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Newsletter

No. 181

October, 1973

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

CR/3562/ck   2762   7 Sept 73

Dear Professor Shapiro,

^{13}CMR chemical shifts of unsaturated fatty acid esters

Very recently we have received our Bruker WH 90 spectrometer, and
outside the periods of initial troubles we have measured the CMR-
spectra of a number of methyl octadecenoates with the double bond
(cis as well as trans) in the positions 8-12.

$$CH_3 \ CH_2 \ CH_2 \ (CH_2)_n \ CH_2 \ CH=CH \ CH_2 \ (CH_2)_m \ CH_2 \ CH_2 \ COOCH_3$$

$$(m=3,4,5,6,7 \ ; \ m+n=8)$$
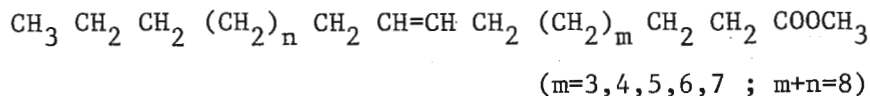
This work can be considered as the start of a systematic study of
^{13}CMR spectra of fatty acid derivatives.

Proton noise decoupled spectra of 0.2-0.5M solutions in $CDCl_3$ with
TMS as internal reference have been registered at 22.63 MHz
(3,000 - 10,000 scans).
The central peak of the $CDCl_3$ triplet was consistently found at
76.8 ppm downfield from TMS. This value is 0.1 ppm lower than
several literature values [1], but such possible errors in the
δ-values are not considered to be unduly disturbing.
The following signals are (nearly) the same in all ten compounds:

CH_3O	:	51.1 - 51.2	ppm
C_1	:	173.5 -173.7	"
C_2	:	34.0 - 34.1	"
C_3	:	24.9 - 25.0	"
C_{18}	:	14.0 - 14.1	"

CR/3562/ck

The methylene carbon atoms in $(CH_2)_m$ and $(CH_2)_n$ give rise to a complex of overlapping signals at 28.8 - 29.6 ppm.
The patterns are very much different for the positional isomers mentioned above, but there is similarity between the spectra of the cis- and trans-compound of the same positional isomer.

The other δ-values are reproduced in the table.
They indicate that in a methyl octadecenoate the configuration as well as the position of the double bond can easily be established. From the chemical shift difference of the olefinic carbon atoms the position of C=C up to 11 cis and 11 trans can be located. Very interesting is the observation that this difference is multiplied by a factor of about two each time the double bond "steps" towards the ester group. With the restricted number of channels available the relative error becomes larger as the difference becomes smaller. Extrapolating the cis series to α,β-unsaturated acids by multiplying Δ=10.3 with 2^6 leads to a difference of 659 Hz=29 ppm, which is very close to literature values for this type of compounds [2].

From the 12-position onwards, the atoms C_{16}, C_{17} and C_{18} will be more and more influenced by the approaching double bond.
The chemical shifts of these atoms can then be used for locating the double bond. Probably the chemical shift difference of the olefinic carbon atoms will increase again as they come nearer to the end of the carbon chain.
As far as the cis/trans discrimination is concerned the neighbouring CH_2 carbons are very useful. They differ about 5.3 ppm for the two isomers.
Perhaps surprisingly, within a CH_2 CH=CH CH_2 group the chemical shift difference between the two olefinic carbon atoms is much more sensitive to long range effects than are the CH_2 groups.

Yours sincerely,

UNILEVER RESEARCH VLAARDINGEN

Dr J. Bus

References
1) G.C. Levy and J.D. Cargioli, J. Magn. Res. 6 143 (1972)
2) E. Lippmaa, T. Pehk, K. Andersson and C. Rappe, Org. Magn. Res. 2 109 (1970)

Table

	8 cis (m=3)	9 cis (m=4)	10 cis (m=5)	11 cis (m=6)	12 cis (m=7)
$\underline{C}H_2C=C\underline{C}H_2$	27.1[*]	27.1	27.2	27.2	27.2
	27.2	27.2			
$=C_{m+5}$	129.2	129.3	129.3	129.4	129.5
$=C_{m+6}$	129.6	129.6	129.5	129.5	
$\Delta^{C=C}$ (Hz)	10.3	5.6	2.9	1.5	0–1
C_{17}	22.7	22.7	22.6	22.6	22.6
C_{16}	31.8	31.9	31.8	31.7	31.5
	8 trans	9 trans	10 trans	11 trans	12 trans
$\underline{C}H_2C=C\underline{C}H_2$	32.4	32.5	32.5	32.5	32.5
	32.5				
$=C_{m+5}$	129.7	129.8	129.9	129.9	129.9
$=C_{m+6}$	130.1	130.0	130.0	130.0	
$\Delta^{C=C}$ (Hz)	10.2	5.9	3.7	2.2	0–1
C_{17}	22.7	22.7	22.7	22.6	22.5
C_{16}	31.9	31.8	31.8	31.7	31.4

[*] Chemical shift δppm downfield from TMS.

CARLETON UNIVERSITY

OTTAWA CANADA
K1S 5B6

DEPARTMENT OF CHEMISTRY

August 29, 1973

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

Title: Conformational Preferences of Spiro-
Aziridines by Low Temperature ^{13}CMR

Dear Barry,

Undergraduate student Robert Kohler has been engaged in the
title study here this summer as part of his B.Sc. thesis project.
Attempts to determine the conformational energy of I by electric
dipole moments (1) have proved unsuccessful. Furthermore 'HMR
cannot be applied to the problem due to the accidental overlap
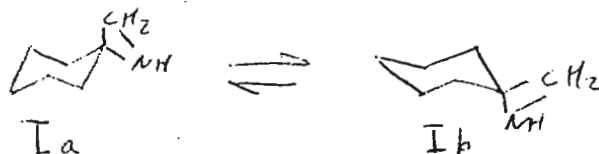
of the aziridine methylene resonance (δ=1.45) with the cyclohexane
ring methylene protons. We hoped that ^{13}CMR might afford a solution
and accordingly a sample of I, 61% ^{13}C enriched at the exo-methylene
position was prepared. (Needless to say we are not blessed with
F.T. here!)

Below -80°C in CD$_2$Cl$_2$ solution the singlet at δ=31.84 for the
aziridine methylene carbon separates into completely resolved components
separated by 6.4 Hz. The resonance of higher integrated intensity
appearing at lower field is assigned to conformer Ib. -ΔG$^{\circ}$ is 0.16
Kcal/Mole.

Interestingly we find the chemical shift difference between the
aziridine methylene carbons of <u>cis</u> and <u>trans</u>-4-<u>t</u>-butylcyclohexane
spiro-aziridine to be 17.5 Hz, indicating a significant pertubation
by the 4-<u>t</u>-butyl group.

(at 25.2 MHz)

We are presently attempting to compare the ring current effects of oxirane, aziridine, episulfide and cyclopropane using various models.

Please credit this contribution to John ApSimon's subscription.

Best regards,

G.W. Buchanan
Assistant Professor

GWB/jd

1. Jones, Katritzky, Lehman, Richards & Scattergood, J.C.S. Perkin II, 1972, 41.

Do you need a signal averager...or a general purpose computer?

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NICOLET NIC-80 DATA SYSTEMS

The new NIC-80 Series data acquisition and processing system combines the benefits of a hard-wired signal averager with the advantages of a general purpose computer. The result is an easy-to-use data system that permits the scientist to concentrate on his research rather than on electronic data processing.

The NIC-80 Series offers digitizing speeds of up to 10 microseconds with 12-bit resolution, high resolution timing of up to 1 microsecond, high timing accuracy (100 nanoseconds), 20-bit word length to eliminate double precision programming, easy interface with a wide range of experiments through specialized hardware and software, extensive processing capability through available software, flexible control of experimental variables through keyboard entries, continuous display even at high data rates, a broad selection of peripheral equipment, and the most thorough applications assistance offered anywhere. For ultra-high-speed applications, digitizing speeds of up to 10 nanoseconds can be achieved with an optional transient recorder.

The NIC-80 Series is presently offered in three different configurations which differ only slightly in hardware design but have a unique software package for each system. For example, the NMR-80 System contains complete programs for Ft nmr work. The MED-80 System is oriented to biomedical applications where the statistical analysis of bioelectric potentials is the task. A third system, called the LAB-80 System is a general purpose laboratory data system designed for use with various spectrometers or other laboratory instruments.

Included in all of the above systems is the hardware for on-line CRT display of incoming data or processed data as well as software for the control of x-y or y-t recorders.

Options and accessories include a high-speed paper tape reader, a disk memory unit, a silent keyboard/printer, x-y or y-t recorders, a transient recorder, paper tape punch, and magnetic tape interface.

NMR-80 capabilities include: complete programs for Fourier transform nuclear magnetic resonance work including routines for data acquisition, signal averaging, data processing, display, plotting, digital readout, theoretical spectrum calculation, automatic spin lattice relaxation time measurements, iterative fitting of theoretical and experimental spectra, as well as dozens of other minor routines.

Call or write to discuss your averaging and processing requirements.

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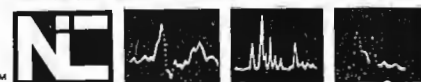
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THE LILLY RESEARCH LABORATORIES

ELI LILLY AND COMPANY · INDIANAPOLIS, INDIANA 46206 · TELEPHONE (317) 636-2211

August 30, 1973

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

Dear Barry:

My communication on the separable contributions of induction and polarization to the chemical shift appeared in Tetrahedron Letters, January, 1973, page 55.

In order to examine some of these ideas with regard to normal paraffins, I have replaced hydrogen with fluorine on the terminal methyl of normal decane and fluorine and oxygen on carbon-10 in nonadecane (C^{19}) and have had gratifying results. All of the effects observed in carbon-13 spectra seem to have been reversed by the opposite electronegativities and opposite signs of dipoles, as shown in the Figure. We are preparing this work for publication.
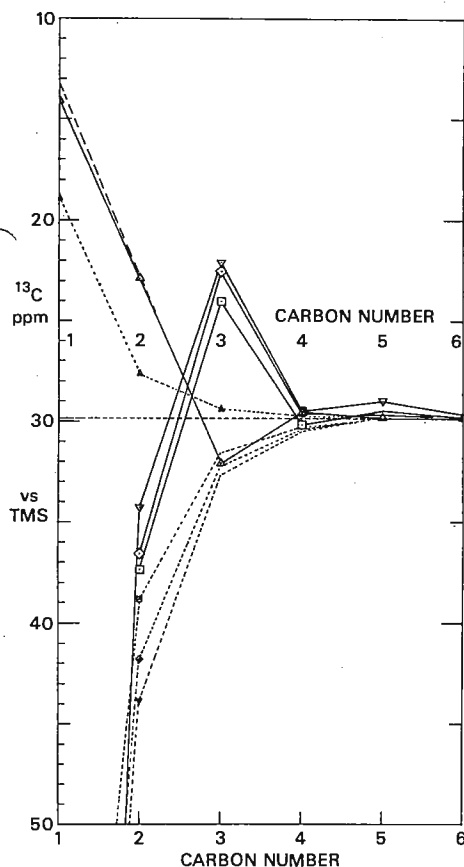
Sincerely yours,

ELI LILLY AND COMPANY

Harold Boaz

Harold Boaz, Ph.D.
Physical Chemistry Research
Department MC525

HB:vr

Figure

Chemical shifts for C^{13} are plotted vs. carbon number from the polarizing group. These data are connected by solid lines. Derived induction curves are dotted. $\triangle$, CH_3; $\triangledown$, CF_3; $\diamondsuit$, CF_2; $\square$, CO_2.

Eidg. Technische Hochschule
Zürich-Hönggerberg

Institut für Molekularbiologie
und Biophysik

Tel. (051) 57 57 70

Prof. Dr. K. Wüthrich

8049 Zürich, September 4, 1973   KW/as

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

Hyperfine shifts of the ^{13}C NMR. in low spin ferric porphyrin complexes
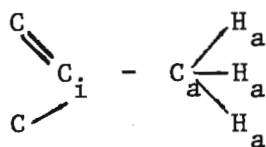

Dear Barry,

　　We have recently studied the ^{13}C NMR. spectra of the zinc(II)
and the dicyano iron(III) complexes with porphin, tetraphenylporphin,
protoporphyrin IX, and deuteroporphyrin IX, and from these data the
hyperfine shifts of the carbon-13 resonances in the iron complexes were
obtained.[1-3]　　Here we would like to report a couple of observations which
might be of interest to others who are working with paramagnetic species.

　　The relatively simple spectrum of the fourfold symmetrical iron(III)
porphin dicyanide complex shows that pseudocontact shifts arising from
the electron spin localized in the π-orbitals of the ligand atoms make
an important contribution to the ^{13}C hyperfine shifts of the aromatic car-
bons. A preliminary estimate indicates that the ligand localized pseudo-
contact shift of the ^{13}C NMR. of an aromatic carbon atom is of the order
60 - 80 ppm if 1% of an unpaired electron is localized in its π-orbital.

　　The contact shifts of the ^{1}H and ^{13}C resonances of the side chains
in iron(III)protoporphyrin IX dicyanide are related to the spin density
ρ_C^π on the ring carbon atoms to which they are bound by a relation of the
type proposed by McConnell for aromatic protons

$$A^I = Q^I \rho_C^\pi \tag{1}$$

where A^I is the contact coupling constant of the nucleus. The sign and
size of the empirical coefficient Q^I depend on whether the electron-nucle-
us coupling is mainly through spin polarization, or hyperconjugation, res-
pectively. For the fragments I and II in Fe(III)(protoporphyrin IX)(CN)$_2$
the following are representative values for the contact shifts, where a
negative sign indicates shifts to lower field at fixed frequency:

$$
\text{I} \qquad\qquad C\!\!=\!\!C_i - C_a \begin{cases} H_a \\ H_a \\ H_a \end{cases}
$$

$$
\text{II} \qquad\qquad C\!\!=\!\!C_i - C_c \begin{cases} C_d \\ H_c \\ H_c \end{cases}
$$

I   II

$$\Delta\nu_c^C(a) \approx + 45 \text{ ppm} \qquad\qquad \Delta\nu_c^C(c) \approx + 39 \text{ ppm}$$

$$\Delta\nu_c^H(a) \approx - 12 \text{ ppm} \qquad\qquad \Delta\nu_c^H(c) \approx - 3 \text{ ppm}$$
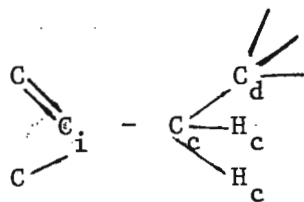
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Delta\nu_c^C(d) \approx - 54 \text{ ppm}$$

The downfield shifts for the protons a and c, and the carbon resonance d indicate that for these nuclei hyperconjugation with the unpaired electron is the dominant coupling mechanism. It had been shown earlier by several authors that in this case the coefficient Q^I in equation (1) can depend markedly on the molecule studied, and is also a function of the sterical arrangement of the aliphatic substituent with respect to the plane of the aromatic ring. Therefore the spin density distribution which one computes solely from the observed contact shifts of H_a, H_c, and C_d through equation (1) is beset with much uncertainty. On the other hand the observation of the contact shifts of the carbon atoms a and c, which are mainly due to spin polarization, yield a more reliable value for the spin density localized in the aromatic carbon atom C_i. In fragment I this means that the coefficient $Q_{CCH_3}^H$ for the methyl protons can now be measured. A preliminary estimate shows[3] that it is of the order of 40 MHz, i.e. rather small compared to what is generally reported for organic radicals.

In fragment II the sterical arrangement of the side chain is now in principle accessible for investigation by NMR. Since $\Delta\nu_c^C(a) \approx \Delta\nu_c^C(c)$, the different contact shifts of the protons a in I, and c in II, respectively, must come from the occurrence of different values for the coefficients Q^I, and as mentionned above these are in turn related to the torsion angle about the $C_i - C_c$ bond. The same information can in principle be obtained independently from the observation of $\Delta\nu_c^C(d)$ in II.

Sincerely yours,

Rudolf Baumann   Kurt Wüthrich

References

1) K. Wüthrich and R. Baumann, Helv.Chim.Acta 56, 585 (1973)
2) K. Wüthrich and R. Baumann, Ann.New York Acad.Sci. (in press)
3) K. Wüthrich and R. Baumann, Helv.Chim.Acta (in press)

The University of Western Ontario, London, Canada

Faculty of Science
Department of Chemistry

September 6, 1973

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

Dear Barry

A Stereochemical Assignment for Sesquiterpenes from Angular Methyl ^{13}C Shieldings.

        Having been reminded that it's time to renew the nonfinancial portion
of my subscription to the TAMU newsletter, it seemed that the results of a recent
examination of some natural products might be of interest to a reader or two.
In collaboration with Dr. Albert Stoessl of the Department of Agriculture, some
sesquiterpenes which are antifungal metabolites have been studied by ^{13}C nmr to
establish the relative orientation of their vicinal methyl groups. These materials
are eremorphilane derivatives and the parent, capsidiol, (1), exhibits three
methyl signals at 9.5, 21.1 and 32.4 ppm which were readily assigned to the sec-
ondary, vinyl and angular methyl carbons, respectively, by selective proton de-
coupling since the methyl protons are well separated at 0.88, 1.74 and 1.37 ppm,
respectively. The angular methyl carbon is the most deshielded one which has
been encountered in this laboratory through the examination of a few dozen steroids
and several methyldecalin derivatives. Because of its low field position we
can immediately conclude that the vicinal methyls must be trans. This is inter-
esting since all other eremorphilanes possess cis-vicinal methyls. A further
point to be established was the stereochemistry of the isopropenyl group. Since
this group can be equatorial whether β or α (2 and 3), a distinction between the
two possibilities is difficult but from the ^{13}C results for aristolochene (4),
whose configuration is known, and the data for a series of model compounds the
angular methyl shieldings for 2 and 3 can be estimated and we would expect 2 to
have the less shielded methyl carbon. Thus one can tentatively conclude that the
isopropenyl group and angular methyl carbon in 1 are cis. This was subsequently
established by an x-ray study of 1 by Dr. George Birnbaum (NRCC, Ottawa).

        Since the angular methyl carbon in epicapsidiol (the 1-epimer of 1)
absorbs at 30.1 ppm, the syn-axial interaction of the 1-hydroxyl in 1 deshields
its angular methyl by 2 ppm. This is an additional example of the downfield
trend generally observed for syn-axial δ effects which have been noted for a
variety of alcohols [e.g. J. Mag. Res. 10, 227 (1972)].
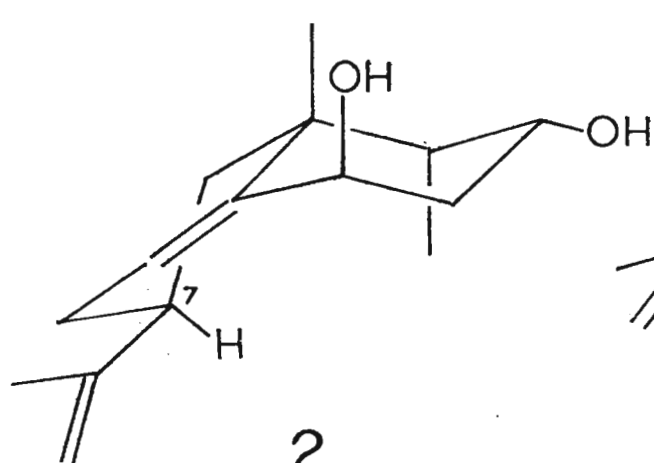
        Best regards.

                                                    Sincerely
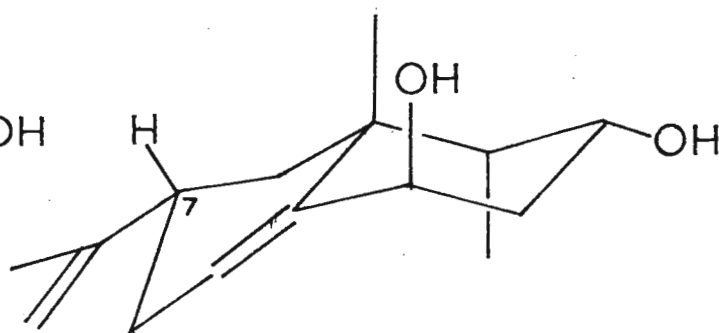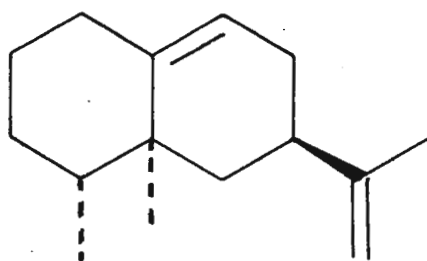
                                                    Jake

                                                    J. B. Stothers
                                                    Professor of Chemistry

JBS/et
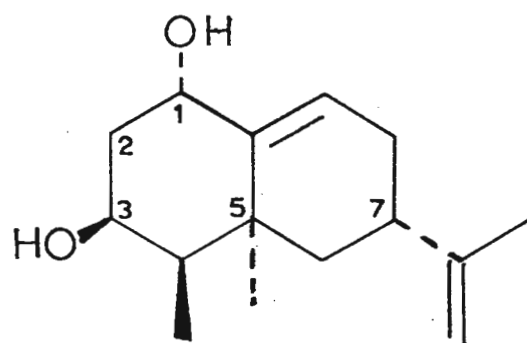
1

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3

4

DEPARTMENT OF ORGANIC CHEMISTRY

The University of Sydney

SYDNEY, N.S.W. 2006

September 6, 1973

IN REPLY PLEASE QUOTE:

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

Dear Barry,

"*Cis*" and "*trans*" *transoid* homoallylic coupling

We have noted elsewhere[1] that, while VB calculations predict equal values for "*cis*" and "*trans*" *transoid* homoallylic coupling constants, i.e., $\phi = 120°$, $\phi' = 120°$ or $240°$ for "*cis*" and "*trans*" respectively), INDO MO calculations predict substantially different values. We have also noted[1] that results for *transoid* homoallylic coupling constants were scarce.

Mr. R. J. Spear has prepared a series of biindenyls, which should be almost ideally planar, for testing the above prediction. It can be seen from the data shown on the next page that the "*cis*" and "*trans*" homoallylic coupling constants are in fact unequal, in conflict with the VB predictions. Unfortunately, we have no reliable means for relative assignments of H_B and H_C and hence the INDO predictions still await final experimental confirmation. The *numerical* agreement is excellent.

With best regards,

Yours sincerely,

S. STERNHELL

[1] M.Barfield and S.Sternhell, *JACS*, <u>94</u>, 1905 (1972).
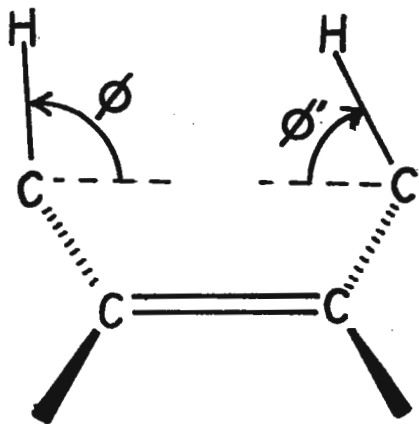
cisoid homoallylic coupling
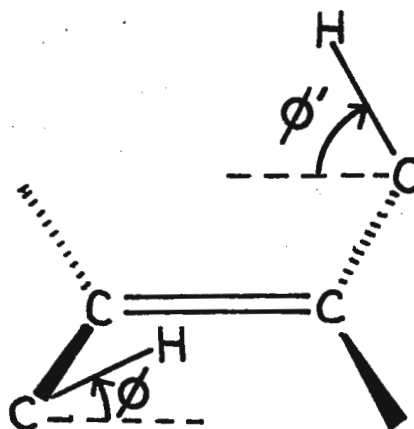
transoid homoallylic coupling
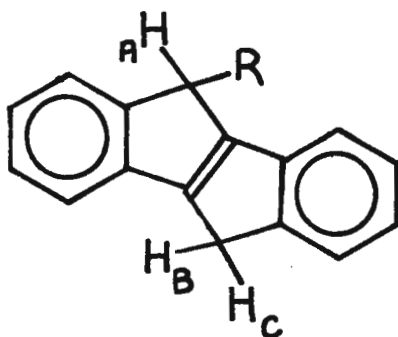
R	J_{AB} [a]	J_{AC} [a]	J_{BC} [a]
H	3.85 ± 0.2 [b]	2.45 ± 0.2 [b]	–
Ph	3.80 ± 0.05	2.30 ± 0.05	-22.2 ± 0.2
$-p-C_6H_4-OMe$	3.86 ± 0.10	2.45 ± 0.10	-22.2 ± 0.2
Calculated[1] INDO	4.22 or 2.59	2.59 or 4.22	–
Calculated[1] VB	2.81	2.81	–

[a] Signs assumed by analogy.

[b] From ^{13}C satellite analysis.

STATE UNIVERSITY OF NEW YORK
AT STONY BROOK

DEPARTMENT OF CHEMISTRY   **STONY BROOK, N.Y. 11790**

September 11, 1973

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

POSITIONS AVAILABLE -

POSTDOCTORAL AND TECHNICAL

Dear Barry:

Several NMR-related positions are now available in my research group and
in the Department of Chemistry. They include:

Postdoctoral Fellows

Preferably with experience in the areas of pulsed NMR, spectrometer
construction and modification, or studies on biological systems,
to work on NMR zeugmatography [TAMUNMRN No. 175, 34 (April 1973);
NATURE, 242, 190-191 (1973)] and its applications in biology and
medicine.

Electronics Technicians

To design, build, modify and/or service NMR and other equipment
(a position as administrative head of a 4-5 man Electronics
Shop is also a possibility for a man with appropriate qualifications).

Computer Programmers

To work on image reconstruction and processing programs, and to
do special minicomputer programming as well as standard
programming on the IBM 370/155 and the IBM 1800 (a position as
supervisor of the Chemistry Computing Center, with an IBM 1800
on-line to a variety of experiments, may also be available to a
suitably qualified applicant).

We are, of course, an equal opportunity employer. All inquiries will be promptly acknowledged and held in confidence. Initial inquiries should include a complete vita and at least two names of people who will provide letters of reference, if such become appropriate.

Finally, applications are invited for admission to our Ph.D. program in Chemistry in the Fall of 1974. One or two positions, with support, may even be available in the Spring of 1974 for suitable applicants.

All initial inquiries should be addressed to me at the above address.

Yours truly,

Paul C. Lauterbur
Professor of Chemistry

PCL:dw

UNIVERSITY OF CALIFORNIA, BERKELEY

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DEPARTMENT OF CHEMISTRY &
Lawrence Berkeley Laboratory

BERKELEY, CALIFORNIA   94720
September 12, 1973

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

Dear Barry:

RE: Enhanced ^{13}C Nuclear Spin Echoes in Solids

I'd like to tell you about some long-lived ^{13}C nuclear spin echoes in
solids which have been produced in my laboratory by Tom Shattuck, a graduate
student. The procedure employed is depicted in figure 1. The first part of
the experiment is simply a single shot cross-polarization version of proton-
enhanced nmr.[1] There are many ways of accomplishing this, and the one employed
here is technically very convenient; one half of the available ^{13}C polarization
(available by an adiabatic transfer) is obtained in one shot[1-3] and no accu-
mulation is necessary with multiple contacts, thus permitting a tremendous
savings in necessary ^{1}H rf power. The additional ^{13}C pulses during the ^{1}H
irradiation produce a Carr-Purcell live train of spin echoes provided the con-
tribution to the decoupled free induction decay from magnetic field inhomoge-
neities dominates the pure ^{13}C $-$ ^{13}C dipolar coupling. This is invariably true
in our case.

Figure 2 shows an atypical result of such an experiment on a small sample
of powdered adamantane with an externally imposed gradient. The oscilloscope
trace also exemplifies the signal observed "in one shot" from natural abundance
^{13}C by this approach. These spin echoes allow several new features of solid
state nmr to be studied.

(a)   Determination of the limiting resolution in high resolution ^{13}C nmr
in solids due to ^{13}C-^{13}C dipolar coupling.

(b)   Determination of the nmr lineshape from randomly distributed coupled
spins, and a check of ideas due to Kittel and Abrahams.

(c)   Complete determination of molecular diffusion tensors in solids by
loss of coherence for a single echo in a Carr-Purcell type A experi-
ment. This extends to solids dynamical work which has been performed
to date only in liquids and recently in liquid crystals.

We have obtained results on all these aspects and they will appear in print
in the near future.[2] Finally, let me point out, for the purposes of acknowledg-
ment, that the experiments were performed on a homebuilt spectrometer constructed
with funds from the E. I. duPont Company and from the U. S. Atomic Energy Com-
mission through the Inorganic Materials Research Division of the Lawrence Berkeley
Laboratory.

Please keep in touch via modes of communication colored anything but blue.

Best regards,

Alex

Alex Pines
Assistant Professor

[1]A. Pines, M. G. Gibby and J. S. Waugh, J. Chem. Phys. $\underline{59}$, 569 (1973).
[2]A. Pines, Proceedings of the First Specialized Colloque Ampere, Krakow, Poland, August 1973 (in press).
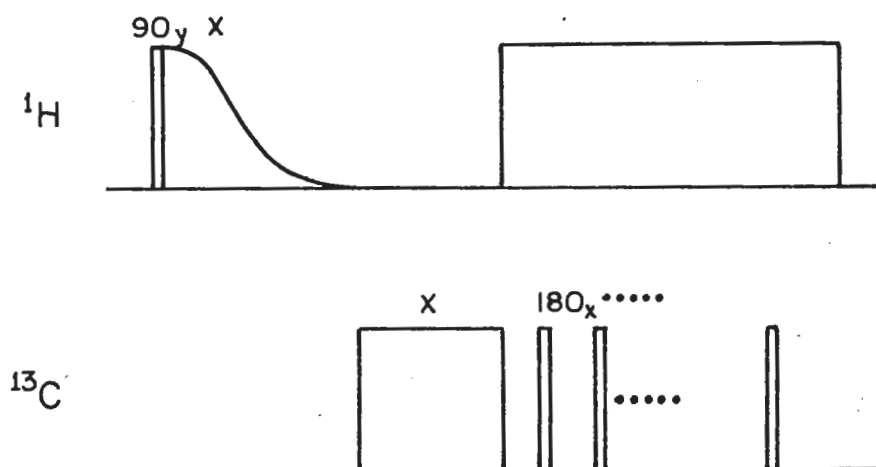[3]J. S. Waugh, private communication.

Figure 1: *Procedure employed for obtaining high sensitivity ^{13}C nuclear spin echoes. Cross-polarization occurs from the demagnetized proton reservoir in the rotating frame. The large ^{13}C magnetization is then treated by a slow train of pulses during strong ^{1}H irradiation.*
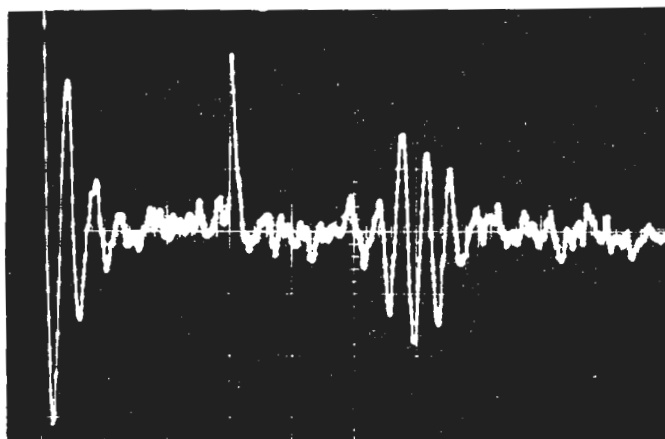
Figure 2: *Oscilloscope trace of ^{13}C detector output in response to sequence of figure 1 with one refocusing ^{13}C pulse. The scale is ~ 1 msec/division.*
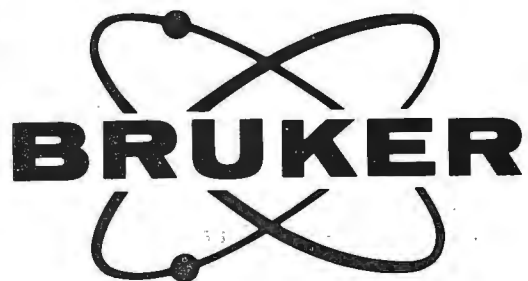
BRUKER

Variable Frequency Nuclear Resonance Pulse Spectrometer
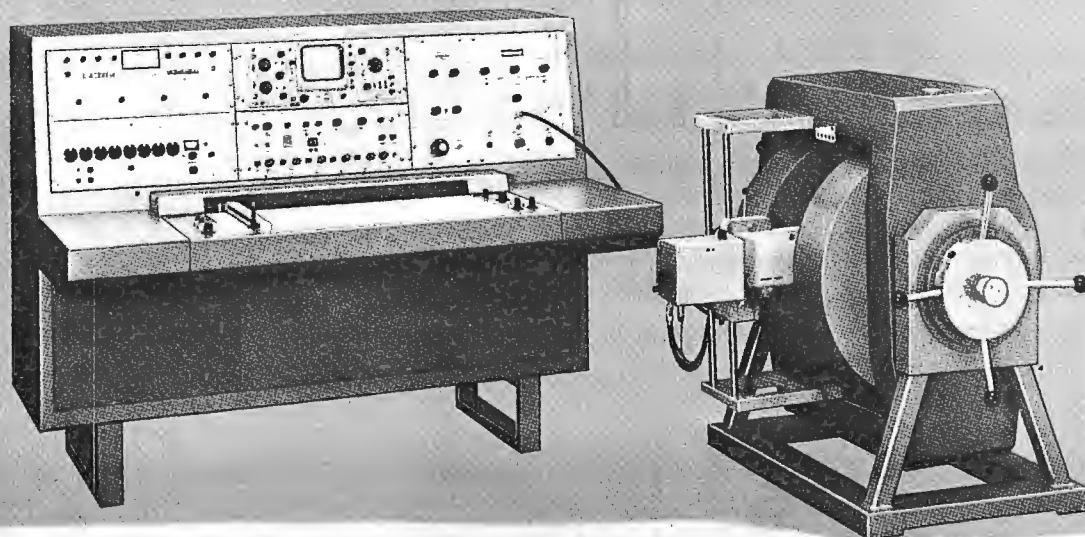
Spin Echo

Fourier Transform

PFP Technique

Double Resonance

NQR

Ferro-Ferri-NMR

SXP 2-200

NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

DEPARTMENT OF CHEMISTRY   September 27, 1973

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

Dear Barry:

We have expanded the stereochemical base in our study of vicinal chemical shift isotope effects (H-C-C-F vs. D-C-C-F). Previously (J. Amer. Chem. Soc., 95, 6150 (1973)), we measured the upfield shift of ^{19}F resonance on the replacement of H by D in cyclohexane systems:

0.15 ± 0.02 0.35 ± 0.02 F

0.18 ± 0.03 0.13 ± 0.02
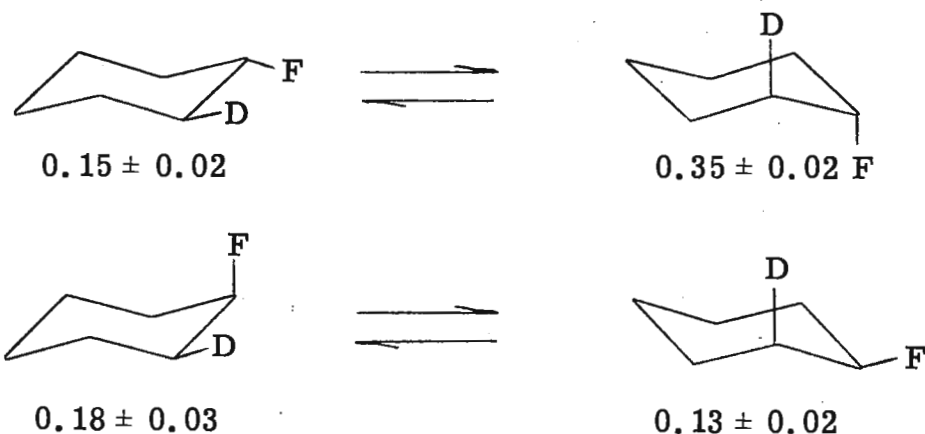
The antiperiplanar relationship was found to exhibit the largest effect (given in ppm under the structures). We have now measured the isotope shifts for the 0° and 120° dihedral relationships by studying the endo-norbornyl fluorides:

0.40 ± 0.06 0.15 ± 0.06

The effect at 120° is essentially the same as that at 180°, and the effect
at 0° is the same as that at 60°. The figure on the next page illustrates
the dependence of the isotope shift on dihedral angle. Superimposed on
the graph are analogous stereochemical data for kinetic isotope effects
in solvolysis reactions. We would welcome any suggested explanations of
our data. We are favoring an angular-dependent inductive effect but are
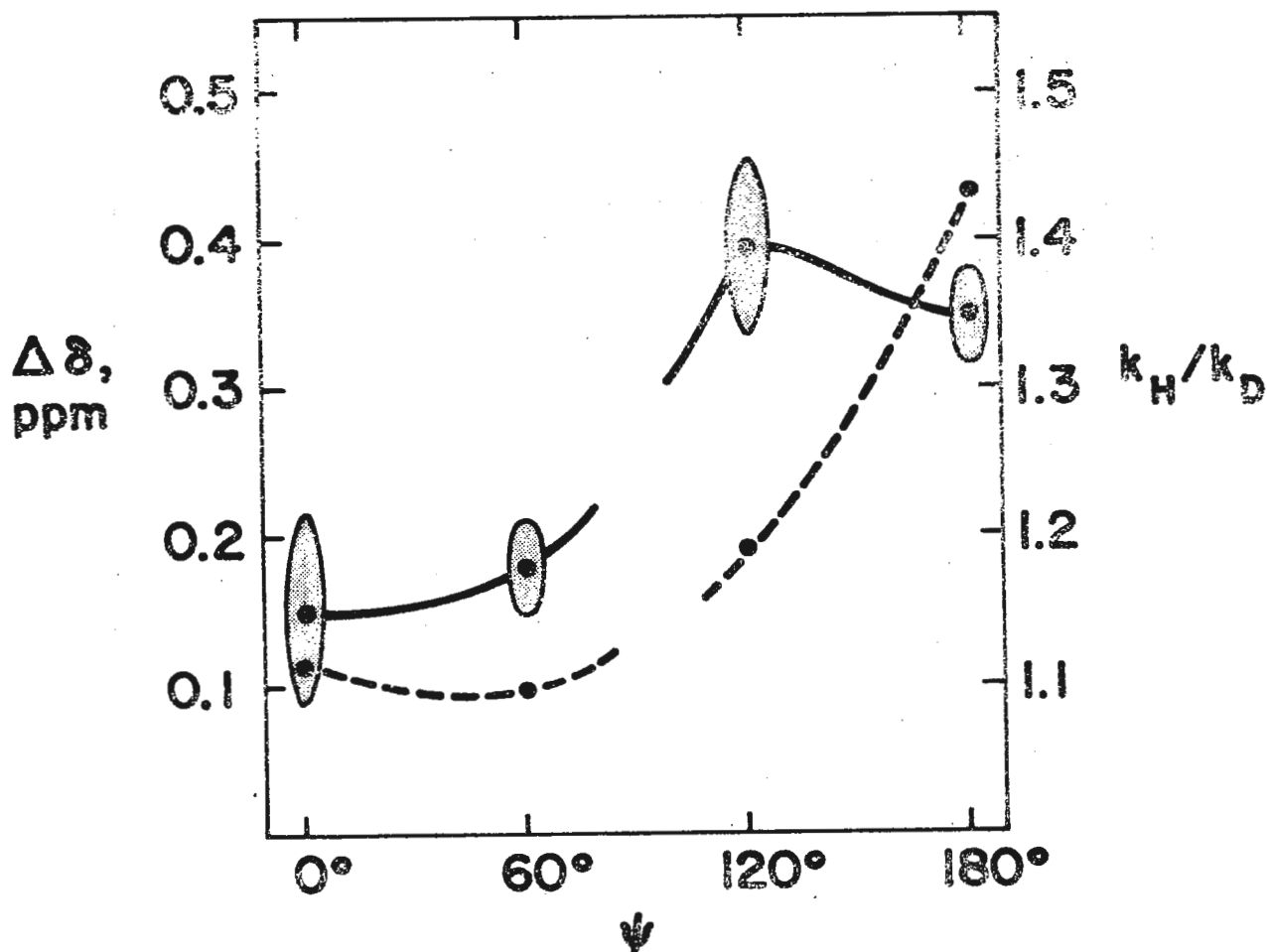by no means sure.

Sincerely,

Joseph B. Lambert

Linda G. Greifenstein

JBL/kp

More on The Stereochemistry of the Chemical Shift Isotope Effect

THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT · ISRAEL   רחובות · ישראל

מכון ויצמן למדע

ISOTOPE DEPARTMENT   מחלקת איזוטופים

September 17, 1973

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

Dear Barry,

The interest in studying the temperature dependence of the shifts in lanthanide complexes has increased recently. We wish to point out now some of the pitfalls. Results will be reported at a later date.

The shifts induced in the substrate resonances, as by now well established, are dependent upon the chemical equilibria between the complexed and uncomplexed forms. Thus the fraction of complexed molecules is temperature dependent. Unfortunately this has usually been ignored in reports of variable temperature work thereby rendering the detailed theoretical analysis virtually meaningless. The reagent protons are also sensitive to complex formation in particular with aromatic substrates (e.g. pyridine). In this case part of the shift is due to aromatic ring currents and to a first approximation should be temperature independent.

For temperature calibrations, while operating in the deuterium lock mode, we prepared a methanol sample containing 10 percent CD_3OH. Our sample was apparently left free from acidic impurities and spin-spin splitting appears in its proton spectrum at temperatures higher than those of the manufacturer supplied one.

Finally, we tried to reproduce the interesting experiment of Cramer and Dubois, JACS, 95, 3801 (1973), who observed at low temperatures (ca. $-100°C$) separate resonances for the 1:1 and 2:1 β-picoline – $Eu(dpm)_3$ adducts in CS_2 solutions. We used $Eu(fod)_3$, which is supposed to be more soluble, but phase separation occured already at about $-30°C$.

Sincerely yours,

Gabriel A. Elgavish   Jacques Reuben

Title: On Variable Temperature Work with Shift Reagents.

JR/sa

SCHEIKUNDIG LABORATORIUM
DER VRIJE UNIVERSITEIT
AMSTERDAM-Z.

De Lairessestraat 174 - Telefoon 71 74 51

AMSTERDAM, September 17, 1973

Uw ref.:

Onze ref.: 73120/CM/aa

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

Dear Dr. Shapiro,

Conformational study of $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-p-xylene by liquid crystal NMR.

In the course of an investigation of molecules with two rotating CH_2X- or CHX_2-groups (X = halogen) by liquid-crystal NMR, we have measured the proton spectrum of $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-p-xylene (in a mixture of two azo-compounds). The spectrum is very broad: about 10.000 Hz. The use of sidebands was avoided by applying an external synthesizer to offset the proton frequency. In a later stage the standard field sweep mode was replaced by a frequency sweep mode. In this way the widths of the outer lines in the spectrum were reduced to acceptable values (about 20 Hz). Several accumulations were needed for a reasonable S/N ratio.

The interpretation of the spectrum was straightforward. Initial values of the ordering parameters were taken from the results of $\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-p-xylene, and with an assumed geometry an initial set of direct coupling constants was obtained. The spectrum was further analysed using a version of LAOCOON III.

A remarkable feature of the spectrum is the large difference between $\sigma_{ring} - \sigma_{CHCl_2}$ in $COCl_3$ (0.9 ppm) and in the nematic phase (-1.5 ppm).

Starting from different models and a varying number of orientation parameters the relative geometry of the proton-skeleton was calculated. From preliminary computations we conclude that the conformations in which the $CHCl_2$ protons are in the plane of the ring protons, predominate. Steric interactions between the $CHCl_2$-groups are neglected and therefore conformations in which the protons are cis or trans relative to each other are assumed equally probable. It was furthermore assumed that the orientation parameter $c_{3z^2 - r^2}$ (z-axis as in figure) has the same value for the "cis"- and "trans"-forms. The calculations do not reveal details of the potential hindering the $CHCl_2$ rotation but the height of the two-field barrier is high enough (e.g. > 5 kcal/mole) to make large deviations from a planar configuration imperceptible.

As there are more variables than dipolar couplings it is impossible to obtain a unique relative geometry but the following values are compatible with a reasonable structure:
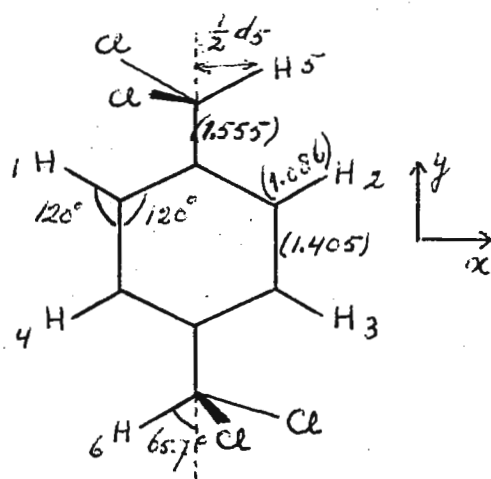
$$d_{14} = 2.491 \ (ass)$$
$$d_{12} = 4.314$$
$$d_{56} = 6.836$$
$$d_5 = 2.033 \ (ass)$$
$$V_2 = \infty \ (ass)$$

With orientation parameters:

$$c_{3z^2 - r^2} = -0.3462$$
$$c_{x^2 - y^2} = -0.4919 \ (cis)$$
$$= -0.7751 \ (trans)$$
$$c_{xy} = 0.0134 \ (trans)$$

The r.m.s. error of the fit is 0.03 Hz. Assuming a C-C distance of 1.405 Å in the ring, and a C-H distance of 1.115 in the $CHCl_2$-group the given values are in accordance with the bond distances shown in parentheses in the figure.

With kind regards,

Sincerely,

C. MacLean   J. Bulthuis   P. Oudega   R. Bouwma

JEOL (U K.) LIMITED

Dr. B.L. Shapiro,   AID/4703/PJB/LSD
Chemistry Department,
Texas A & M University,
College Station,
Texas   843,
America.   20th September, 1973.

Dear Dr. Shapiro,

^{13}C of antibiotics - impurities in deuterated solvents - deuterium decoupling on PS100

Please accept my apologies for the lateness of this contribution.

Over the past year the time available to me for using the nmr instruments has decreased
sharply as a result of a large increase in sales activities with all the demonstration,
technical information and tuition requirements this entails. However, in my free time I
have been continuing with ^{13}C measurements in collaboration with a number of outside
groups. The study of the ^{13}C nmr[1] and biogenesis[2] of rifamycin S has been substantially
completed and provides a clear example of how powerful the technique is in solving a fairly
complex problem in rather a short time (total instrument time was less than ten days).
Further work is being done on the rifamycin series and also (with another group) on the
Aurivertin series, the structure of which is currently not known. I have also been doing
some work on the ^{13}C nmr of unsonicated membranes.[3]

Work on the other nuclei (mostly ^{1}H, ^{31}P and ^{19}F) has been of a more routine nature, but one
important point which has arisen on a number of occasions is the occurrence of various
proton - containing impurities in highly deuterated solvents. There seems little point in
using 99.99% $CDCl_3$ if it contains impurities giving several signals of 10-50 times the area
of the residual $CHCl_3$. I would suggest that all suppliers

1. E. Martinelli, R.J. White, G.G. Gallo, G. Lancini and P. Beynon Tetrahedron 29 inpress
2. R.J. White, E. Martinelli, G.G. Gallo, G. Lancini and P. Beynon Nature 243, 273, (1973)
3. K.M. Keough, E. Oldfield, D. Chapman and P. Beynon Chem Phys. Lipids 10 (1973) 37

JEOL (U.K.) LIMITED

of these materials should specify the maximum total area of all signals in the ^{1}H spectrum as a multiple of the area of the residual protonated solvent peak. For those suppliers without ^{1}H F.T., I would be glad to run a test spectrum in exchange for a 100g sample of solvent! Of course these solvents must be rigorously protected from water vapour in the air, and all glassware used un sample preparation must be scrupulously clean and dry.

One point which may not have occured to some PS100 users is that the ^{2}D lock channel of the crossed-coil proton probe may readily be used for ^{2}D decoupling in CW mode if homonuclear internal or external lock are used. I have so far only required very low irradiation power as the normal shift range and coupling constants are both small, but I tried operating at higher power, with the ^{2}D head amplifier withdrawn as a precaution, without any obvious ill effects.

Yours sincerely,

Peter J Beynon

DR. P.J. BEYNON,
Product Manager.

ת.ד. 2053, טל. 71241
באר־שבע
P.O.B. 2053, TEL. 71241
BEER-SHEVA
ISRAEL

UNIVERSITY OF THE NEGEV

הפקולטה למדעי הטבע
המחלקה לכימיה
FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

מספרנו /OUR REF.:

אוניברסיטת הנגב   Sept. 18th, 1973.   תאריך /DATE:

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

<u>Proton Spin Lattice Relaxation in EBBA</u>

Dear Professor Shapiro,

We have become interested in the mechanism of spin lattice relaxation in the nematic phase. Two mechanisms have been proposed: relaxation due to fluctuation of the order parameter(1), and fluctation of the dipolar spin interaction caused by molecular diffusion(2). Vilfan, Blinc and Doan(3) have shown that the former mechanism dominates in the case of PAA(p-azoxyanisole) while the latter mechanism operates in the relaxation of MBBA (p-methoxybenzylidene-p-butylaniline). They have also shown that by adding CH_2 groups to PAA T_1 is significantly lowered. They claim that the lengthening of the molecule has introduced an additional relaxation mechanism similar to that of MBBA. We have carried this one step further by adding another CH_2 group to MBBA (to get EBBA) and measured T_1 vs temperature over the range of the solid to the isotropic liquid. The results are shown in the figures.

An activation energy of 5.9±1 kcal/mole is found for EBBA as compared to 6±1 kcal/mole estimated from results on MBBA(4). Thus adding the CH_2 group has very little effect on the relaxation in the nematic phase. A significant increase in the activation energy for EBBA was found in going from the nematic to the isotropic phase, the energy for the latter being 8.8±1 kcal/mole. The result for MBBA is 7kcal/mole(4). The increase in activation energy is consistent with the drop in T_1 upon going from the nematic to the isotropic phase as has been observed for MBBA(4).

Vilfan <u>et al</u> (3) have shown that the relaxation in PAA is due to fluctation of the order parameter and is essentially independent of temperature. Adding end chains to PAA reduces T_1 considerably (5) and it has been implied that the relaxation mechanism is similar to that found for MBBA. However, this is inconsistent with the temperature independence of T_1 found for the PAA homologs. In contrast, we have found that the addition of a CH_2 group to MBBA has had little effect on the relaxation behavior of the nematic phase. Perhaps this is due to the differences in temperature ranges for the nematic phases of the PAA series and the MBBA series. In general the nematic phases for PAA and its homologs occur at higher temperatures than the MBBA homologs and at these temperatures perhaps the diffusion is too fast to effectively relax the nuclei.

Sincerely,

Dr. Stephen Marks

1) C.C. Sung, Chem. Phys. Lett.,10, 35,(1971).
2) J.F. Harmon and B.N. Muller, Phys.Rev., 182,400(1969).
3) M.Vilfan, R. Blinc and J.W. Doan, Solid State Commun., 11, 1073 (1972).
4) C.L. Watkins and C.S. Johnson Jr.,J.Phys.Chem., 75, 2452(1971).
5) C.R. Dybowski, B.A. Smith and C.G. Wade, J.Phys. Chem., 75, 3834,(1971).

A plot of T_1 vs T for the solid, nematic and isotropic phases of EBBA.

The circles indicate heating and the squares cooling.
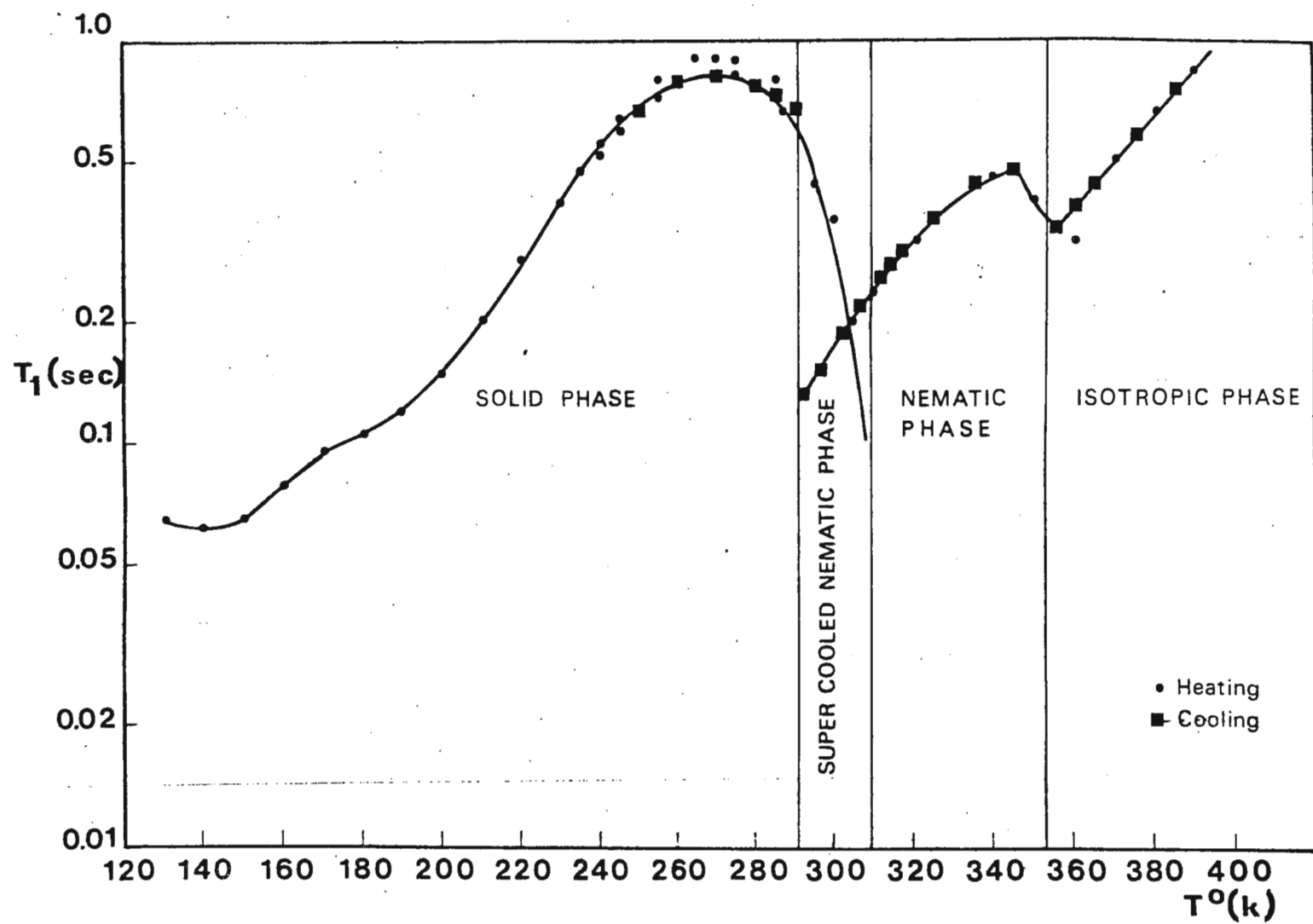
A semilog plot of T_1 vs the reciprocal temperature for the isotropic

and nematic phases of EBBA. The circles indicate heating and the squares cooling.
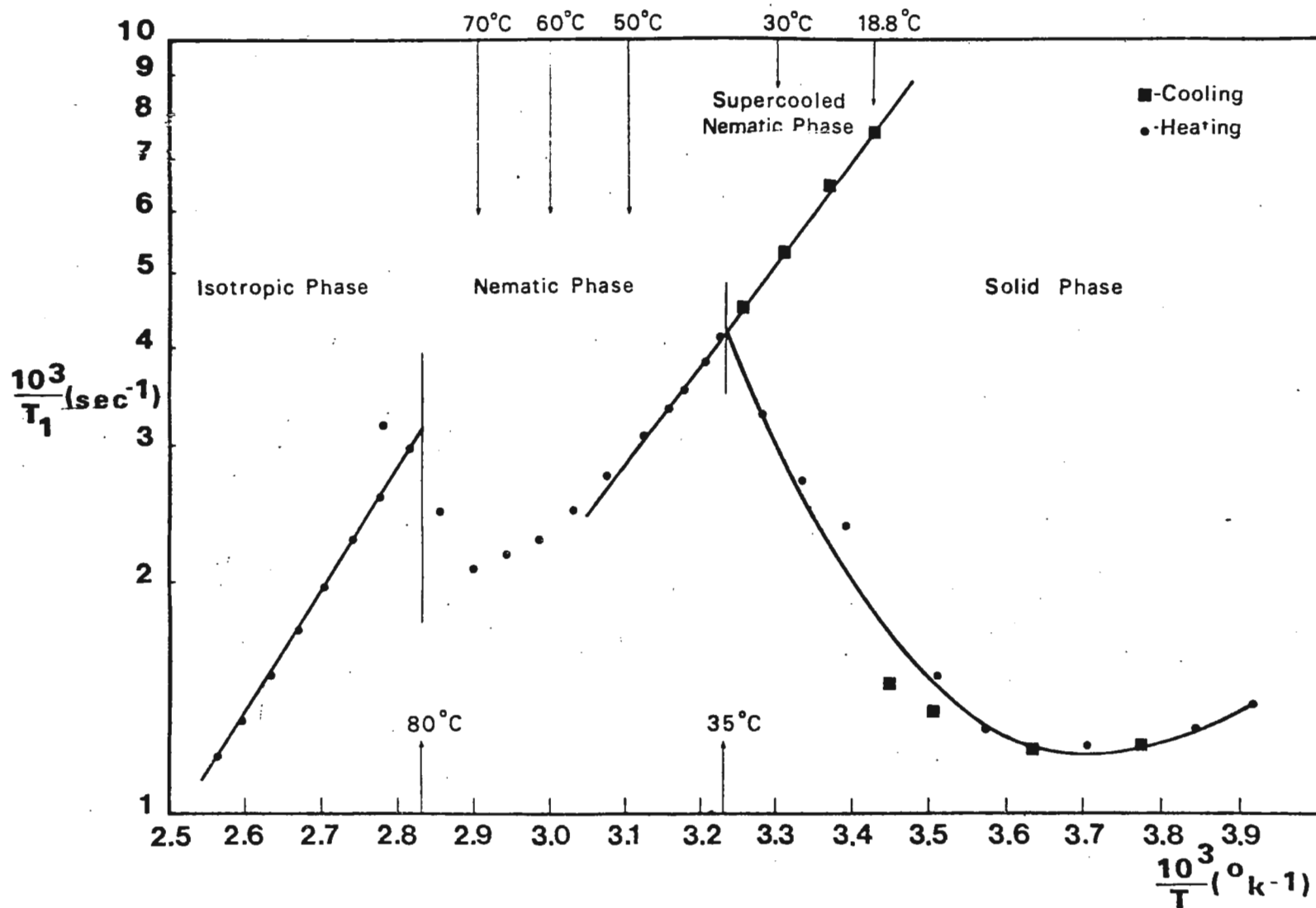
Sept.5, 1973

Dr. Barry Shapiro
Department of Chemistry
Texas A.&.M.
College Station, Texas

Dear Dr. Shapiro:

I am in need of a superstabilizer for a Varian high impedence 12"
magnet, and would appreciate your circulating this information via the
Texas A&M NMR Newsletter.

Sincerely,

Bernard C. Gerstein
229 Research, I.S.U.
Ames, Iowa 50010

THE UNIVERSITY OF NEW BRUNSWICK

FREDERICTON, N.B.

Canada

September 21, 1973

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

Proposed Title: S/N gain in Multichannel Spectrometry

Dear Barry:

For renewal of my subscription to the Newsletter, I would like to offer a few "Gedanken" on the subject of Fourier transform spectrometry. We are all aware of the wonderful signal/noise enhancement that this method has brought to high resolution spectrometry. The usual explanation is in terms of the multichannel procedure, roughly as follows.

The spectrum $S(\omega)$ is digitized into M (some thousand) spectral samples S_m with due attention paid to the sampling theorem. Instead of measuring the amplitude S_m of each element one after the other as with the field or frequency sweep methods, the free induction decay $f(t)$ is measured and digitized into M elements f_ℓ. Each f_ℓ is a linear combination of all spectrum channels S_m (multichannel measurement):

$$f_\ell = \sum_{m=0}^{M-1} w_{\ell m} S_m, \qquad [1]$$

and the weighting coefficients

$$w_{\ell m} = \exp(2\pi i \ell m/M)$$

follow from the Fourier transform relation between spectrum

and free induction decay. The matrix $w_{\ell m}$ has certain desirable properties (e.g. orthogonality) that make it easy to invert Eq. [1], for example with the fast Fourier transform algorithm, to obtain the spectrum. It is remarkable that this procedure, under certain conditions, leads to a signal/noise enhancement by a factor

$$F_m = [\sum_{\ell} |(w^{-1})_{m\ell}|^2]^{-1/2} = \sqrt{M}. \qquad [2]$$

The value $\sqrt{M}$ achieved in this case is the maximum that can be obtained with any matrix w whose coefficients satisfy the requirement $|w_{\ell m}| \leq 1$. Sufficient conditions for Eq. [2] are that the noise which causes measurement inaccuracies, is stationary, has zero mean, is white in the detector bandwidth and independent of the signal, i.e. the same for the measurement of a sample f_ℓ as for an element S_m under identical measurement conditions (bandwidth and time). These conditions are probably well satisfied if the noise arises in the detector as in NMR and IR spectroscopy, but they are not satisfied in the UV or visible range where photon noise (signal dependent) may be dominant.

We thus need to measure the free induction decay. It would seem only logical to apply the multichannel procedure a second time: Digitize f(t) into M samples f_ℓ and, instead of measuring these one after the other, measure some quantity X, whose M samples X_k are linear combinations of the f_ℓ (multichannel measurement):

$$X_k = \sum_{\ell=0}^{M-1} v_{k\ell} f_\ell. \qquad [3]$$

Hopefully, another factor $\sqrt{M}$ will evolve in the signal/noise ratio.

What quantity do we use for X? The spectrum samples S_k would do, since they satisfy Eq. [3] with

$$v_{k\ell} = \frac{1}{M} \exp(-2\pi i k\ell/M)$$

and have all the required characteristics. Measuring the spectrum point by point is a genuine multichannel procedure to measure the free induction decay. The only snag is that

the resulting S/N enhancement factor, calculated from Eq. [2] with v in place of w, comes out to be $1/\sqrt{M}$. This multi-channel method thus gives a S/N reduction, which is not surprising since the overall enhancement in combination with the first method must give F = 1 (i.e. no gain).

However, another quantity is available to be used for X. The discrete convolution of an input signal represented by samples i_k, with the spin system's impulse response function samples f_ℓ can be written in the form [3] with

$$v_{k\ell} = i_{k-\ell},$$

and X is thus the output signal $\sigma(t)$. It satisfies the requirements listed earlier, and the input signal can be chosen to yield a multichannel advantage F up to $\sqrt{M}$. In fact, the maximum value $\sqrt{M}$ is reached when the i_k are derived from a binary pseudorandom noise sequence for which $v_{k\ell}$ becomes a cyclic Hadamard matrix. This is particularly convenient because it permits Eq. [3] to be inverted by means of the fast Hadamard transform algorithm, and the problem of having an odd number of sample points for the fast Fourier transform is then easily solved.

These considerations have been confirmed experimentally and it may be said that, in principle, pseudonoise spectrometry involves a second multichannel process with advantage $\sqrt{M}$. However, because of the limited ability of the spin system to dissipate power, this enhancement does not permit a reduction of the measurement time below that required in pulsed Fourier transform spectrometry. Instead, it permits a reduction of the peak transmitter power and of the receiver dynamic range by a factor M.

Comments will be greatly appreciated.

Sincerely yours,

R. Kaiser.

R. Kaiser, Professor

RK:seb

RAMAN RESEARCH INSTITUTE
BANGALORE 6

LIQUID CRYSTAL LABORATORY

Professor C.L.Khetrapal   September 6, 1973
Dr. A. C. Kunwar

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

Title: Some recent NMR work at the Raman Research Institute

Dear Professor Shapiro,

        At the Raman Research Institute, our group would
continue to work on the NMR of molecules dissolved in thermo-
tropic and lyotropic mesophases.   Currently, we are engaged
in the study of the conformation of 2,2'-bithiophene in a
thermotropic mesophase and some investigations on molecules
dissolved in a lyotropic mesophase.

        The molecule bithiophene seems to exist neither in a
single planar form nor a non-planar one.   The results indicate
that it exists as a mixture of cis and trans planar conformations.

        A lyotropic mesophase formed by a mixture of sodium
sulphate, decanol, dodecyl sulphate and heavy water is used to
study the PMR spectra of pyridazine, pyrimidine and pyrazine.
Since the ordering of the molecules is much lower in this case
compared to that in thermotropics, some of the dipolar couplings
could be guessed fairly accurately already from the first order
analysis of the spectra.   The geometry information and the
order parameters are derived in each case.   Ratios of the
inter proton distances thus determined are compared with those
obtained from the studies in the thermotropic mesophase.

        Like in thermotropics, the S-value along the C_2-axis
of symmetry is found positive and that perpendicular to the
plane is negative in pyridazine and pyrimidine.   The S-value
in the ring plane along an axis perpendicular to the C_2-
axis is negative for pyrimidine and positive for pyridazine.
Unlike in thermotropics, for pyrazine it was possible to
determine the signs of the order parameters in this phase
under the assumption of the signs of the indirect spin spin
couplings.

                                Yours sincerely,

                        C.L. Khetrapal   Ajit Chand Kunwar

                        (C.L.Khetrapal)   (A.C.Kunwar)

September 10, 1973

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

Dear Barry:

Long Range ^{13}C-^{13}C Coupling Constant

Your blue notice reaches us at a bad time. We have spent the past
few months attempting to get our Bruker HX-90 running as a ^{13}C spectro-
meter. Although the instrument has run quite well as a $^{1}H/^{19}F$ spectro-
meter we have encountered several stability problems while trying to
obtain ^{13}C data in the CW mode. Consequently we have obtained very
little experimental data at this time.

However, our Amoco Oil division has recently obtained a sample of
hexadecane enriched to 90% at C-1. A ^{13}C spectrum of this sample was
obtained at Varian's Application Laboratory and is shown in Figure 1.
The sample was run neat and without an added reference. The most
intense line was assigned the chemical shift of 29.4 ppm down field
from TMS and the shifts of the remaining lines were calculated with
respect to this line. The peak assignment was straightforward using
the equation of Grant and Paul. Five of the eight carbons were
individually detected while the remaining three were overlapped. The
^{13}C-^{13}C couplings were found to be $^{1}J_{1,2}=34.6$ Hz, $^{2}J_{1,3}\approx 0$ Hz, $^{3}J_{1,4}=$
4.0 Hz.

Sincerely,

G. J. Ray   E. M. Banas   R. W. Dunlap

GJR:EMB:RWD:slk

---

[1]D. M. Grant and E. G. Paul, J. Am. Chem. Soc., **86**, 2984 (1964).

Figure 1
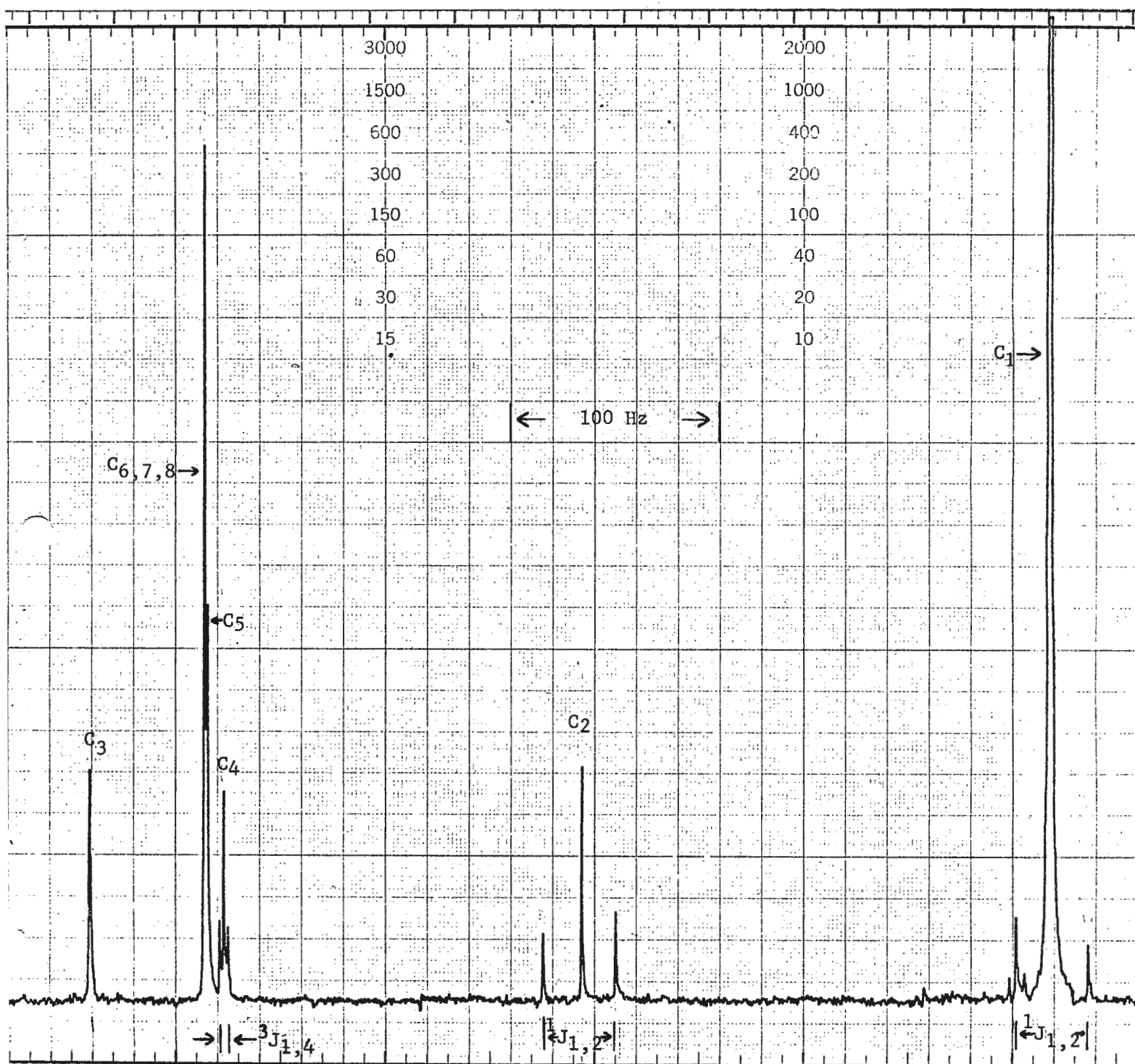
Figure 1

IBM

September 27, 1973

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

Dear Barry:

Wiebren Veeman, who is visiting my laboratory for a year, has started to
look at some spectra of ^{13}C in single-crystal acetic using the Bleich-
Redfield double-resonance technique. A spectrum at –180°C is shown on the
next page, where the methyl and carboxyl carbon resonances are well resolved
into bands $\sim$ 150Hz wide. The crystal structure has 4 molecules/unit cell
and therefore, one expects 8 lines for a general orientation. For the
spectrum shown here, the orientation is such that the 4 molecules are nearly
magnetically equivalent. Spectra at other orientations show two lines in
the carboxyl region. Since we are operating at 5.4 kgauss (5.783 MHz for
^{13}C), we stand little chance of resolving all eight peaks. We hope to
remedy this situation soon.

Sincerely yours,

C. S. Yannoni
bat
Attachment
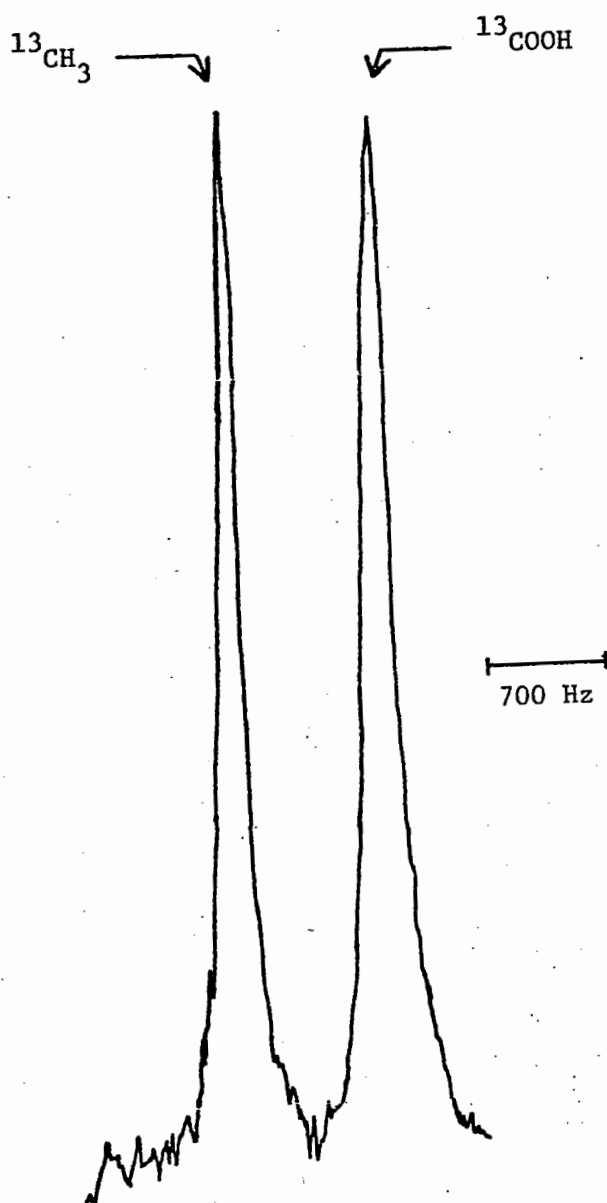
^{13}C Spectrum of CH$_3$COOH Crystal at -180°C (Single 3-minute scan)

THE UNIVERSITY OF BRITISH COLUMBIA

VANCOUVER 8, CANADA

DEPARTMENT OF CHEMISTRY

August 22, 1973.

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

Dear Barry,

Thank you for your kind invitation for me to reinstate
myself in the "club"; my delinquency was caused by my sabbatical
leave which effectively pre-empted much of my time during the
past year. Part of my year was spent at Oxford University where I
was extremely impressed with Rex Richard's group; both the equip-
ment and the incumbents are excellent!

As you may know, Caroline Preston has been using our
Fourier Transform spectrometer to measure the proton T_1-values of
a wide variety of organic molecules $\{$Chem. Comm., 1319 (1972)
and Carbohydrate Res. 27, 286-8 (1973) give some data for pyranose
carbohydrate derivatives$\}$. The variations that we observe appear
to have very useful diagnostic potential at the chemical level
and at the physical level support the anticipated dominance of
intramolecular dipole-dipole relaxation.

Of course the problems of data reduction are considerably
greater than those encountered in carbon-13 studies, due to the fact
that one is trying to deal with spin-coupled multiplets. This
difficulty is further enhanced by the fact that one has an incredible
wealth of data from any one spectrum and, as an organic chemist,
one is generally interested in intercomparing a wide range of
compounds.

Even if we had a fully automated T_1-spectrometer, I suspect
that we would still favour measuring a substantial number of parti-
ally relaxed spectra by hand; problems of "varying" base-line etc.
are significant here. We generally measure at least 20 partially

relaxed spectra and use a computer to give us an estimate of the individual T_1-values. We then recalculate a "final" T_1-value using all the data points obtained during the period 0 sec to $(T_1 + 10-20\%$ $T_1)$ sec. All this amounts to is a "mindless" weighting of the early points. For the most part the difference between the "preliminary" and "final" value is only about 10%, although it can be higher.

Evaluating the "true" T_1-value of a spin coupled multiplet can be very difficult if there is extensive cross relaxation. However we find that for the majority of spectra the T_1-values of the individual transitions are identical, within experimental error.

If any other groups have additional experience in handling proton T_1-data that they would wish to share, either via this news-letter of private correspondence, we would be glad to hear from them.

With all best wishes,

L.D. Hall   C.M. Preston

AUTHOR INDEX