. Litchman and E.W. Randall, J. Mag. Res.,
   1975, 19, 255.

2. R. Freeman and H.D.W. Hill, J. Mag. Res., 1971, 4, 366.

PHASE ANOMALIES

cf. Freeman and Hill, J. Magn. Res., 1971, 4, 366

^{15}N 10.1367 MHz

S.W. 5000 Hz

Pulse width 7 µs (13°)

Repetition time 0.25 s.

Pulses 234,000

Data points 2K

$NO_3^{\ominus}$?
↓

$NO_3^{\ominus}$

$\overset{|}{C}=O$ $\overset{|}{C}=O$
$\overset{|}{N}R$ $\overset{|}{N}H$

REAL

IMAGINARY

Université de Nancy I

LABORATOIRE
DE CHIMIE THÉORIQUE

Case officielle N° 140 - 54037 NANCY Cedex
Tél. 27.00.24 (Poste 2049 et 2051)

D. CANET — J.-P. MARCHAL

NANCY, le 29 September 1977

Professor B.L. SHAPIRO
Texas A and M University
College of Science
College Station Texas 77843
U.S.A.

Suggested title : Indirect measurement of $^2J15_N1_H$.

Dear Professor Shapiro,

· In previous communications (1), we showed that ^{15}N chemical shift and $^1J15_N1_H$ are easily extracted from proton spectra by combining double irradiation (at the ^{15}N frequency) and difference spectroscopy. We wish to point out that $^2J15_N1_H$ and sometimes $^3J15_N1_H$ can be obtained as well though a careful analysis of off-resonance $^1H\{^{15}N\}$ spectra when observing the signals corresponding to the proton directly bonded to the nitrogen atom. This is exemplified by the included spectrum ($(CH_3)_3CCONHCH_3$) : lines down correspond to normal satellites and lines up to the relevant off-resonance spectrum. It is apparent that the multiplet structure (which arises from coupling between the N$\underline{H}$ proton and the CH_3 attached to nitrogen) is different in the off-resonance spectrum. Calculations made on the basis of the double resonance hamiltonian confirm that this effect is due to the $^2J15_N1_H$ between ^{15}N and the CH_3 protons. This allows the determination in magnitude and sign of this coupling constant. Details will hopefully be published soon.

Yours sincerely.

J.-P. MARCHAL   D. CANET

(1) J.-P. Marchal and D. Canet, J. Am. Chem. Soc., 97, 6581 (1975)
    J.-P. Marchal and D. Canet, TAMU NMR Newsletter Nr 209, 24 (1976)

20 Hz
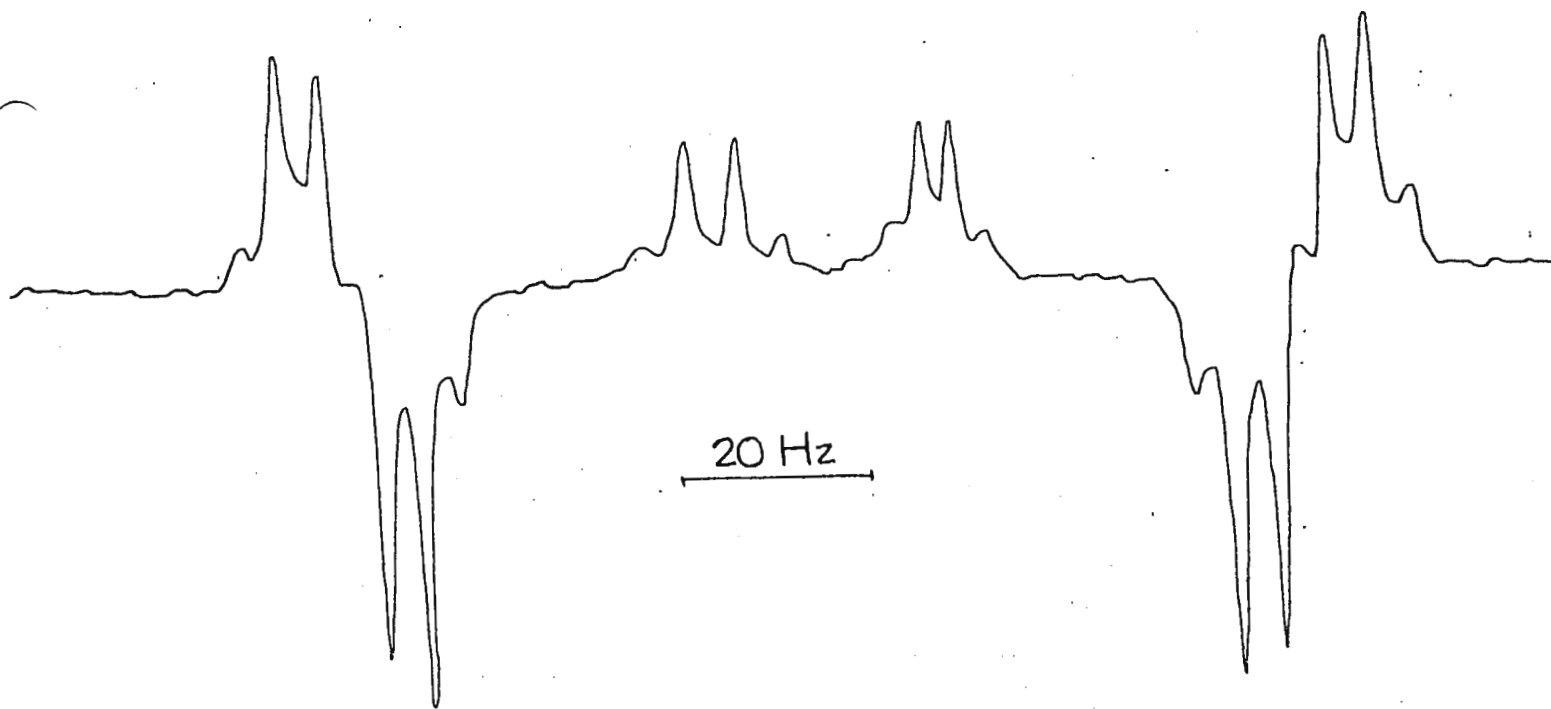
Position open: Research Associate at the M.S. or Ph.D. level to work on

pulsed NMR and NQR work in the area of Solid State Physics and Electronics.

Appointment will be approximately for 10 months or one year in the first in-

stance starting December 1.   Salary will depend on experience.   Contact:

Professor P. K. Kadaba, Electrical Engineering Dept., University of Kentucky,

Lexington, KY 40506 or phone (606) 258-2966 or 257-1855.

APPROACH THE SPEED AND SENSITIVITY OF PULSE FT-NMR ON YOUR CW SPECTROMETER USING A NICOLET NMR-80 DATA SYSTEM FOR RAPID SCAN CORRELATION NMR SPECTROSCOPY
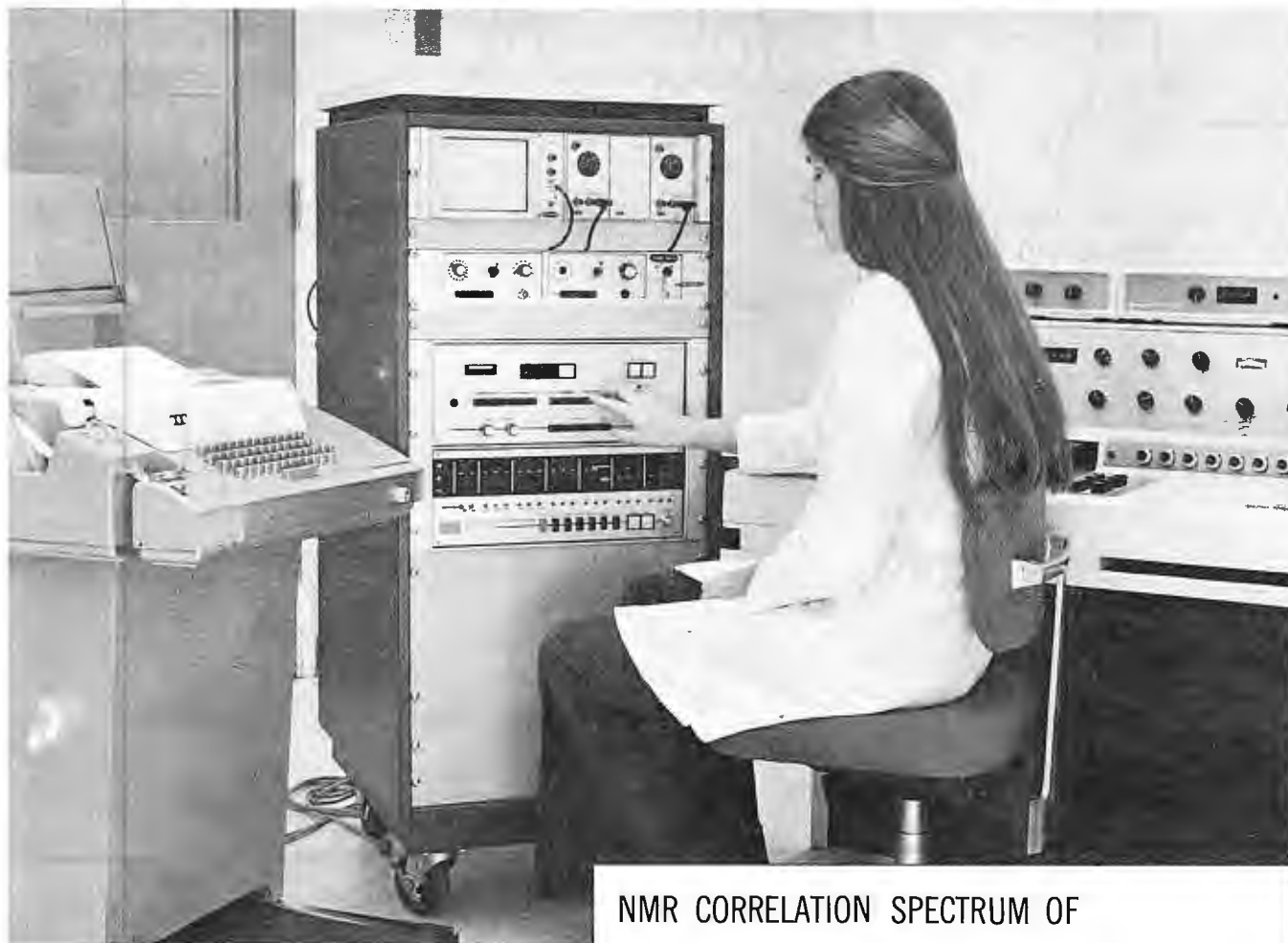
Rapid scan correlation NMR spectroscopy offers these advantages over CW techniques:

1) Greater sensitivity per unit time,
2) Greater sample throughput per unit time, and
3) The ability to follow fast reactions and produce meaningful data.

Rapid scan correlation NMR spectroscopy offers these advantages over pulsed techniques:

1) Power distribution over spectrum is exactly square and independent of sweep width.
2) Large solvent resonances can be avoided by sweeping only a small part of the total spectrum.
3) Resolution is increased because the final spectrum occupies all of data memory.

NMR CORRELATION SPECTRUM OF

50 µg ∝-ionone in spherical microcell
128 scans, 11 sec. per scan
TOTAL TIME 23 min.
Signal/Noise (Peak to Peak) of methyl peaks = 36:1
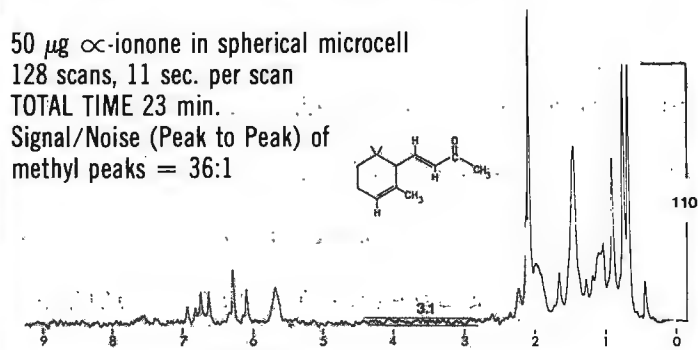
This spectrum of 50 micrograms of ∝-ionone was obtained by correlation NMR in 23 minutes. Normal CW averaging techniques would require over 4 hours.

For more information on the Nicolet NMR-80 data system for rapid scan correlation NMR spectroscopy please write or phone.

NICOLET INSTRUMENT CORPORATION

5225 Verona Road
Madison, Wisconsin 53711
Telephone: 608/271-3333

Photo and spectrum supplied by Varian Instrument Division, Palo Alto, CA.

University of Illinois at Urbana-Champaign

School of Chemical Sciences
Urbana, Illinois   61801

October 6, 1977

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

Dear Barry:

Flashing Lights, NMR and O_2 Evolution

The common denominator in the above title is in the experiments we
have been performing lately on chloroplast preparations in our attempts
to unravel more of the mysteries of photosynthesis. It is well known that
Mn is an essential ingredient for the light stimulated evolution of O_2 by
green plant chloroplasts. We have recently completed a frequency and tem-
perature study of T_1 and T_2 water proton relaxation times in pea chloro-
plasts. Analysis of the data by means of the Solomon-Bloembergen-Morgan
equations yields a set of relaxation parameters which agree well with those
obtained by other workers on Mn containing biological systems. Specifically,
we have found that the relaxation rates are dominated by the chemical ex-
change rate $(1/\tau_M)$ and by the Mn electronic relaxation rate via the symmetry
distortion rate $(1/\tau_V)$ of the paramagnetic complex. Values for the correla-
tion times and the parameter B (which is related to the zero field splitting
among other things) are $\tau_V = (20\pm2)\times10^{-12}$ sec, $\tau_M = (2.2\pm0.2)\times10^{-8}$ sec and
$B = (0.90\pm0.09)\times10^{19}$ $(rad/sec)^2$. In addition, a sizeable "outer sphere" con-
tribution was needed to satisfactorily fit the data. A plot of $T_{1,2}$ data vs.
frequency together with the fit (solid line through the points) and the
"outer sphere" contribution are shown in Figure 1. With the addition of oxi-
dants (e.g., ferricyanide) or reductants (tetraphenylboron) to the chloro-
plast suspensions the relaxation data showed the same frequency dependence
as above, however, it became clear that the relaxation rates were sensitive
primarily to the Mn(II) content of the chloroplast membranes and that the
higher Mn oxidation states were not being monitored. The above results,
coupled with the demonstrable dependence of the relaxation rates on the mea-
sured Mn concentrations in the chloroplasts, show that the water proton re-
laxation rates of chloroplasts are sensitive to the amount of Mn(II) present.

Previous work in this laboratory (1) has demonstrated the existence of
an interesting effect of light flashes on the $1/T_2$ relaxation rate of chloro-
plast suspensions. Specifically, a periodic variation in the $1/T_2$ relaxa-
tion rate with the number of light flashes is observed. A similar experiment
in which the O_2 yield is measured as a function of flash number is a well-
known technique for investigating the O_2 evolution of chloroplast preparations.

From the T_2 measurements described above it seems clear that the oxidation state of the Mn in the chloroplast membranes is related to the chloroplasts' O_2 evolution apparatus.

The O_2 yield response pattern to light flashes has been successfully fit to a four-step model (2) in which an oxidizing equivalent is generated with each light flash. According to this model, when four equivalents are accumulated the water is oxidized to O_2 and four electrons are transferred. Figure 2 shows a $1/T_2$ response pattern in part (a) and an O_2 yield pattern in part (b) for the same chloroplast sample. The closed circles represent the experimental data and the open circles show the theoretical fits. In part (b) the data were fit to the model mentioned above and using the parameters obtained from that fit, a theoretical fit of the $1/T_2$ data was made using a suitably modified version of the O_2 yield model.

Our modification of the O_2 yield model suggests that:
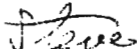
1)   the O_2 evolution process is correlated with the oxidation state of Mn in the chloroplast membranes, and

2)   the transfer of electrons by water is not a concerted process that occurs once every four light flashes but instead occurs during intermediate flashes.

More complete descriptions of this work are being prepared for publication. Credit for this work should also be given to Tom Wydrzynski, Paul G. Schmidt and Govindjee.

                                        Sincerely,

                                        H. S. Gutowsky
                                        H. S. Gutowsky

                                        S. B. Marks
                                        signature

HSG:SBM:nw

(1)   T. Wydrzynski, N. Zumbulyadis, P. G. Schmidt, H. S. Gutowsky and Govindjee, Proc. Nat. Acad. Sci. U.S.A., 1196, 78 (1976).

(2)   B. Kok, B. Forbush and M. McGloin, Photochem. Photobiol., 457, 11 (1970).
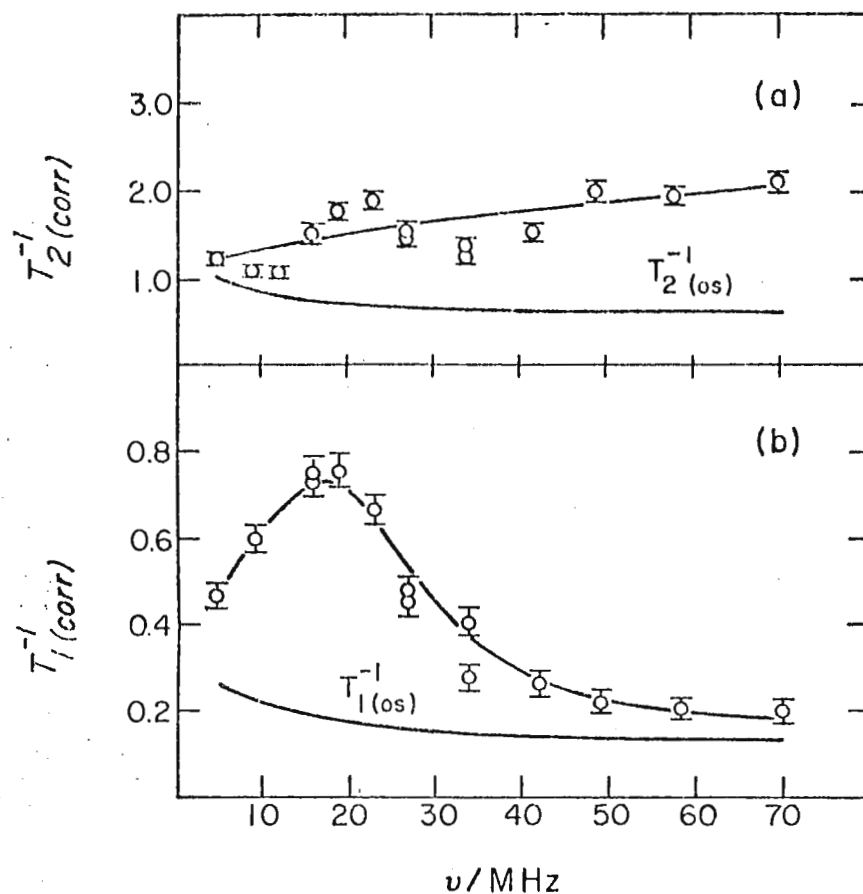
Figure 1: T_1^{-1} and T_2^{-1} vs. frequency data for pea chloroplasts at 25°C. The relaxation rates have been corrected (corr) by subtracting off the relaxation rate for an appropriate "Mn free" sample.
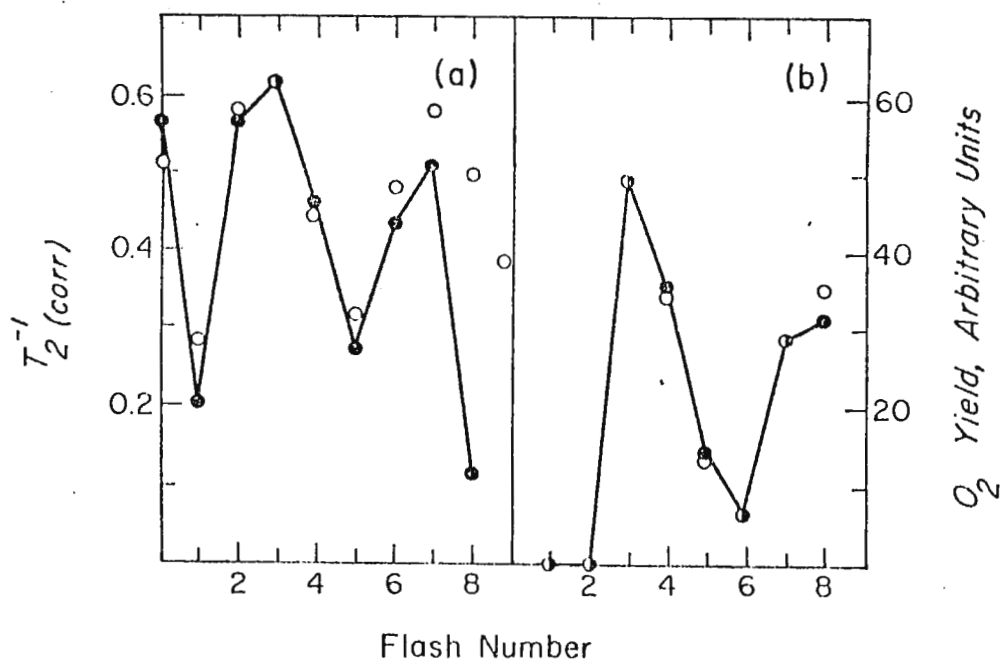
Figure 2: T_2^{-1} (a) and O_2 yield (b) data for pea chloroplasts at 25°C and pH 6.7 obtained in response to a series of short (0.6 µs) flashes of light spaced 4 seconds apart.

Prof.Dr.H.Kessler
Institut für Organische Chemie
der Johann Wolfgang Goethe-Universität
Frankfurt am Main
Laboratorium Niederrad

D-6000 Frankfurt/Main 70
Theodor-Stern-Kai 7
Chemie-Mehrzweckgebäude
Telefon 63 01 - 6032/33

Professor B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843   September 30, 1977

Title: Extension of the DNMR-3 Program for the Calculation
       of the Ionization Barrier in Tritylchloride.

Dear Professor Shapiro,

Sorry for being so late.

During our studies of ionizational barriers of ionogenic compounds
in solution[1] we came across the problem to calculate the AA'BB'C
$\rightleftharpoons$ DD'EE'F exchange between the covalent and ionic form of trityl
chloride in SO_2. The DNMR-3 program in the common version[2] is not
able to handle this complex exchange. Besides of some smaller
changes we therefore extended in the program the dimension of the
B-submatrix from 48 to 72 and the maximum number of lines from 136
to 272. Because of the limited number of core words the program has
been equipped with an overlay structure of 6 segments and occupies
now 62 566 words (decimal) at the UNIVAC 1108. Finally, it works
and requires about 6 minutes CPU time for a typical spectrum
(Figure 1).

The problems of many static parameters was solved using a 270 MHz-
^{1}H-NMR-spectrum of tritylchloride at high temperatures (30°C) and
trityl hexachloroantimonate which were fitted by the LAOCOON 3.
The chemical shift values in the low temperature spectrum has to
be refitted in the slow exchange region.
The free enthalpie of activation for the ionization results in
$\Delta G^{\ddagger}_{204}$ = 10.15 kcal/mol which compares excellent to our results of
the deuterated compound ($\Delta G^{\ddagger}_{209}$ = 10.12 kcal/mol)[1].

1) M.Feigel and H.Kessler, Angew.Chem.Int.Ed. <u>16</u>, 256 (1977);
   Chem.Ber., in press, and references cited.

2) D.A.Kleier and G.Binsch, DNMR 3 Program 165, Quantum Chemistry
   Program Exchange, Indiana University 1969.

To our experience the computing of exchange broadened complex ^{1}H-NMR-spectra is not the limiting factor for complete line shape analysis but the drastic increasing amount of temperature depending variables (chemical shifts, coupling constants, T_2's) creates problems.

Sincerely yours,

M. Feigel   *H. Kessler*

(M.Feigel)   (H.Kessler)

Figure 1

ϕ_3C-Cl SO_2/CD_2Cl_2 10/1

^{1}H -NMR

$P_{ion}/P_{cov} \approx 0.02$

20 Hz

T = 275 K

$P_{ion}/P_{cov} = 0.631$

$k_i = 54.9 \, sec^{-1}$

T = 204 K

$P_{ion}/P_{cov} = 2.17$

$k_i \approx 10 \, sec^{-1}$

T = 186 K

ion   cov.
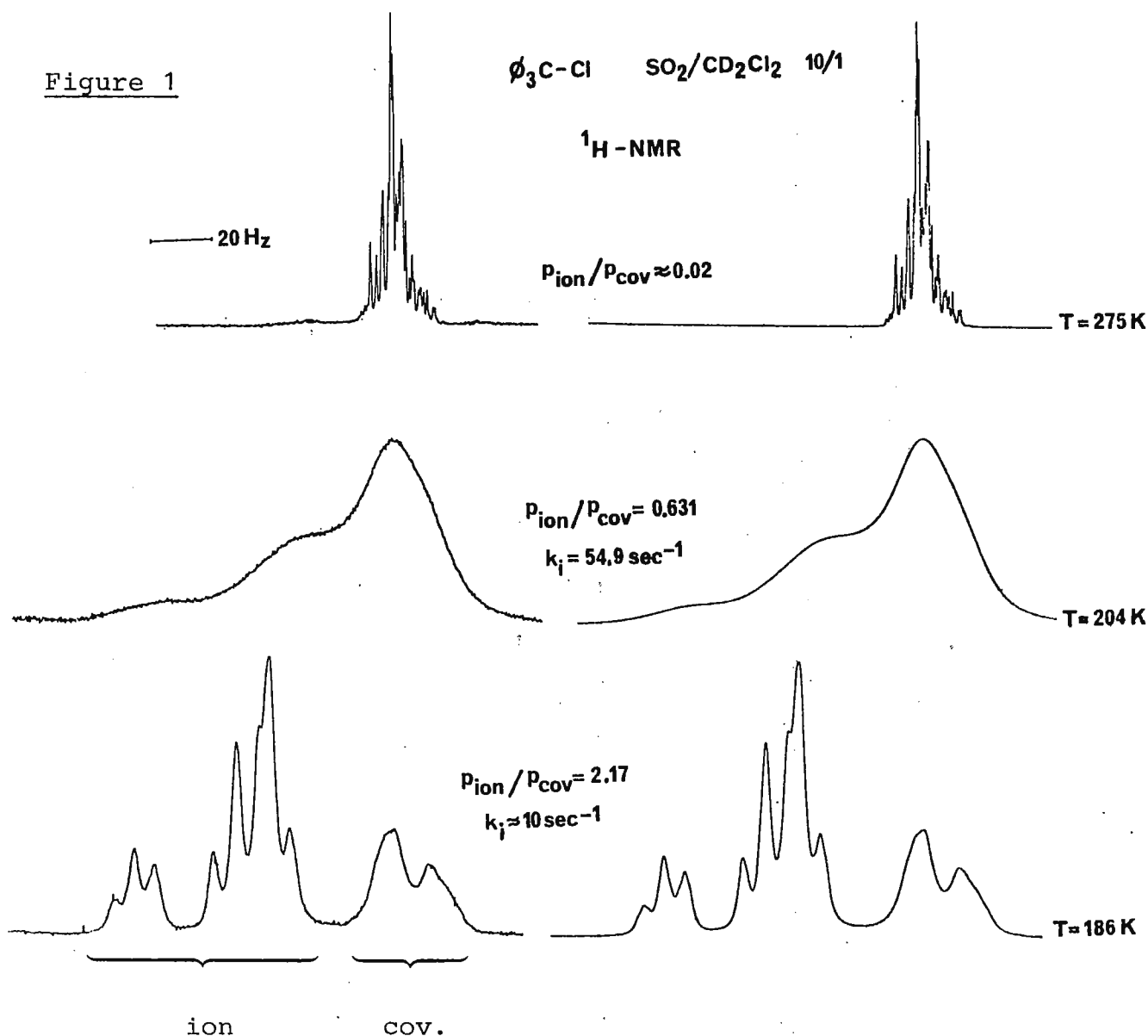
The Commonwealth of Massachusetts

University of Massachusetts

Amherst 01003

POLYMER SCIENCE & ENGINEERING
MATERIALS RESEARCH LABORATORY
OFFICE OF THE DIRECTOR

Room 701
Graduate Research Center
(413) 545-0433

October 4, 1977

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

"Fluorine NMR Studies of a Modified Albumin"

Dear Barry:

I left Santa Barbara in August for a sabbatical and your "blue note" has just caught
up with me.

We have been exploring the use of 2,6-dinitro-4-trifluoromethylbenzenesulfonate (I)
as a reagent for tagging the amino groups of proteins. Under the

$$\underset{CF_3}{\overset{SO_3^-}{\underset{}{NO_2 \diagdown \diagup NO_2}}} \quad \mathbf{I}$$
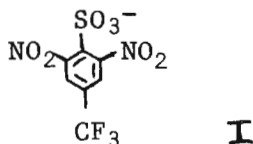
appropriate conditions I appears to react fairly selectively with two lysine residues
of human albumin (1) and one of these residues has been tentatively identified as
lys-199 in the sequence (2). A sample of modified protein was prepared and worked up
by a procedure involving extended dialysis against water. The Figure shows the fluo-
rine nmr spectrum of this protein at pH 3.9 in 0.15 M NaCl (Curve A). The band at
about 14 ppm appears at the chemical shift expected for a derivatized lysine but the
signal at 12.5 ppm has the same shift as expected for a modified tyrosine or, for that
matter, has the same shift as I. The protein sample was dialyzed against 0.01 M
p-toluenesulfonate whereupon the spectrum in curve C was obtained. It thus appears
that albumin can bind I tightly at certain sites but that reaction of these sites is
not possible; the non-covalently bound I can be chased from the protein by molecules
of similar structure such as p-toluenesulfonate.

Sincerely yours,

Tom

K.E. Katz   J.T. Gerig

(1) Gerig and Reinheimer, J. Am. Chem. Soc. 97, 168 (1975).
(2) Gerig, Katz and Reinheimer, submitted to Biochim. Biophys. Acta.
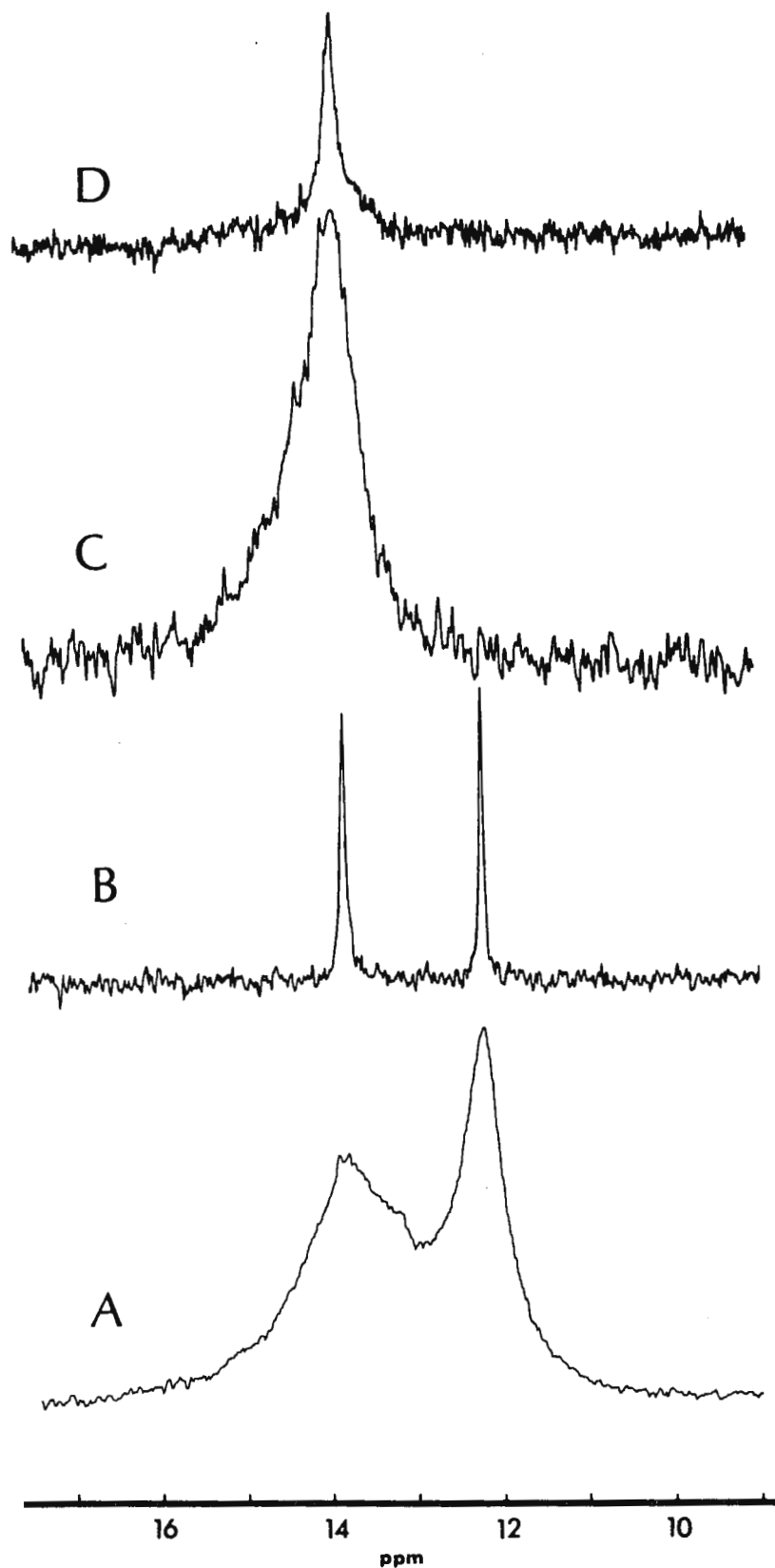
Caption for Figure. (A) Fmr spectrum of human albumin with 1.1 covalently attached 2,6-dinitro-4-trifluoromethylphenyl residues, as judged by absorbance at 416 nm. (B) Fmr spectrum of same protein dissolved in 8 M urea. (C) Fmr spectrum of protein used for scan A after dialysis against 10 mM p-toluenesulfonate. (D) Fmr spectrum of protein used for C in 8 M urea. Peak positions are given relative to internal trifluoroacetate.

Standard Oil Company (Indiana)
Amoco Research Center
P.O. Box 400
Naperville, Illinois 60540
312-420-5111

October 6, 1977

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

Dear Barry:

Practical Application of Rapid Scan Fourier Transform Spectroscopy

We recently interfaced our Bruker HX-90 spectrometer with a NIC-80
computer and an NIC-301 signal conditioner to do Rapid Scan Fourier
Transform Spectroscopy (RSFT). The system has proven very useful in
the analysis of polyolefins. We are particularly interested in
quantitatively determining the degree and type of unsaturation present
after polymerization. In the past, we used a rather tedious ^{1}H CW
technique to determine this. Since the relative amount of unsaturation
is always extremely small, a single CW scan gave only marginal results.
Occasionally, time consuming ^{1}H CW signal averaging had to be used to
increase the signal to noise ratio. Attempts to increase the signal to
noise by using ^{1}H FT techniques were unsuccessful due to dynamic range
problems caused by the intensity of the aliphatic resonances. The RSFT
technique allows us to increase the precision of the results thru signal
averaging in about the same amount of time it took to accumulate a
single scan. It also eliminates the dynamic range problem we ran into
when attempting to use the ^{1}H FT experiment since only the olefinic
portion of the spectrum is excited. Figure 1a shows the full 1200 Hz
spectrum of a typical polyolefin. We have added an internal standard
to the sample for use in the quantitative analysis. The region of
interest is marked by the two horizontal lines. Figure 1b shows a
300 Hz expansion of this area recorded in the normal single scan ^{1}H CW
mode. Note the noise and drift in the integral. Figure 1c shows the
same area after 100 scans using the RSFT technique. The flatter
integral and increased S/N make the analysis considerably easier. We
feel this technique has many applications for this type of sample.

In the process of running these samples, we had the opportunity to use
a few software packages. Because of its phase and integration routines,
we chose the Bruker package for this analysis. It also seems to give

better lineshapes after processing than the others. We have found the
Nicolet software to be extremely useful when baseline corrections or
add-subtract routines are needed.

We hope this contribution will beat the dreaded pink notice.

Sincerely,

R. W. Dunlap
Mail Station F-9

G. J. Ray
Mail Station F-9

/sls

Figure 1a
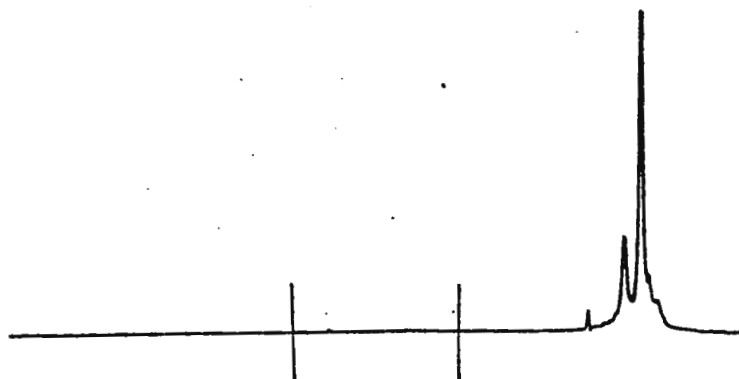
Figure 1b
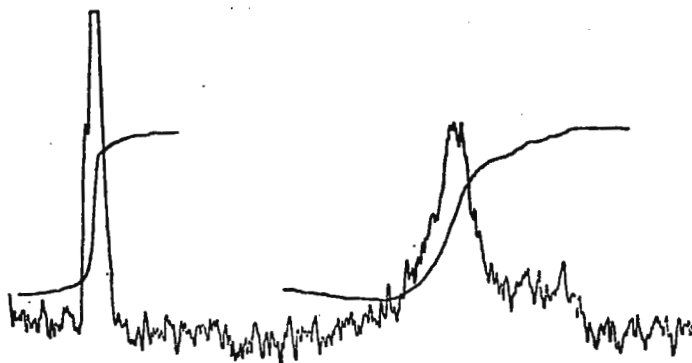
Figure 1c
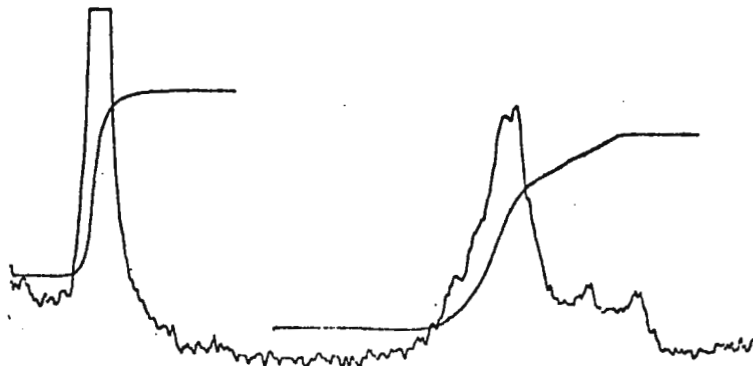
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DEPARTMENT OF CHEMISTRY
LOS ANGELES, CALIFORNIA   90024

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

Dear Barry:

Title: "^{29}Si Spectra of Transition Metal Silanes"

We have observed what we believe to be the first ^{29}Si spectra of a silicon directly bonded to a transition metal. The previous attainment of these spectra was impeded by long T_1 values, negative NOE factors and chemical reactions with relaxation agents such as $Cr(acac)_3$. Based largely on the success of Jakobsen and co-workers[1] and our own success in the study of fluorosilanes[2], we employed the selective population transfer technique (SPT) in the acquisition of these spectra.

The molecule we first chose to study was $(CH_3)_3SiMn(CO)_5$, prepared from the reaction of $(CH_3)_3SiCl$ with the manganese carbonyl anion. The samples were run in a 12mm tube with benzene-d_6 serving as both lock and solvent.

In a ^{29}Si{^{1}H} experiment involving a gated decoupling sequence to eliminate the negative NOE, the signal-to-noise ratio was ~2.5 : 1 after 7000 transients (15 hours). A dramatic improvement was obtained by using the SPT method (τ=.09 seconds, H_2=75dB on a Varian XL-100 spectrometer). The S/N ratio was improved by a factor of 2-3 and the expected decet structure was clearly visible after 2000 transients.

The resonance appeared at 10.8ppm downfield from external hexamethyl-disiloxane. This is well within the range of ^{29}Si shifts found for other compounds of the type Me_3SiX^3 (i.e. Me_3SiH, δ=-23.17 and Me_3SiF, δ=+25.4 from hexamethyldisiloxane).

It is noteworthy that the chemical shift of the ^{29}Si in this complex is not drastically different from the other trimethylsilyl derivatives. It appears that the direct bonding of a metal does not effect ^{29}Si shifts like it effects ^{1}H shifts.

In a forthcoming publication, we will present the chemical shifts and where possible, T_1 and coupling constant data for a series of metal-silane complexes including derivatives of Fe, Co, Ni, Mn, Mo and Pt. Theoretical considerations and comparisons with analogous ^{119}Sn spectra will be included.
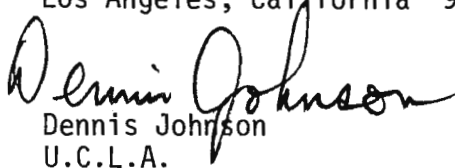
Sincerely yours,
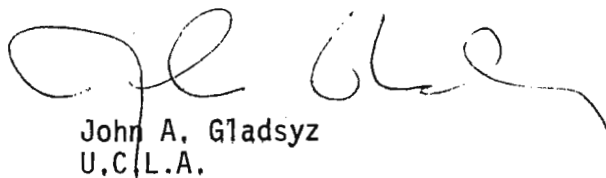
Kenneth L. Servis
Deparment of Chemistry
University of Southern California
Los Angeles, California 90007

Stephen Li
U.C.L.A.

Dennis Johnson
U.C.L.A.

John A. Gladsyz
U.C.L.A.

1. S.A. Linde, H.J. Jakobsen and B.J. Kimber, J. Amer. Chem. Soc., 97, 3219, (1974)
2. K.G. Sharp, K.L. Servis and S. Li, manuscript in preparation
3. R.K. Harris and B.J. Kimber, J. Mag. Res., 17, 174, (1975)

KENT STATE UNIVERSITY

KENT, OHIO 44242

CHEMISTRY
(216) 672-2032

October 19, 1977

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

Dear Barry:
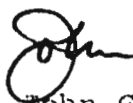
We have a tenure-track opening for an analytical chemist
at the Assistant Professor level. While we prefer some one
interested in computer interfacing we will be happy to consider
(and we may well end up hiring) an individual with almost any
other specialty. We do require that the Ph.D. be in analytical
chemistry.

We were very fortunate to hire Mark Greenberg, who is
presently our only analytical chemist. Mark is a first-rate
man and a pleasure to interact with. The department is com-
mitted to development of the analytical division.

Despite unfavorable publicity, our situation is now better
in most respects than at any time in the last 10 years. We
now have a dean, a provost and a president whose priorities are
in tune with ours. The department contains more young, produc-
tive people than ever before; our biochemists have gotten two
career development awards; and we have just taken delivery on
the first Varian FT-80 Fourier-transform multinuclear nmr spec-
trometer in these parts. Our affiliations with the Northeast
Ohio Universities' Medical College (BS-MD program) and with
the Liquid Crystal Institute give us some advantages.

Of course we have a shortage of money, and our total size
will be stagnant for some time. But we can set a good analyti-
cal person up in business, and we will be grateful for any candi-
dates you might direct our way.

Best regards,

John Gordon
Acting Chairman

JG/rmb

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Professeur Bernard L. Shapiro
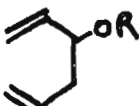
Texas   Aand   M University

College of Science

College Station

Texas 77 843.

Cher Professeur Shapiro,

Nous avons synthétisé une série de monoéthers d'hexadiènes — 1,5 substitués en position 3 du type avec R = Me, Et, Ac, Si (Me)3.

La structure de ces produits est établie par RMN ^{1}H et ^{13}C. Les spectres RMN ^{13}C sont donnés dans le tableau.

Nous avons en outre, étudié la stéréochimie de la transposition de Cope de ces composés.

Les produits de réarrangements c'est à dire les éthers d'énols obtenus conformément au schéma (1) sont caractérisés par RMN ^{1}H et ^{13}C.

Schéma I :
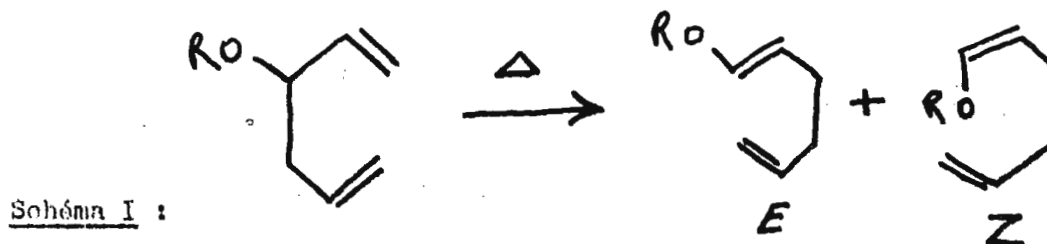
Les spectres RMN ^{13}C sont donnés dans les tableaux.

Les spectres RMN ^{13}C ont été enregistrés à 15,8 MHz sur des solutions

dans CDCl3 (TMS en référence interne) sur un spectrographe BRUKER WP 60 à impulsions.

Les spectres sont normalement obtenus avec découplage des protons par une bande de bruit (DPB).

Nous avons également enregistrés certains spectres sans découplage des protons (S.D) pour attribuer les différents signaux à l'aide des structures fines.

Nous remercions bien vivement le Professeur Chuche qui nous a aimablement assisté dans toutes les phases de ce travail (Faculté des Sciences de Reims).

Bien cordialement vôtre.
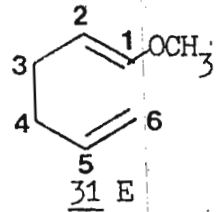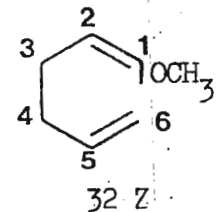
R. Abdelhédi
Assistant
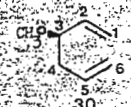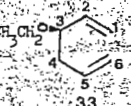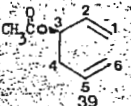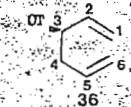
M. L. BOUGUERRA.
Professeur

Déplacement chimique des différents carbones des éthers d'énol
$\underline{31}$ et $\underline{32}$ (Valeur en p.p.m par rapport au TMS) solvant CDCl3
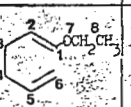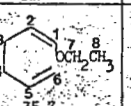
Isomères	$\delta\ C_1$	$\delta\ C_2$	$\delta\ C_3$	$\delta\ C_4$	$\delta\ C_5$	$\delta\ C_6$	$\delta\ C_7$	% de cha isomèr
31 E	147,77	102,36	27,50	35,27	138,79	114,86	59,44	55% $\pm$ 2
32 Z	146,56	106,24	23,50	34,06	138,42	114,50	55,79	45 % $\pm$ 2

* Les pourcentages indiqués sont la moyenne des pourcentages déterminés à partir des carbones C_3, C_4, C_5 et C_6.

Déplacement chimique des différents carbones des molécules 30, 33, 36, et 39
(Valeur en p.p.m par rapport au TMS) solvant $CDCl_3$
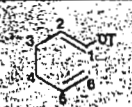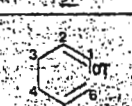
Molécule	δC_1	δC_2	δC_3	δC_4	δC_5	δC_6	R $-CH_3$	$-CH_2$
CH_3O ... 30	117,11	36,66	82,69	40,13	134,72	116,8	56,15	
CH_3CH_2O ... 33	116,69	139,27	80,86	40,25	134,9	116,38	15,36	60,8
CH_3CO-O ... 39	117,84	136,54	73,58	38,98	133,63	116,63	20,88	
OT ... 36	116,63	141,03	73,46	42,62	134,84	113,65		

Déplacement chimique des différents carbones des éthers d'énol
35 et 34 (Valeur en p.p.m par rapport au TMS) solvant $CDCl_3$

Isomères	δC_1	δC_2	δC_3	δC_4	δC_5	δC_6	δC_7	δC_8	% de chaque isomère *
OCH_2CH_3 ... 34 E	145,67	106,18	27,62	35,27	138,42	114,81	64,60	15,30	55 ± 2 %
OCH_2CH_3 ... 35 Z	145,10	103,39	23,56	34,12	138,85	114,44	67,51	24,81	45 ± 2 %

* Les pourcentages indiqués sont la moyenne des pourcentages déterminés à partir des carbones C_3, C_4, C_5 et C_6.

Déplacement chimique des différents carbones des éthers d'énol
36 et 37 (Valeur en p.p.m par rapport au TMS) solvant $CDCl_3$

Isomères	δC_1	δC_2	δC_3	δC_4	δC_5	δC_6	% de chaque isomère *
OT ... 37		111,28	27,19	34,96			44 ± 1 %
OT ... 38		110,67	23,25	33,99			56 ± 1 %

Les pourcentages indiqués sont la moyenne des pourcentages déterminés à partir des carbones C_3 et C_4.

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MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811

Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,   13th October, 1977.
Texas 77843,
U.S.A.

Dear Professor Shapiro,

Gated Decoupling with the BNC-12

Some time ago we purchased a BNC-12 computer to use with our Bruker
HFX-13 instrument. Unfortunately we did not have enough money to buy a full
interface and so we were unable to perform decoupler gating under computer
control. It may be of interest to tell how we got around this problem very
cheaply. We use the Bruker FTNMR programme B08-51218, and if we change the
contents of both locations 5561 and 5572 to 4104, then executing either
instruction "BB" or "DO" through the teletype gives a 1.5 v pulse (400 nsec)
at the "Pulse 2" connector of the computer frame. An edge-triggered flip-
flop circuit converts this pulse to a gating 0 or 5 v dc level for operating
a ring modulator on the input to the ^{1}H decoupler.

Additionally, "on the cheap" we have bought a broad-band power amplifier,
mixers, and built a board-band pre-amp, which has allowed us to perform a
successful multinuclear conversion (after Traficante et al J. Magn. Resonance,
1974, 15, 484) for ca. £500. We thank Ms. J. Elliot for stimulating this
latter effort.

Again, if any readers are interested, please contact us for details.

Yours sincerely,

Dr. G.E. Hawkes   Mr. G.S. Coumbarides

Please credit this contribution to Ed. Randall's account.

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Professeur PIERRE LASZLO

Institut de Chimie
Université de Liège
Sart-Tilman par 4000   Liège 1, Belgique

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

October 12, 1977

I Gotta Right to Sing in Praise of Sodium NMR.

Dear Barry,

We were alerted by a recent article of N.S. Poonia, Inorg. Chim. Acta, **23**, 5 (1977), to the possible complexation of Na^+ by o-phenanthroline - assuredly better known as a superior complexant of transition metal cations.

These are the results obtained when o-phenanthroline displaces DMF solvent molecules from the 0.1 M sodium salicylate ion pair :
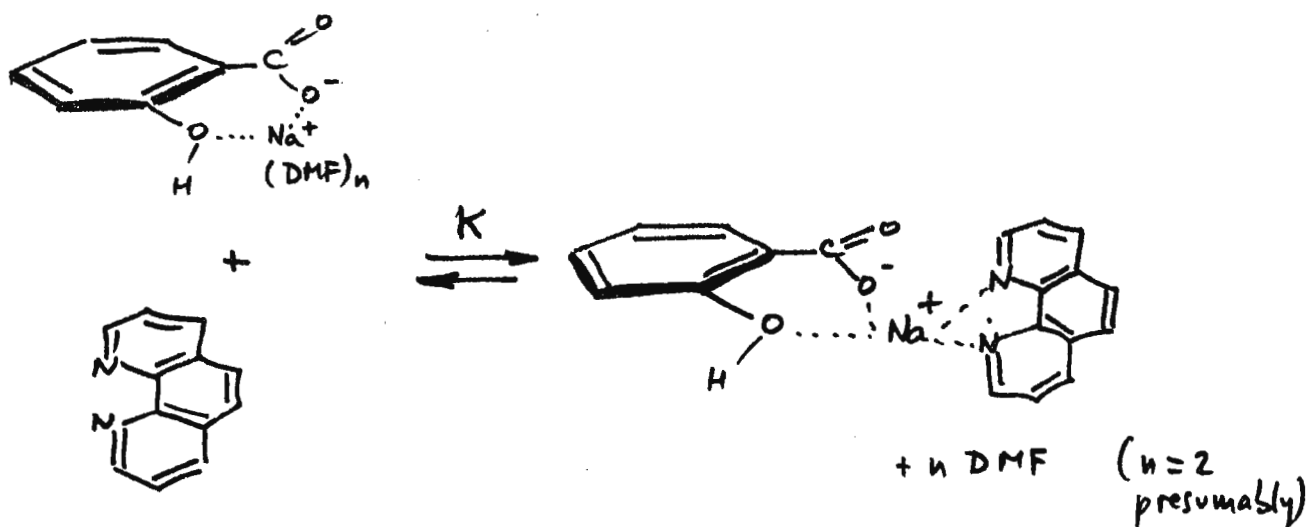
While the initial state is characterized by δ = -2.4 and $\Delta\nu_{1/2}$ = 175 Hz $(cP)^{-1}$, the final state answers to δ = + 3.3^5 and $\Delta\nu_{1/2}$ = 310 Hz $(cP)^{-1}$.

The downfield shifts result from the greater donicity of the coordinating atoms in o-phenanthroline, as compared to DMF. The increase in the linewidth is consistent with an increased asymmetry of the local charge distribution in going from an all-oxygen solvation sphere to a two oxygens + two nitrogens situation.

The apparent equilibrium constant $K = 9,7 \, M^{-1}$ is derived from the chemical shift observed as a function of the (o-phenanthroline)/(salicylate) concentration ratio, using the formalism of D. Live and S.I. Chan, J. Am. Chem. Soc., **98**, 3769 (1976). The observed linewidths (fast exchange limit) are likewise analyzed to yield $K = 9,2 \, M^{-1}$, _i.e._ both sets of data agree nicely.

Should you want to feel yet better, we recommend the following recipe : cook fresh artichokes, remove the leaves, top each heart with a poached egg, and coat the whole dish with sauce Gribiche; serve cold.

With warmest regards,

Cordially yours ,

André Cornélis   Pierre Laszlo
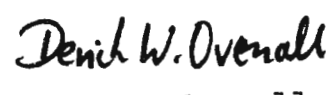
($HOCH_2OH$) and the methanol hemiacetal (CH_3OCH_2OH). On addition of a small amount of the enriched formaldehyde solution to a 10% lime processed gelatin solution in D_2O, the first new peak to be observed is that of the lysine methylol (71 ppm). Within about 3 hours, the arginine methylol peak appears at 65 ppm and slightly before this, a broad peak appears at 59 ppm which we assign to an arginine-lysine crosslink,

$$
\begin{array}{c}
\overset{+}{NH_2} \\
\parallel \\
-NH-C-NH-CH_2-NH-CH_2-\,.
\end{array}
$$
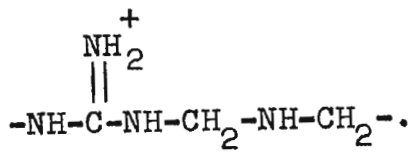
Even after two weeks, there is a large amount of unreacted polyoxymethylene present. We believe that this is responsible for the "afterhardening" phenomenon observed in this process.

Sincerely,

Stephen K. Taylor (2)   Fredric Davidson   Derick W. Ovenall

---

(1) A full account of this work will appear in the Journal of Photographic Science and Engineering.

(2) Photo Products Department, Du Pont Experimental Station.

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CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
EXPERIMENTAL STATION

October 19, 1977

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

Dear Barry:

^{13}C NMR Study of the Crosslinking of Gelatin by Formaldehyde

Although the crosslinking of proteins by formaldehyde is of importance in photography, tanning, biology and medicine, the basic reactions are not fully understood. One initial reaction is the formation of methylol groups on lysine. Kinetic evidence suggests that crosslinks form between the lysine methylol and a different unknown methylol.

Recently, we have used ^{13}C nmr to study the crosslinking of D_2O solutions of gelatin with 90% ^{13}C enriched formaldehyde (1). The ^{13}C resonances from formaldehyde derived addition compounds and crosslinks can be readily picked out from the background of gelatin carbon atom resonances.

Peak assignments were facilitated by model compound studies and by studying the reactions between ^{13}C enriched formaldehyde and D_2O solutions of synthetic polylysine and polyarginine.

The ^{13}C nmr spectrum of a methanol stabilized ^{13}C enriched formaldehyde solution shows that, in water, the major components present are polyoxymethylene in equilibrium with formaldehyde hydrate

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Department of Chemistry / 303·753-2436

October 11, 1977

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

Field Dependent AB Coupling Patterns

Dear Barry,

Recently we have become interested in the problem of calculating line positions and intensities for AB spin systems when the magnetic field strength is not constant. The need to account for the changes in magnetic field strength across a spectrum is particularly severe for two coupled electron spins observed in epr spectra, but may also become significant in field swept nmr spectra taken at low field strengths when coupling constants are large.

We have obtained the following expressions for the positions of the four lines in an AB pattern at constant frequency, ν_o, for two spins with g values g_1 and g_2, and coupling constant, J, in $\sec^{-1}$.

$$H_1 = \frac{2}{(g_1+g_2)}\left[\frac{h\nu_o}{\beta} - \frac{1}{2}\frac{hJ}{\beta}\right] - \frac{1}{2}\frac{2}{(g_1+g_2)}\left[H_1^2(g_1-g_2)^2 + \left(\frac{hJ}{\beta}\right)^2\right]^{1/2}$$

$$H_2 = \frac{2}{(g_1+g_2)}\left[\frac{h\nu_o}{\beta} + \frac{1}{2}\frac{hJ}{\beta}\right] - \frac{1}{2}\frac{2}{(g_1+g_2)}\left[H_2^2(g_1-g_2)^2 + \left(\frac{hJ}{\beta}\right)^2\right]^{1/2}$$

$$H_3 = \frac{2}{(g_1+g_2)}\left[\frac{h\nu_o}{\beta} - \frac{1}{2}\frac{hJ}{\beta}\right] + \frac{1}{2}\frac{2}{(g_1+g_2)}\left[H_3^2(g_1-g_2)^2 + \left(\frac{hJ}{\beta}\right)^2\right]^{1/2}$$

$$H_4 = \frac{2}{(g_1+g_2)}\left[\frac{h\nu_o}{\beta} + \frac{1}{2}\frac{hJ}{\beta}\right] + \frac{1}{2}\frac{2}{(g_1+g_2)}\left[H_4^2(g_1-g_2)^2 + \left(\frac{hJ}{\beta}\right)^2\right]^{1/2}$$

These equations differ from those given in the standard nmr texts in that the energy difference between the coupled spins is dependent on the observing field strength and will be different for each transition.

Professor Shapiro
October 11, 1977

The relative intensities of the four transitions are given by:

1. $(g_1 \cos \theta - g_2 \sin \theta)^2 / (g_1 \cos^2 \theta + g_2 \sin^2 \theta)$

2. $(g_1 \cos \theta + g_2 \sin \theta)^2 / (g_1 \cos^2 \theta + g_2 \sin^2 \theta)$

3. $(g_2 \cos \theta + g_1 \sin \theta)^2 / (g_2 \cos^2 \theta + g_1 \sin^2 \theta)$

4. $(g_2 \cos \theta - g_1 \sin \theta)^2 / (g_2 \cos^2 \theta + g_1 \sin^2 \theta)$
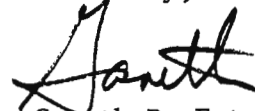
where the angle is defined by

$$\cos 2\theta = \frac{H_i(g_1 - g_2)}{\left[H_i^2(g_1 - g_2)^2 + \left(\frac{hJ}{\beta}\right)^2 \right]^{1/2}}$$

Thus θ depends on the strength of the observing field. Aasa and Vänngård have shown that on converting from constant field to constant frequency calculations it is necessary to divide the intensities by g.[1] This is achieved above by dividing the usual intensity factors by the weighted average of g_1 and g_2 for each transition.

We have not found a treatment of field-dependent AB splitting in the literature. If any reader knows of a treatment paralleling (or contradicting!) the above, please tell us.

Sincerely,

Gareth R. Eaton
Associate Professor

Sandra S. Eaton
Assistant Professor
(University of Colorado, Denver)

[1] R. Aasa and T. Vänngård, _J. Mag. Res._ **19**, 308(1975).

GRE:mel

DEPARTMENT OF CHEMISTRY   **TUFTS UNIVERSITY**   MEDFORD, MASSACHUSETTS 02155

October 11, 1977

Dr. B. L. Shapiro
TAMUNMR Newsletter
College of Science
Texas A&M University
College Station, Texas   77843

"Correlation is Possible on an HA-100"

Dear Barry:

Your readers may be interested to know that we have dragged our
HA-100 kicking and screaming into the third generation of nmr experi-
ments by performing correlation spectroscopy (currently proton only)
on it. It simply requires in addition to a computer, the removal of
the sweep oscillator amplifier card (J1324) from the lock box and the
connecting of an externally controlled audio frequency source to the
jack marked "sweep osc out" (J1307) at the rear of the lock box.

In our case we happened to have a surplus HP-5103A frequency
synthesizer with remote searching capabilities which we used to
sweep the audio sideband range from 2500-3500 Hz. Clearly an audio
VCO would do. In our first iteration this has been accomplished by
using the scope voltage output from the computer, our departmental
PDP-11, and using it to step through 4096 voltage increments which
when properly attenuated and biased could be used to select, in theory,
any frequency range we desired. Spectra obtained of phenylethanol
using a single 300-second sweep and 10 30-second sweeps before and
after correlation are attached.

The problems we still need to overcome are that the voltage
output after biasing and attenuation is not perfectly reproducable
and that it is limited to 4096 points. We are currently building
a digital interface which will allow us to manually "push" any of
the buttons on the synthesizer under computer control and thus allow
larger numbers of points to be swept. If anyone has a manual for
this synthesizer,we would like to get a copy. HP has not been too
helpful.

At present we are using the method described by Gupta, Ferretti
and Becker(1) for performing correlation, which leads to a reduction
in the number of points by 2, but allows frequency domain phase correc-
tion. Once we have optimized various parameters we may allow the user
the option of the method developed by Steve Patt which produces all
real points after the correlation and transform but which requires

Dr. B. L. Shapiro   October 11, 1977

phase correction in some pseudo-time domain, "flying blind."
Needless to say we have written Fourier transforms which allow the
maximum possible dynamic range by overflow detection as we have
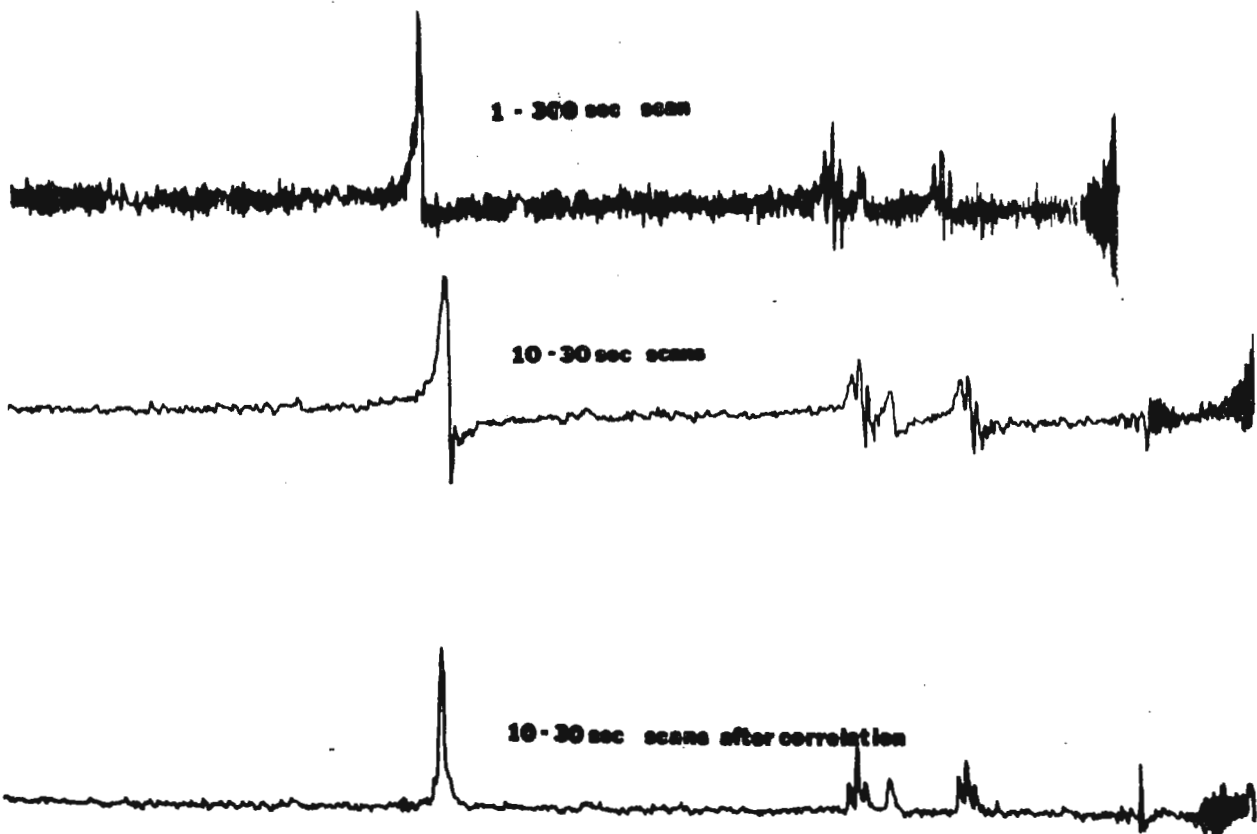described elsewhere.(2)

(1) R. K. Gupta, J. Ferretti, and E. D. Becker, J. Magn. Resonance
     13, 275-290 (1974).

(2) J. W. Cooper, I.S. Mackay and G. B. Pawle, J. Magn. Resonance
     28, 000 (1977).

                              Sincerely,

                              Jim

                              James W. Cooper
                              Assistant Professor

JWC/nmc

Southern Research Institute

October 20, 1977

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

Title: ^{13}C Spectra of Some Retinoids

Dear Barry:

We have recently been working with some derivatives of retinoic acid and have found ^{13}C nmr of tremendous value, both in proof of basic structure and proof of isomeric purity. In connection with this, we have relied heavily on the report of some very useful work by Gerhard Englert (Helv. Chim. Acta, 58 (8), 2367-2390 (1975)).

We now have data on four derivatives not included in his paper, which I hope will be of use to others working with retinoids. It is interesting that the chemical shift differences from a change of solvent are greater than those from a change of R. The nearly invariant chemical shifts of the chain carbons is a great help in checking on isomerism.

Sincerely,

Martha Thorpe
Senior Chemist

MT: sdb
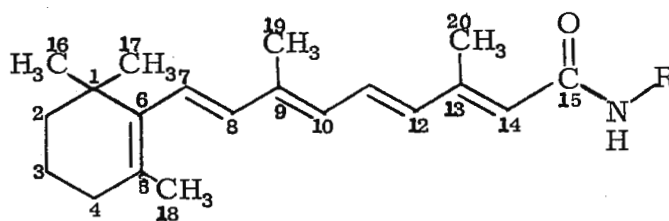
^{13}C Chemical Shifts of Some Retinoids (ppm downfield from internal TMS)

Carbon	R $-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH-CH_3$ $\text{21}\quad\text{22}\quad\quad\text{23}\quad\text{24}$ CDCl$_3$	R $-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$ $\text{21}\quad\text{22}$ CDCl$_3$	R $-CH_3$ 21 CDCl$_3$	R $-CH_2-CH_2-OH$ $\text{21}\quad\quad\text{22}$ CDCl$_3$	DMSO–d$_6$
1	34.30	34.30	34.35	34.28	33.86
2	39.74	39.74	39.81	39.71	39.30
3	19.29	19.29	19.36	19.29	18.82
4	33.14	33.14	33.19	33.14	32.63
5	129.78*	129.86*	129.69*	129.64*	128.72*
6	137.84	137.79	137.94	137.82	137.38†
7	128.28	128.43	128.21	128.31	127.14
8	137.40	137.36	137.48	137.38	137.14
9	138.79	139.13	138.54	138.79	137.38
10	130.00*	130.49*	129.74*	129.76*	129.11*
11	129.66*	129.66*	129.57*	129.91*	130.12*
12	135.58	135.39	135.78	135.56	136.38†
13	149.39	150.26	148.08	148.76	145.89
14	120.76	120.23	121.68	121.32	123.19
15	167.14	168.38	167.94	168.48	166.42
16, 17	28.99	28.99	29.01	28.99	28.77
18	21.71	21.74	21.71	21.71	21.44
19	12.83	12.86	12.86	12.86	12.52
20	13.68	13.83	13.63	13.68	13.12
21	41.36	41.60	26.10	42.36	41.58
22	170.37	173.14		61.98	60.11
23	61.38				
24	14.14				

* Assignments may be interchanged.
† Assignments may be interchanged.

19 October 1977

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

Dear Professor Shapiro

Hammett and Stilbenes – an Undergraduate ^{13}C N.M.R. Experiment

As a departure from the usual type of letter, we offer the following as an interesting undergraduate experiment which involves synthetic and physical organic chemistry as well as a useful introduction to assignment techniques in ^{13}C n.m.r. spectroscopy. Each member of a class of 18 3rd year chemistry students selected a particular m- or p-substituted trans-stilbene for preparation.
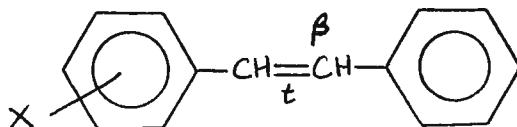
After spending a few hours discovering the different nomenclature systems in Chemical Abstracts and hence the appropriate properties of the materials being synthesised, each student prepared a substituted stilbene by means of the Wittig reaction using benzyl chloride and the appropriately-substituted benzaldehyde. Where the aldehyde was not available, a synthesis was found and performed. Each stilbene was then submitted, as a 0.04M solution in $CDCl_3$, for analysis by ^{13}C n.m.r. The resultant spectra were assigned by the students, making use of various assignment techniques such as additivity relationships, peak height differences due to symmetry and/or relaxation times, etc. Of particular interest were the shieldings for the β-carbons. These values for the m-substituted stilbenes were plotted as a function of σ, with the latter values being derived from least-squares fitting of ^{13}C n.m.r$_1$ data from other series of m-substituted aryl compounds in $CDCl_3$ and CCl_4.^{1} The line so constructed (corr. coeff. = 0.9968) (Fig. 1) was used to read off σ values for the p-substituents (the results demonstrate that for +R substituents σ values intermediate between σ and σ$^+$ are obtained, while for -R substituents σ$^-$ gives better agreement with the data than σ).

In a few cases where the assignment of the β-carbon resonance could not be made unambiguously, the reverse approach was used. The shielding value which gave the more reasonable σ value was chosen, thus illustrating an alternative assignment technique.
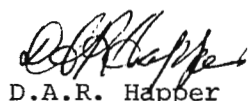
There are no prizes for working out why the results from only 14 substituted stilbenes appear on the graph.

Other series of β-substituted styrenes could be used, thus permitting variation in the types of syntheses involved.

Yours sincerely

J. W. Blunt

D.A.R. Happer

(and 18 others)

Reference:
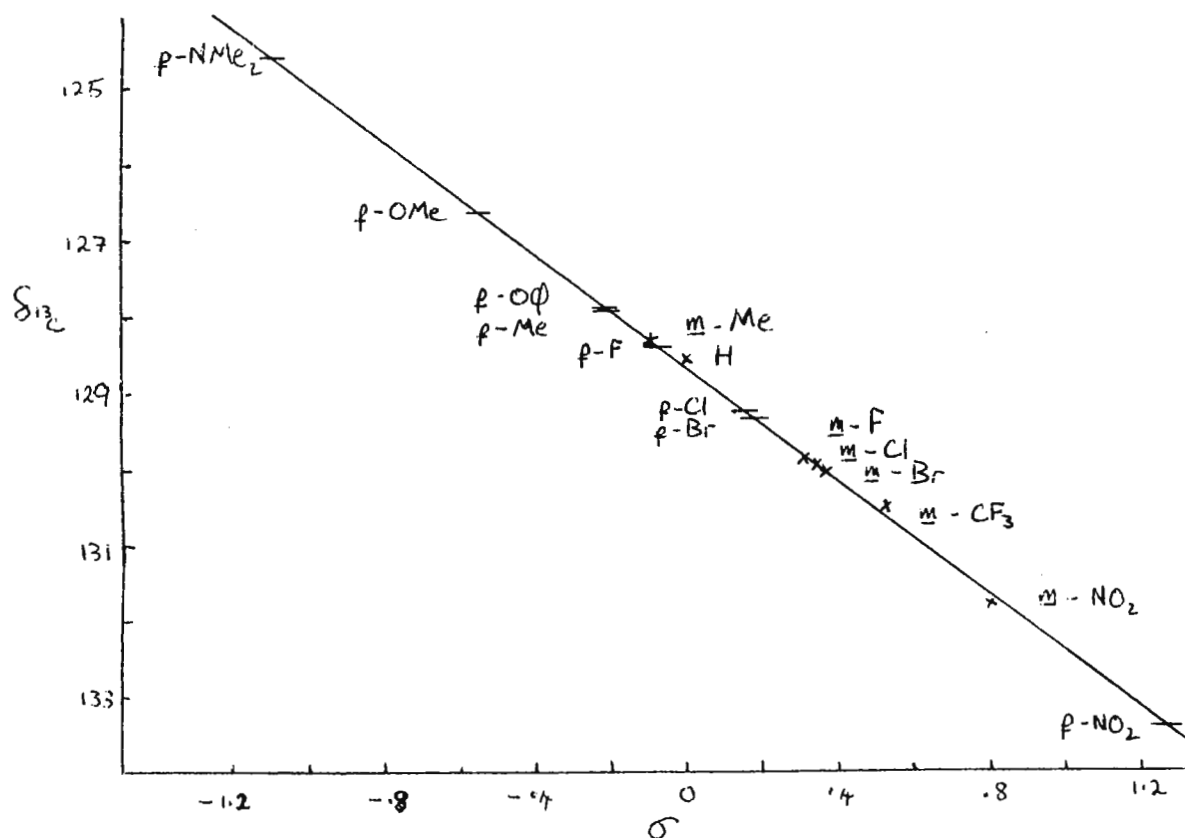1   D.A.R. Happer, S. M. McKerrow and A. L. Wilkinson, Aust. J. Chem., 30, 1715 (1977).

Fig. 1. ^{13}C Shieldings for C-β as a Function of σ.

from Prof. G. Hägele   D-4000-Düsseldorf, 17.10.77
Institut für Anorganische   Universitätsstrasse 1
und Strukturchemie der   G.F.R.
Universität Düsseldorf

Dear Professor Shapiro!

Here a quick reply to your red reminder.:
Recently we looked into the chemistry of fluorinated cyclo-
butanes and cyclobutenes. Bromination of C_4F_5H led to a
20/80 % mixture of cis and trans $C_4F_5HBr_2$. We analyzed the
spectrum of $C_4F_5H-[AB]_2CX$-spin-system at 14.1 and 21.1 kGauss.
We found data given in table 1.
Fortunately the specific resonances of cis and trans isomers
$C_4F_5HBr_2$ do not overlap too much. Results from ABCDEX-analysis
are listed in table 2. Signs of couplingconstants were checked
by systematic variations in iterative treatment. Double reso-
nance studies will follow.

Yours sincerely

Gerhard Hägele and Rainer Dittrich

Table 1

Shifts: δ_F and δ_H [ppm]

A	B	C	X
49.21	44.47	57.94	5.879

Coupling constants [Hz]

AA'	BB'	AB	AB'
199.86	196.52	-12.52	27.89

BC	AC	AX	BX	CX
5.17	20.07	-1.62	9.66	-7.00

rms: 0.097
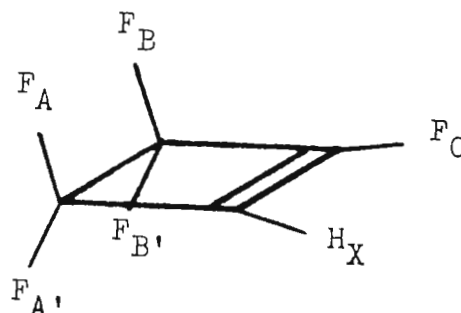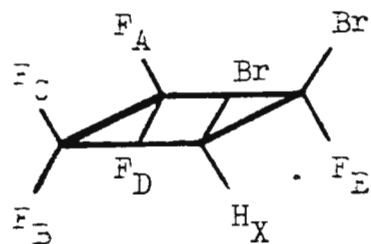
cis-1,2-Dibrom-2,3,3,4,4-penta-fluorcyclobutan (I)

Spinsystem: ABCDEX

trans-1,2-Dibrom-2,3,3,4,4-penta-fluorcyclobutan (II)

Spinsystem: ABCDEX

δ_A	δ_B	δ_C	δ_D	δ_E	δ_X	RMS
51.81	47.58	43.59	32.40	43.75	4.832	0.18

$^2J_{FF}^{BC}$	$^2J_{FF}^{AD}$	$^3J_{FF}^{AC}$	$^3J_{FF}^{BD}$	$^3J_{FF}^{AB}$	$^3J_{FF}^{CD}$
+212.49	+206.42	−11.39	−7.00	+5.34	+4.31

$^3J_{FH}^{BX}$	$^3J_{FH}^{CX}$	$^4J_{FH}^{DX}$	$^4J_{FH}^{AX}$	$^3J_{FH}^{EX}$
+11.64	+10.05	+8.30	−1.79	+16.70

$^3J_{FF}^{DE}$	$^3J_{FF}^{AE}$	$^4J_{FF}^{BE}$	$^4J_{FF}^{CE}$
−8.32	−0.97	−5.77	+13.36

δ_A	δ_B	δ_C	δ_D	δ_E	δ_X	RMS
52.00	47.57	42.39	37.49	32.93	4.743	0.046

$^2J_{FF}^{AC}$	$^2J_{FF}^{BD}$	$^3J_{FF}^{AB}$	$^3J_{FF}^{CD}$	$^3J_{FF}^{AD}$	$^3J_{FF}^{BC}$
+210.43	+209.54	−10.31	−7.25	+5.12	+4.60

$^3J_{FH}^{AX}$	$^3J_{FH}^{CX}$	$^4J_{FH}^{BX}$	$^4J_{FH}^{DX}$	$^3J_{FH}^{EX}$
+9.94	+9.15	+7.61	−2.23	+10.99

$^3J_{FF}^{DE}$	$^3J_{FF}^{BE}$	$^4J_{FF}^{CE}$	$^4J_{FF}^{AE}$
−8.39	−6.17	−0.14	+8.70

δ in ppm bezüglich C_6F_6 bzw. TMS

J und RMS in Hz

(Isomerengemisch zu 50Vol% in CCl_4, gemessen bei 21.1 kGauss)

Universität Regensburg

FACHBEREICH CHEMIE

8400 REGENSBURG,
Universitätsstraße 31 — Postfach
Telefon (0941) 9431

Professor Bernard L. Shapiro   October 19, 1977
Department of Chemistry
Texas A and M University
College Station, Texas 77843
U.S.A.

Dear Professor Shapiro:

This letter is to initiate my subscription to TAMU NMR Newsletter.

IS THE INTERPRETATION OF H-1 NMR CHEMICAL
SHIFTS OF BENZYLIDENEANILINES RIGHT ?

For benzylideneanilines I substituted in the benzaldehyde ring the chemical shift of the CH= proton can be well correlated with the substituent reactivity constants σ. However, for derivatives II such a correlation is on a low confidence level and moreover, the slope has surprisingly opposite sign.
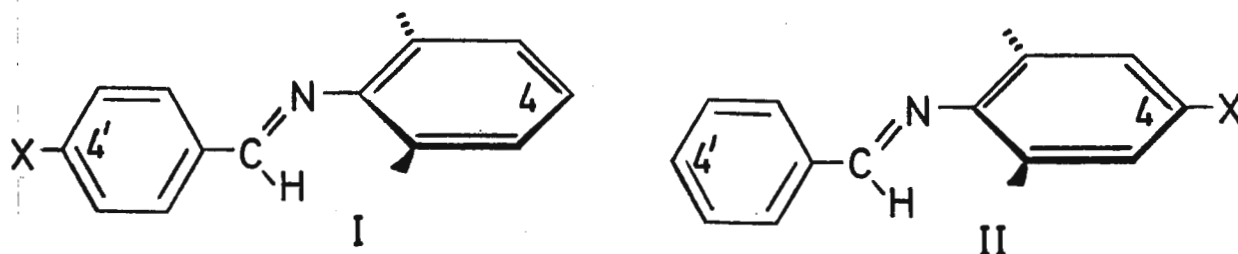
Attempts were made to account for this peculiarity of II by the weakening of electronic interaction between substituent and CH= hydrogen due to the twist of the molecule (1) or by the decrease in through-bond transmission effect and the increased contribution of the through-space field effect (2). All those explanations involving only changes caused by electron distribution seem to be problematic, since it can be infered from H-1 (3), C-13 (2), and also from F-19 (4) spectra of 4,4'-disubstituted benzylideneanilines that the transfer of a substituent effect from position 4 to 4' in II is the same or nearly the same as in the opposite way from the 4' to the 4 position in I.

According to our finding, this anomalous effect is really caused by the twist of the molecule, but our explanation (3) differs substantially from the previous ones.

It is known, that the angle of twist in benzylideneaniline molecule is about 60°. This is due to a compromise between conjugation of N-π electron and N-n electrons with the π-system of molecule and the steric hindrance by proximal hydrogen atoms (i.e., CH= and 2-H in aniline ring). The change in electron density introduced by a substituent can substantially affect this equilibrium value and hence vary the twist angle and the steric arrangement of proximal hydrogens. E.g., electron-donating group increases electron density in the system and shifts NMR signals to higher field. Simultaneously, however, due to the increase of N-C(aryl) bond order the angle of twist can decrease. For a value less than 50° the distance between azomethine H and 2-H is shorter than the sum of van der Waals radii and the corresponding distortion of electron clouds causes low-field shift. Moreover, the deshielding contribution of ring current is increased. Both these effects oppose the electron density effect in such a way that the change in chemical shift is nearly compensated. Similar consideration applies also for electron-withdrawing groups which can increase the twist angle and shift the CH= signal to higher field. A shift in the same direction was observed when the twist was increased by substitution in 2 and 6 positions (6).

In a series of para-disubstituted benzenes with one constant composite substituent (e.g., Ph-CH=N-) and another variable simple substituent, the chemical shifts of hydrogens in ortho and meta positions correlate (5) with substituent increments a_i, the slope of this correlation being near unity. That applies for 2'-H and 3'-H in benzylideneanilines I and for 3-H but not for 2-H in II: the slope is near zero and the correlation is very poor. This finding supports our conclusion about the important role of the twist angle on the chemical shifts of proximal hydrogens because the increase in twist diminishes the effect of van der Waals repulsion and also decreases the contribution of the diamagnetic anisotropy of the N=C bond.

Comments are welcome.

Sincerely yours,

Miroslav Holík

(on sabbatical leave from Lachema
CS-621 33 Brno,Czechoslovakia,
until February 1978)

1. J.S.Sandhu,D.Mago,and B.J.Wakefield, Tetrahedron Letters 1091(1975)
2. N.Inamoto et al., Tetrahedron Letters 3617(1974), 3701(1975)
3. M.Holík,J.Běluša,and J.Břicháček, Coll.Czech.Chem.Commun.,in press
4. S.K.Dayal and R.W.Taft, J.Am.Chem.Soc. 95, 5595 (1973)
5. M.Holík, Org.Magn.Resonance 9, 491 (1977)
6. A.S.Al-Tai,D.M.Hall,and A.R.Mears, J.C.S.Perkin II, 133 (1976)

THE UNIVERSITY OF NEW BRUNSWICK
FREDERICTON, N.B.
CANADA

PHYSICS DEPARTMENT

SHORT SINE TABLES INTERPOLATED, and V3520 MAGNET COOLANT CONTROL WANTED

Dear Barry:

October 24, 1977.

Fast Fourier transform minicomputer programs require values of the sine function at arguments $2\pi k/N$, where N is the number of real data points in the array that is to be transformed, and k is an integer. Usually, N is a power of 2, and the symmetry of the sine function then permits all required values to be derived from those in the first quadrant $0 < k < N/4$. There appear to be three possibilities to generate these N/4 sine values:

   (i)   storage in a look-up table,
   (ii)   computation by means of a software subroutine,
   (iii) generation by means of hardware.

Our FFT program utilizes method (ii) with a 65 word subroutine which approximates the sine function with a 7th order polynomial (only 4 terms required since even powers vanish) with absolute rms error less than 2^{-15}, which is all that is required for our 16 bit computer. Method (i) cannot give greater accuracy but enjoys a speed advantage since it takes less time to look up a table stored in memory than to go through the polynomial evaluation. As usual, the speed advantage is at the expense of greater storage requirements because the quarter sine table must be stored for the largest data array that will be operated upon. Of course, the appropriate address decoding routine and a sine table of just the required length for a particular transform could be loaded separately from the FFT program, but this seems awkward.

We were thus interested to read of J.W. Cooper's observations (TAMU 226/20 and preprint) made by combining methods (i) and (ii). Professor Cooper used a coarse sine look-up table with linear interpolation between tabulated values. His empirical results on a 20 bit computer transforming a N=16K array show that a table of 128 words is sufficient. Longer sine tables bring identical results, but reduction of the table length by only a factor 2 from 128 to 64 words leads to "complete garbage in which the spectrum could not even be observed", and this is confirmed in Fig. 4 of Professor Cooper's preprint. We were sufficiently perplexed by this sudden change in going from a 128 to a 64 point table to attempt the following analysis.

The error $\varepsilon(x)$ of the linear interpolation of a function $y(x)$ between tabulated values $y(x_n)$ and $y(x_{n+1})$ is a 2nd order polynomial that vanishes at x_n and at x_{n+1},

$$\varepsilon(x) = y''(\bar{x}) \frac{(x - x_n)(x - x_{n+1})}{2!} \qquad [1]$$

where $y''(\bar{x})$ is the 2nd derivative at some $\bar{x}$ between x_n and x_{n+1}. The method can easily be extended to higher order interpolation, see for example R.W. Hamming, Numerical Methods for Scientists and Engineers, McGraw-Hill, Ch.8. In using the interpolated sine for the digital Fourier transform of $f(t)$, what is computed is the discrete equivalent of

$$F(w) = \int f(t) [\sin(wt) - \varepsilon(wt)] dt \qquad [2]$$

and similarly for the cosine transform. The error in the Fourier transform
is then bounded by

$$E \leq \varepsilon_{max} \int |f(t)|\, dt \quad , \tag{3}$$

where

$$\varepsilon_{max} = \frac{h^2}{8} = \frac{\pi^2}{32M^2} \tag{4}$$

is obtained from eq. [1] with the interpolation interval

$$h = X_{n+1} - X_n = \pi/(2M) \tag{5}$$

for M tabulated points. Some values from eq. [4] with $\pi^2 \approx 8$ are

M	=	512	256	128	64	32
ε_{max}	$\approx$	2^{-20}	2^{-18}	2^{-16}	2^{-14}	2^{-12}

The integral $\int |f(t)|\, dt$ is greater than the tallest line in the spectrum but
probably smaller than the sum of all lines. Strictly, eq. [2] is used in each
of the $\log_2 N$ passes of the FFT algorithm. The total error bound [3] might
thus be multiplied with $\log_2 N$ or, if scaling occurs between all passes, with
a factor 2. Actually, scaling need not occur between all passes, but either
the first or the last $\log_2 M$ passes do not require interpolation of the sine
table, and we will take a factor 2 to allow for these effects. (One may note
that, since scaling reduces the error from early passes, a FFT algorithm that
requires interpolation in the early passes is preferable to one needing it
for the late passes). So, for a quarter sine table with 128 entries, we expect
to see a spectrum error of order 2^{-15} times the true spectrum, and for a 64
point table the error should be 4 times greater. The former error may well
be hidden in the round-off error of the Fourier transform computations, the
latter might just become visible for a transform of a 16K point array on a 20
bit computer, as used by Professor Cooper.

If this analysis is roughly correct, we do not understand the "complete
garbage" obtained with a 64 point sine table, nor the sudden break in the
magnitude of the error in going from 128 to 64 points. We would be pleased to
receive comments from interested readers.

I wish to thank Professor W.R. Knight of our Mathmatics Department for
helpful discussions, and Professor J.W. Cooper for a preprint of his paper.

On another subject, we would like to purchase a used Varian V3520 magnet
coolant control unit for a high impedance 12 inch electromagnet as used with
HA-60 or HA-100 spectrometers, or equivalent. Would readers having such a
unit for sale please establish contact with me (506)-453-4723).
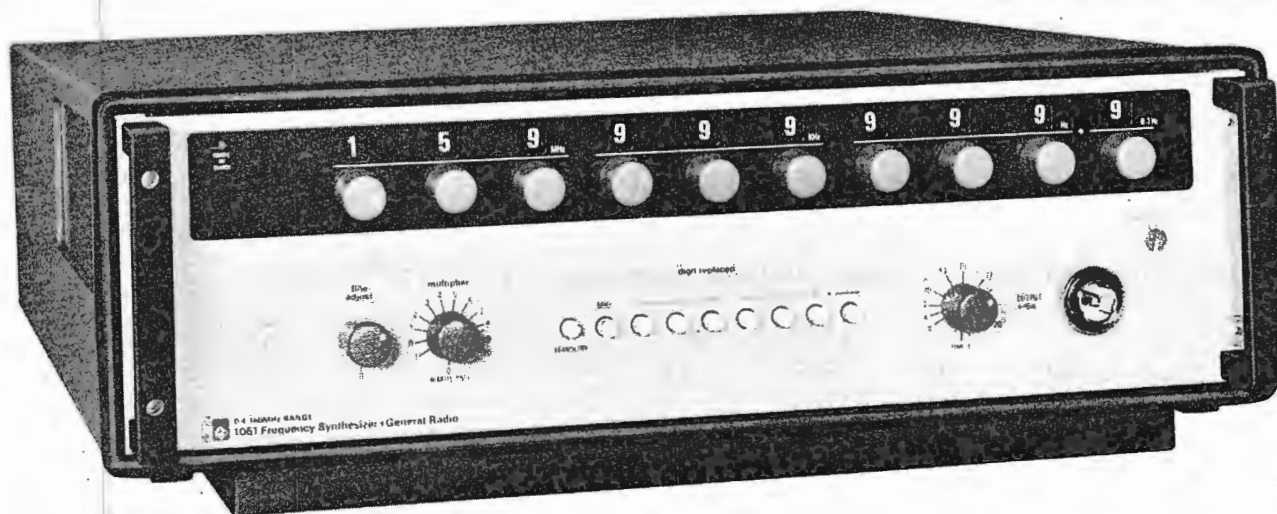
<div style="text-align:right">

Sincerely yours

Professor R. Kaiser

</div>

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

October 25, 1977

Building 2, Room B2-08

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

Title: Tyrosine residues of RNase by ^{13}C-NMR.
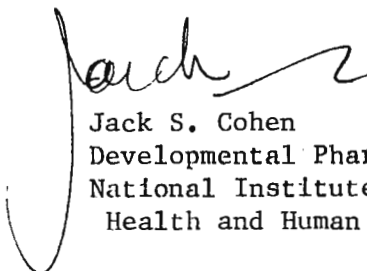
Dear Barry:

Soon after returning from a very peaceful and pleasant year at the Weizmann Institute in Israel my peace of mind was disturbed by the receipt of your blue reminder.

The number of accessible (normal) and buried tyrosine residues out of the six present in ribonuclease has been a subject of dispute for over 15 years. By a variety of methods, including spectrophotometric titration, solvent perturbation, chemical modification and X-ray crystallography various numbers have been arrived at, usually indicating 3 buried and 3 accessible residues. (For a review see ref. 1). By carrying out NMR titrations of the six resolved ^{13}C$^\zeta$ resonances of ribonuclease at 67.8 MHz (Fig. 1), we have been able to show that four resonances (peaks 1-4) titrate normally, one has a high pK (peak 5) and is partially buried, and one does not titrate at all up to pH 11 (peak 6) and is consequently buried (Fig. 2). Further details will be published elsewhere (2).

During my stay in Israel I carried out a study of 90% ^{13}C-methyl methionine β-galactosidase (MW 460,000)(3) and wrote a review on "NMR studies of biologically relevant isotopes other than hydrogen (^{1}H)" intended principally for biochemists, which will appear in Critical Revs. in Biochemistry.

Sincerely,

Jack S. Cohen
Developmental Pharmacology Branch
National Institute of Child
 Health and Human Development

JSC:ell

Refs: (1) F. M. Richards and H. W. Wyckoff in The Enzymes, (Boyer, P. D. ed). Vol. 4, p. 647-806, Academic Press, N. Y. 1971.

 (2) W. Egan, H. Shindo and J. S. Cohen, in preparation.

 (3) J. Yariv, J. S. Cohen, A. J. Kalb (Gilboa), L. Jacobson and Y. Schechter, in preparation.
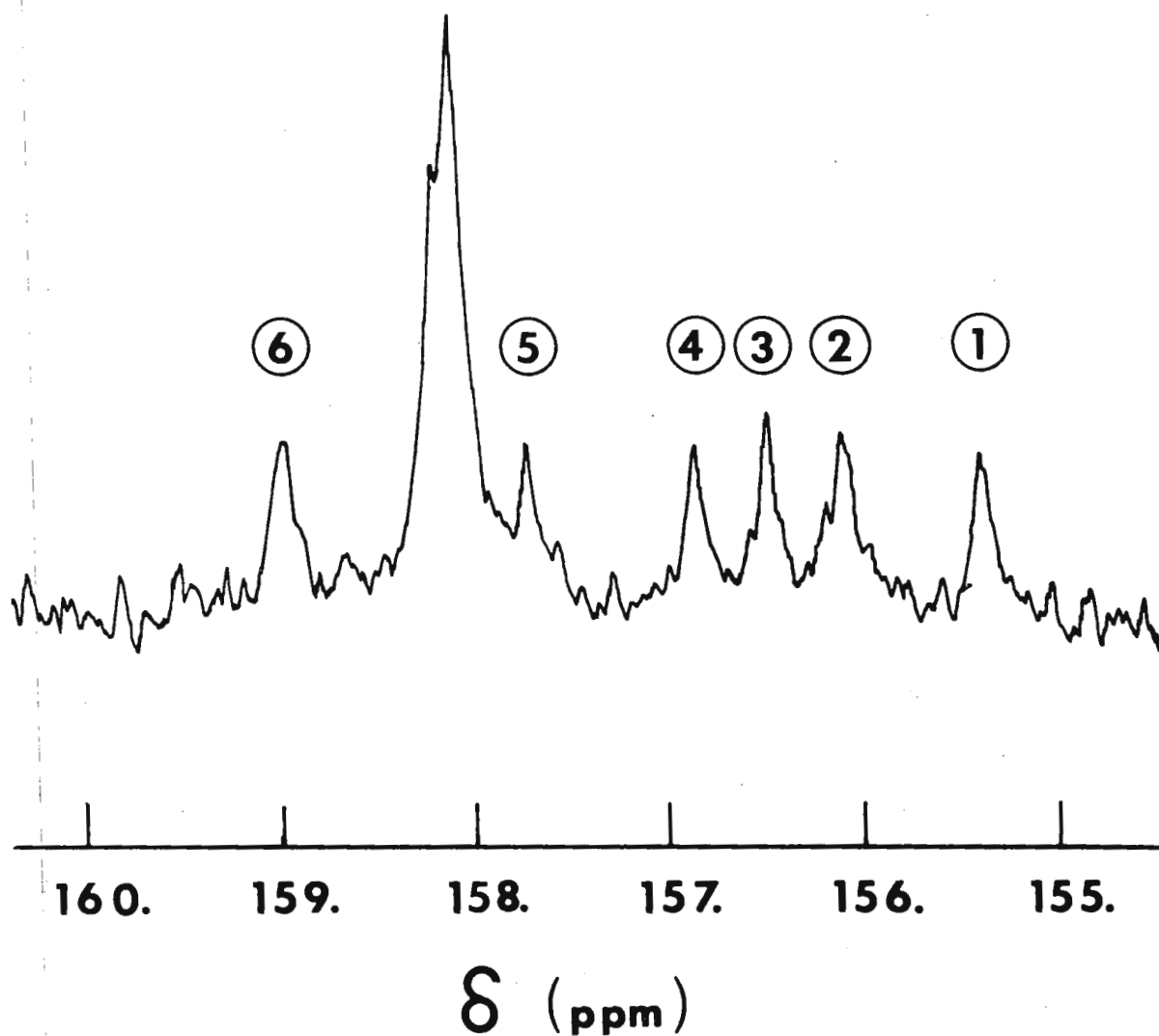
Fig.1 ^{13}C NMR spectrum of tyrosine C^ζ and arginine C^ζ resonances of bovine ribonuclease A (ca. 20 m$\underline{M}$ in 0.1$\underline{M}$ NaCl, pH 2.25, 20°C). Spectral parameters were: 67.898 MHz observation frequency, 15151.5 Hz sweep width, 32,768 acquisitions, 16 K data points with 16K zero filling, 0.54 sec acquisition time, 1.5 sec delay time: quadrature phase detection was employed in the acquisition of the spectrum. The free induction decay signal was exponentially multiplied to produce a 2.5 Hz additional line broadening.
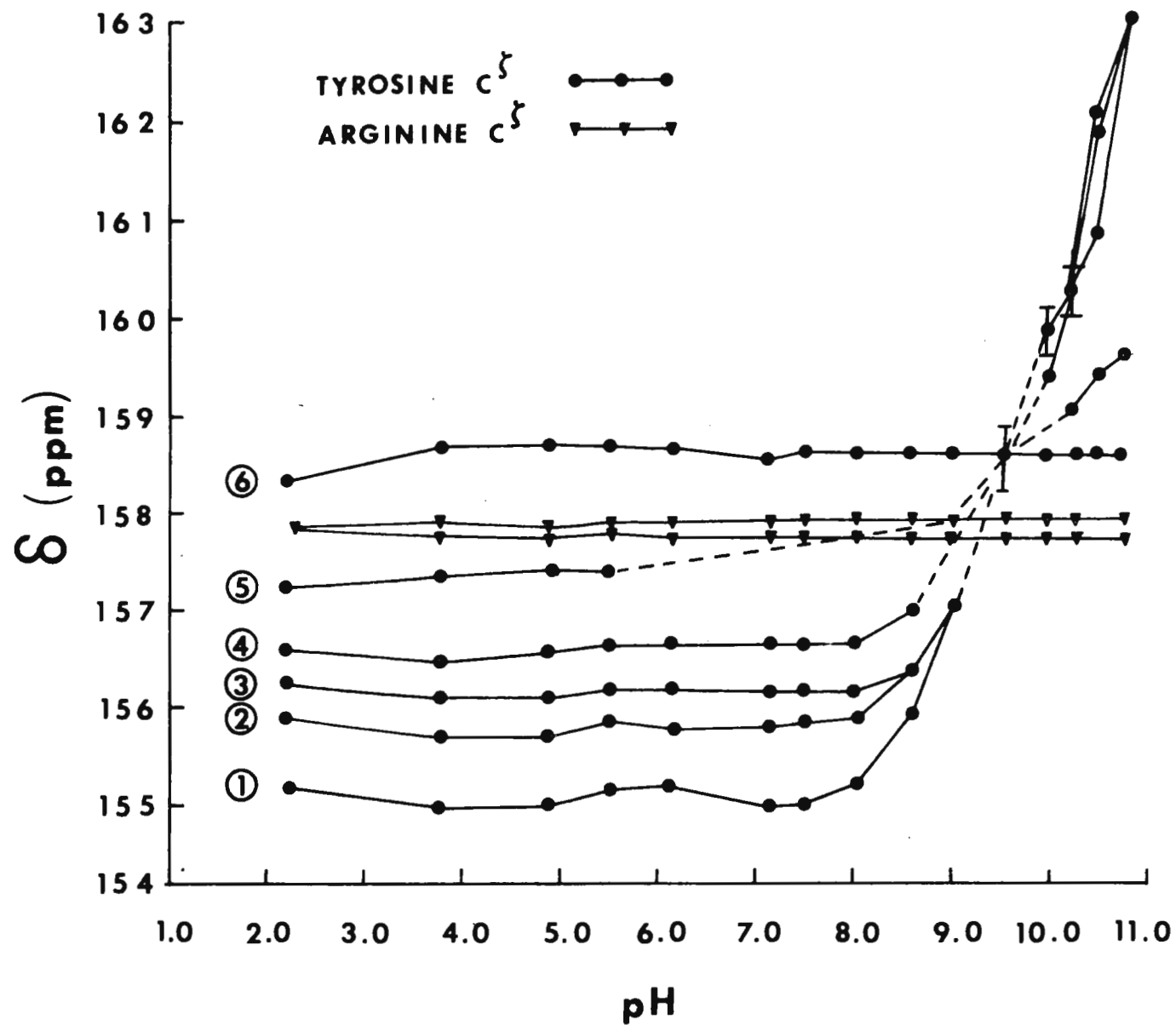
Fig.2 NMR titration curve of the tyrosine C^{ζ} (-●-●-) and arginine C^{ζ} (-▼-▼-) ^{13}C resonances of ribonuclease A.