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Deadline Dates: No. 205: 6 October 1975
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All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
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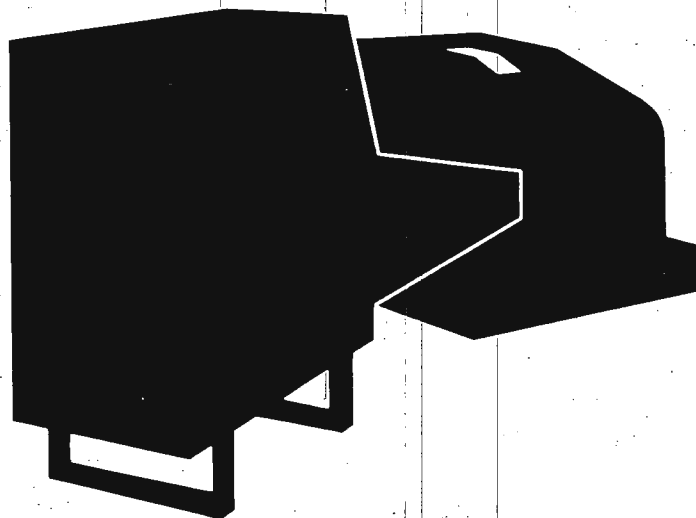
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Newsletter

POLICIES AND PRACTICAL CONSIDERATIONS
(Revised Version of 1 August 1975)

1. _Policy_: The TAMU NMR Newsletter (née MELLONMR, then IIT NMR Newsletter) is envisaged as a means for the rapid exchange of information between active workers in the field of nuclear magnetic resonance. As such, it will serve its purpose best if the participants impart whatever they feel will be of interest to their colleagues, and inquire concerning whatever matters interest them. Since the participant is clearly the best judge of what he considers interesting, our first statement of policy is "We print anything". (This is usually followed by the mental reservation "that won't land us in jail".) Virtually no editorial functions are performed, although I feel the time has come when contributions dealing with the likes of how to clean spectrometer cooling coils, still another discovery of non-equivalent methylene protons, etc., should not be considered adequate. The TAMU NMR Newsletter is not, and will not become, a journal. We merely reproduce and disseminate exactly what is sent in. Foreign participants should not feel obliged to render their contributions in English.

2. _Finances, Subscriptions and Advertising_: The Newsletter is wholly self-supporting, and depends for its funds on advertising, donations, and particularly individual subscriptions, for which we are now forced to charge the substantial rate of $60.00 per year for a single subscription. A 50% academic or personal discount is available. Organizations and individuals are also invited to consider becoming a Contributor or Sponsor of the Newsletter and to have their organization's name appear in the appropriate list in each month's Newsletter, as well as the satisfaction of knowing they are helping keep this non-profit Newsletter in a solvent configuration. We will be happy to provide further details to anyone interested.

A major, indeed essential, source of funding to support the Newsletter is advertising. We earnestly solicit present and potential participants of the Newsletter to seek advertising from their company or institution. Our rates are modest and the need is great. Please inquire for all details.

Participation is the prime requisite for receiving the TAMU NMR Newsletter; _in order to receive the Newsletter, you must make at least occasional contributions to its contents_. We feel that we have to be ruthless in this connection and the following schedule is in effect: Eight months after your last contribution you will receive a "Reminder" letter. If no contribution is then forthcoming ten months after your last contribution, you will receive the "Ultimatium" letter, and then the next issue will be your last. If you are dropped from the mailing list, you can be reinstated by sending a contribution, and you will receive back issues (as available) and forthcoming issues at the rate of nine per contribution. Frequent contributions are encouraged, but no "advance credit" can be obtained for these. In cases of joint authorship, either contributor, but not both, may be credited - please indicate to whose account credit should be given.

PLEASE NOTE: A subject of considerable interest and concern to several present and potential TAMU NMR Newsletter participants - as well as to ourselves - is whether the Newsletter ought to contain material which either appears essentially simultaneously in the formal literature (or is presented at a meeting) or is definitely scheduled to appear very shortly (i.e., within a few weeks) after it would appear in the Newsletter. Our attitude is that a TAMU NMR Newsletter contribution should not duplicate, summarize or abstract material which has been published or which will appear in the formal literature within a small number of weeks of the Newsletter account. On the other hand, let it be firmly emphasized that if the appearance in a journal is several months away - as is frequently the case - a brief account (as an abstract with or without a "Preprint Available" notice, a separate informal account, a selection of material from the manuscript, or what have you) sent in to the TAMU NMR Newsletter fulfills one of the very functions which we feel this Newsletter can provide. We trust that a participant will in each case himself apply the criterion of whether or not his contribution will communicate some subject matter to the Newsletter audience before they could read it elsewhere.

3. _Public Quotation_: Public quotation of Newsletter contents in print or in a talk is expressly forbidden (except as follows), and reference to the TAMU NMR Newsletter by name in the scientific literature is never permissible. We remind you that in order to quote results or use material from the Newsletter, it is necessary, in each individual case, to obtain the prior permission of the author in question and then to refer to the material quoted as a "Private Communication".

If your copy of the Newsletter is shared with other readers, it is your obligation as the actual recipient of the Newsletter to see that these other readers of your copy are acquainted with and abide by the statements of policy and practical considerations.

-2-

4. <u>Practical Considerations</u>: (a) All contributions to the TAMU NMR Newsletter should be sent to the undersigned and will always be included in the next issue if received before the deadline dates, which appear in each issue.

(b) <u>Contributions should on the minimum (NOTE!!!!) number of 8½ x 11" (21 x 27.5 cm) pages</u> <u>printed on one side only. Margins should be between 2 and 3 cm on all sides - *PLEASE* observe these limits</u> <u>if at all possible. Black ink, typing, drawings, etc., essential. We are not equipped to deal with large</u> <u>size pieces of paper - e.g., A-60 charts</u>.

Please conserve space by avoiding double spacing (except where necessary), ultra-wide margins, half-filled pages, etc. In general, please plan and construct your contribution so as to <u>fill</u> the minimum number of pages needed. On the other hand, drawings and spectra lose both eye-appeal and utility when they are too small. Only in very rare and absolutely necessary circumstances will a contribution in excess of three pages - including drawings, figures and references - be accepted. Economic necessity forces this policy.

Since reproductions of various kinds do not themselves reproduce too well, contributors are urged to submit their photographic originals to us (if the size does not exceed 8½ x 11"), and we will be happy to return these if requested. Some law of physics says that photographic reproductions of fuzzy or blurred originals never come out <u>less</u> fuzzy or blurred.

(c) <u>Please provide short titles of all topics of your contributions, as they will ensure</u> <u>accuracy in preparing the title-page index</u>.

(d) Please do not send in manuscripts, theses, books, etc., and ask us to be your consciences in selecting what should and shouldn't go into the Newsletter.

5. <u>Suggestions</u>: They are always welcome.

B. L. Shapiro

B. L. Shapiro
1 August 1975

<u>Address for all contributions and inquiries</u>:

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

(Phone: (713)845-6944)

DEPARTMENT OF ORGANIC CHEMISTRY

THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX

TEL: 051 – 709 - 6022

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

Dear Barry,

Downfield δ Shifts in ^{13}C NMR of Orthosubstituted toluenes.

Downfield 'steric' shifts have attracted some interest recently[1]. The shift of the toluene methyl carbon on ortho alkyl substitution is interesting in this respect and some values are listed below.

δ(Me),ppm from TMS
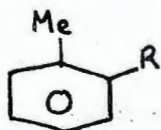
R=H	21.4
R=Me	19.4
R=Et	19.0
R=iPr	19.2
R=^{t}Bu	23.2

1
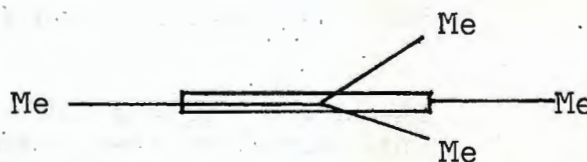
Substitution in toluene of an ortho methyl group produces the well known upfield shift of 2.0 ppm; however, substitution of ortho ethyls or ortho isoporpyl (that is addition of 1 or 2 δ methyl groups) produces an almost identical shift. Thus the δ effects of the added methyls are near zero. In contrast the addition of a third δ methyl, as in the ^{t}butyl compound, produces a large downfield shift of 3.8 ppm, a magnitude not dissimilar to those noted previously[1,2,3] where syn axial interactions were involved. It is unlikely that a pure syn axial interaction is involved here, the shift probably reflects the consequences of two quasi syn axial interactions in a conformation such as 1. On the other hand the data suggest that the dominant conformation in the isopropylic compound lacks any 1,5 Me-Me interactions.

Thus the generality of δ interactions is further established and in this type of system they are a useful indicator of conformation and caution is again drawn to the fact that it is dangerous to associate steric crowding with upfield shifts.

Please credit this to Ray Abraham's account.

With all good wishes

Harry Pearson.

1. J.G. Batchelor, J. Magn. Resonance 18, 212 (1975).
2. S.H. Grover et al, J. Magn. Resonance 10,227 (1973).
3. J.I. Kroschwitz et al, J.Amer.Chem.Soc. 91,5927(1969).

№ 44

1st August 197 5

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

Dear Professor Shapiro,

High Resolution Broad Line ^{13}C NMR in Solids

Thank you for the blue reminder. We have recently become
interested in the proton-enhanced nuclear induction
spectroscopy, developed by J.S.Waugh and A.Pines. This new
tool already combines high sensitivity with high selectivity,
thus having the best of both, in double resonance at least.
It seemed like a good idea to extend these advantages to
single resonance as well, in order to study lineshapes,
relaxation and other aspects of solid-state dynamics. To do
this, the abundant proton spins are spin-locked in the
rotating frame in the usual manner. A single mutual contact
with the rare (^{13}C) spins is established by a strong rf
field, fulfilling the Hartmann-Hahn condition, but the free
induction decays are co-added and Fourier transformed in a
NIC-1085, NIC-293 computer only after a variable delay,
during which the decoupling field is also turned off tempo-
rarily. The free induction decays are registered in the
decoupled mode, thus yielding a series (12 to 20) high
resolution solid state spectra. The (delay) time dependences
of line intensities in these spectra represents the trans-
verse relaxation of groups of nonequivalent ^{13}C nuclei.
Another Fourier transform of data points, corresponding to
these time dependences, gives the shapes of all individual
undecoupled lines that can be resolved in the decoupled
spectrum. The whole "single resonance" spectrum can thus be
reconstituted, but with about 100-fold increased sensitivity
and high selectivity.

A low temperature study of solid norbornadiene, which is a semispherical molecule with fast rotation even at low temperatures, showed that the solid-state ^{13}C lines have different widths with different temperature dependences and shapes that are neither Lorentzian nor Gaussian. The polarization transfer from ^{1}H to ^{13}C nuclei is markedly non-exponential and characterized by different time constants for all groups of nonequivalent carbons in the molecule.

A more full account is going to appear in Chemical Physics Letters.

With best regards,

Sincerely yours,

E.Lippmaa   M.Alla

norbornadiene -75°C
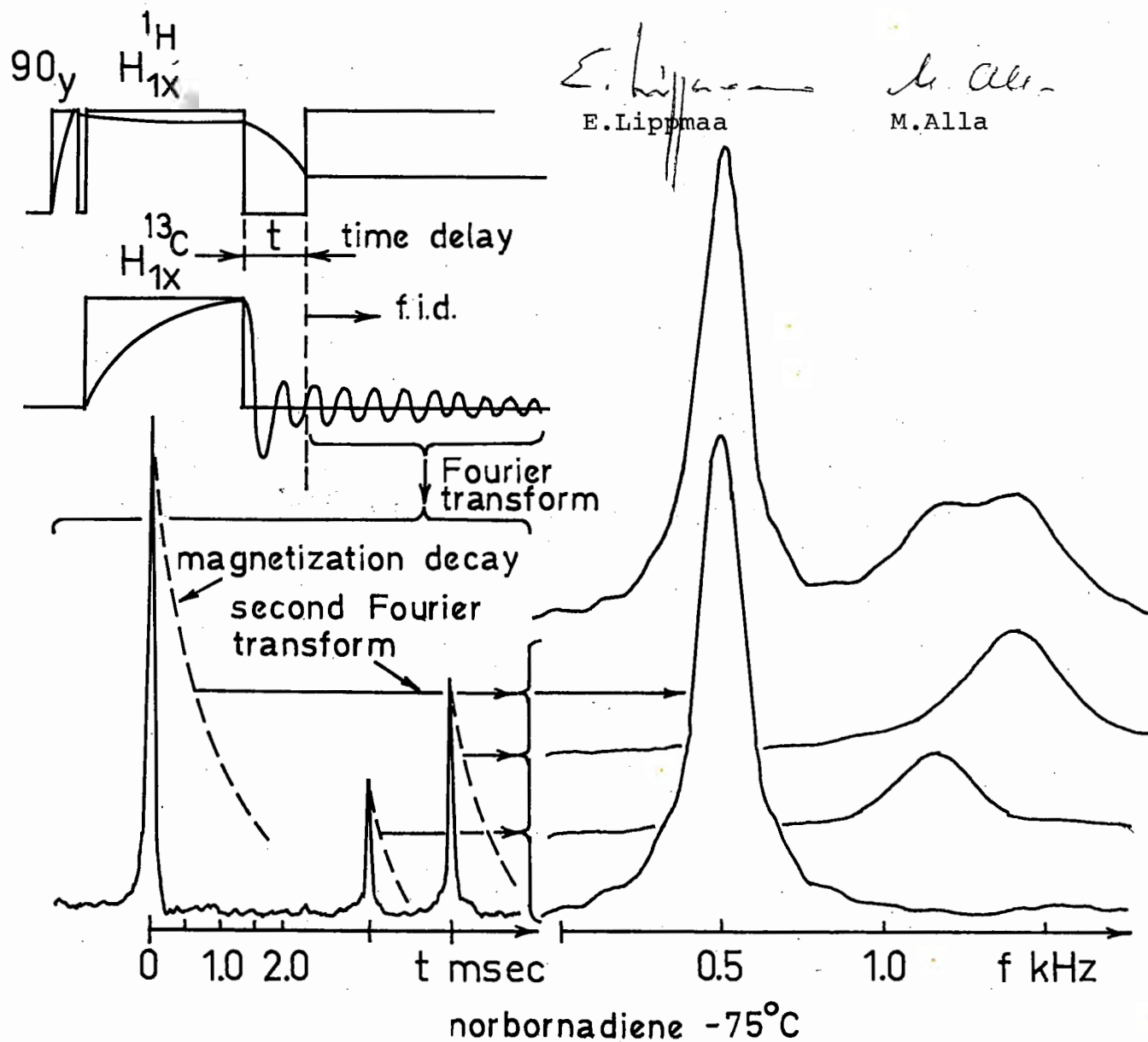
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DEPARTMENT OF CHEMISTRY   BERKELEY, CALIFORNIA   94720

August 4, 1975

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

Dear Professor Shapiro:

RE: NMR Powder Study of Molecular Motion in a Six-Fold Potential

   We have recently joined some other groups in examining the details
of molecular reorientation in solids by observing the effect of the
motion on the powder lineshapes. The theory has been discussed by Luz
et al.[1] (LBA), and by Spiess.[2] The experimental technique is ^{13}C nmr
using proton-enhanced nuclear induction spectroscopy.

   Hexamethyl benzene was one of the first compounds we studied. Motion
in the solid is about the 6-fold axis. In the zero motion limit a typical
asymmetric powder pattern should be seen; in the fast motion extreme the
pattern should be that of a symmetric shielding tensor. The interesting
range is when the molecules are just beginning to reorient. In this case
different patterns will be seen depending upon whether the molecules
rotate diffusively in the plane of the ring or make rapid jumps of 60°
between the equivalent sites. In the latter case, as predicted by LBA,[1]
two anomalous "bumps" should be seen in the powder pattern between σ_{11} and
σ_{22}. These (fondly referred to in one laboratory as "shpitzim") result
from molecules oriented so that two of the three different ring carbons
have approximately the same chemical shift. For these molecules even very
low jump frequencies will satisfy the exchange narrowing condition.

   Some of our results are shown in the accompanying figure. The left
side shows experimental spectra at various temperatures and the right side
theoretical lineshapes at various jump frequencies in Hz. These we calculat-
ed using the standard exchange matrix formalism with powder orientation
averaging by computer, and agreement is seen to be good. The spectra are
also in agreement with those calculated by the elegant expansion techniques
of LBA.[1] The bump at $\sim$ -80 ppm is especially evident in the -130.6° spectrum.
Lineshapes calculated assuming a rotational diffusion model were in total
disagreement with experiment.

   Most of the experimental work was done by David Wemmer, a
graduate student in our laboratory. Our results on the motion in
HMB and other molecules will be published shortly.

Best regards,

Dr. David Ruben

1. Z. Luz, A. Baram and S. Alexander, should be appearing about this time.

2. H. W. Spiess, Chemical Physics 6, 217 (1974).

σ (ppm from benzene)
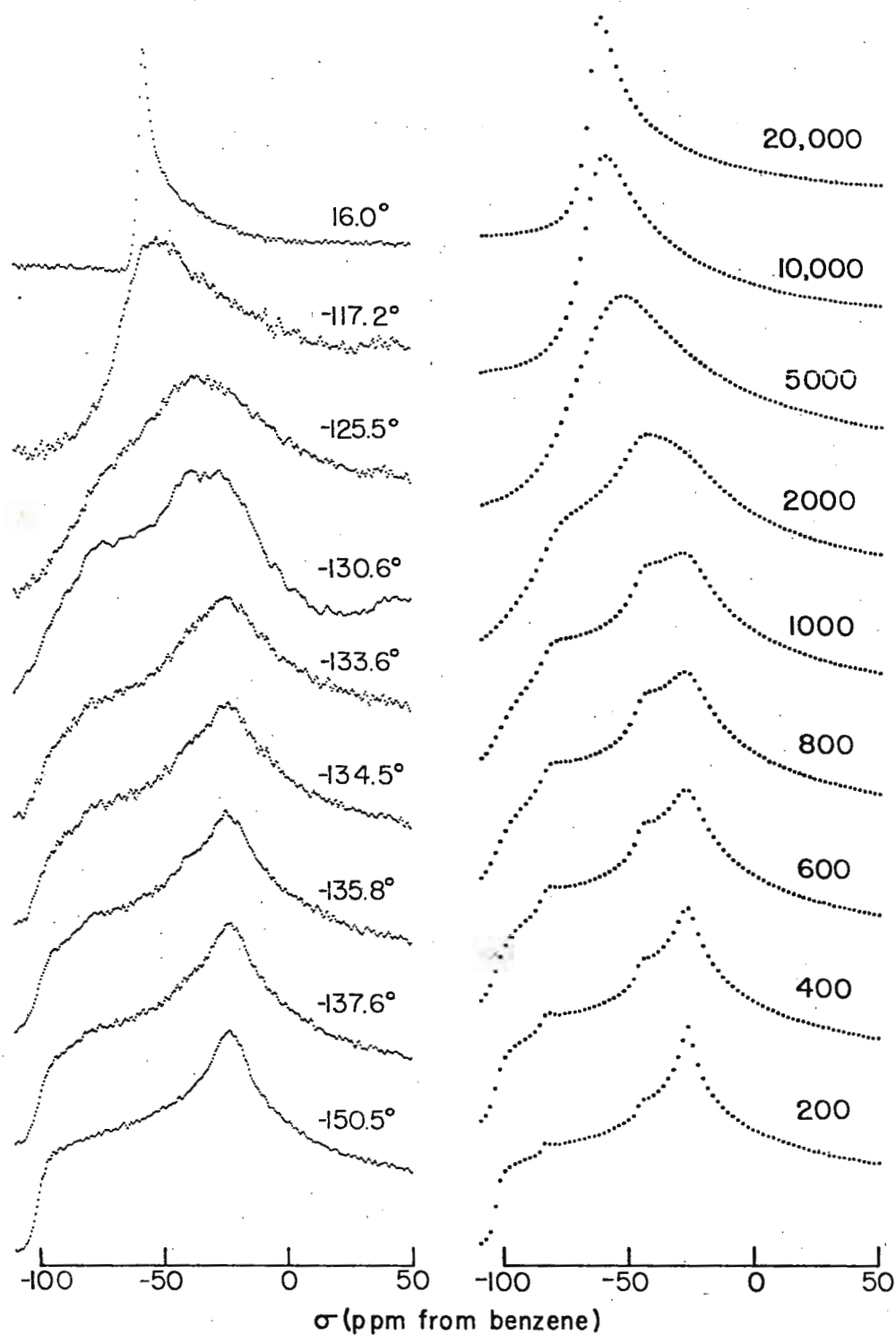
XBL 753-5947A

DR:crh

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TEL. NO. 812—

August 6, 1975

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

Effect of $^{13}C-^{14}N$ Dipolar Interactions

on T_1 Values and Intensities

of Nonprotonated Carbon Resonances

Dear Barry:

We have shown (R. S. Norton and A. Allerhand, JACS,
in press) that $^{13}C-^{14}N$ dipolar interactions can contribute
significantly to the relaxation of a nonprotonated carbon
that is directly bonded to one or more nitrogen atoms. We
have shown that if the T_1 values of the protonated carbons
of a rigid large organic molecule are measured, then one can
make fairly accurate predictions of the T_1 and NOE values of
nonprotonated carbons within the same molecule, without
invoking relaxation mechanisms other than the $^{13}C-^1H$ and
$^{13}C-^{14}N$ dipolar ones (at 14.2 kG). As far as we know, earlier
workers have not considered the possible importance of $^{13}C-^{14}N$
dipolar contributions to ^{13}C relaxation (of nonprotonated
nitrogen-bearing carbons), probably because of the very low
gyromagnetic ratio of ^{14}N. However, the short C-N bond
length partly compensates for the low gyromagnetic ratio.

Spin-lattice relaxation times and integrated intensities
of the resonances in proton-decoupled natural-abundance ^{13}C
Fourier transform nmr spectra of adenosine-5'-monophosphate
and guanosine-5'-monophosphate (in H_2O and D_2O, at 40-44°, at
15.18 MHz, in 20-mm sample tubes) were compared with calculated
values that take into account $^{13}C-^1H$ and $^{13}C-^{14}N$ dipolar
relaxation. In each case, T_1 values of methine carbons of the
base were used to obtain a rotational correlation time, which

was then used, together with interatomic distances from crystallographic data, to compute T_1 values of nonprotonated carbons. Nonprotonated carbons which are directly-bonded to nitrogens and which have no hydrogens two bonds removed yielded theoretical T_1 values strongly affected by $^{13}C-^{14}N$ dipolar interactions. For carbons in this category, calculated T_1 values which include $^{13}C-^{14}N$ dipolar interactions are in much better agreement with experimental values than calculated values which consider only $^{13}C-^{1}H$ interactions. Integrated intensities were calculated by considering variations in the nuclear Overhauser enhancement that result from differences in relative contributions to $1/T_1$ from $^{13}C-^{1}H$ and $^{13}C-^{14}N$ dipolar relaxation. The calculated intensities are in excellent agreement with the experimental ones.

Best regards,

Adam Allerhand
Professor of Chemistry

AA:esm

DEPARTMENT OF CHEMISTRY

OTTO MAASS CHEMISTRY BUILDING (514) 392-4467

McGILL UNIVERSITY

August 6, 1975.

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

Dear Dr. Shapiro:

Assignment of ^{13}C Signals Using a ^{1}H Coupled Spectrum

We would like to demonstrate that two-bond and three-bond

^{13}C-H coupling constants ($^{2}J_{CH}$ and $^{3}J_{CH}$, respectively) can be used to assign

the ^{13}C signals unambiguously. When all the protons are decoupled, myo inositol

has four ^{13}C signals with the intensity ratios 1:2:1:2 from the low field.
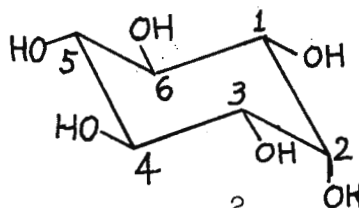
Knowing the following[2], one can simply predict the ^{13}C signal

patterns when protons are coupled:

$^{2}J_{CH}$ $^{3}J_{CH}$

∿5 Hz

∿0 Hz
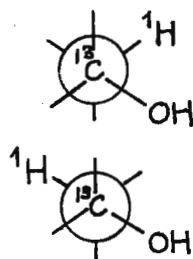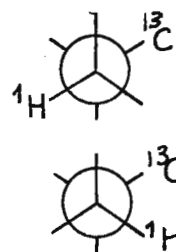
∿5 Hz

∿0 Hz

Dr. Barry Shapiro   August 6, 1975

Carbon	Expected Couplings	Doublet Patterns*
2	$^1J_{CH(2)}$	singlet
5	$^1J_{CH(5)}$, $^2J_{CH(4,6)}$	triplet
1	$^1J_{CH(1)}$, $^2J_{CH(2,6)}$	triplet
4	$^1J_{CH(4)}$, $^2J_{CH(3,5)}$, $^3J_{CH(2)}$	quartet

*Each carbon resonance will exhibit a large doublet due to one
directly bonded proton.
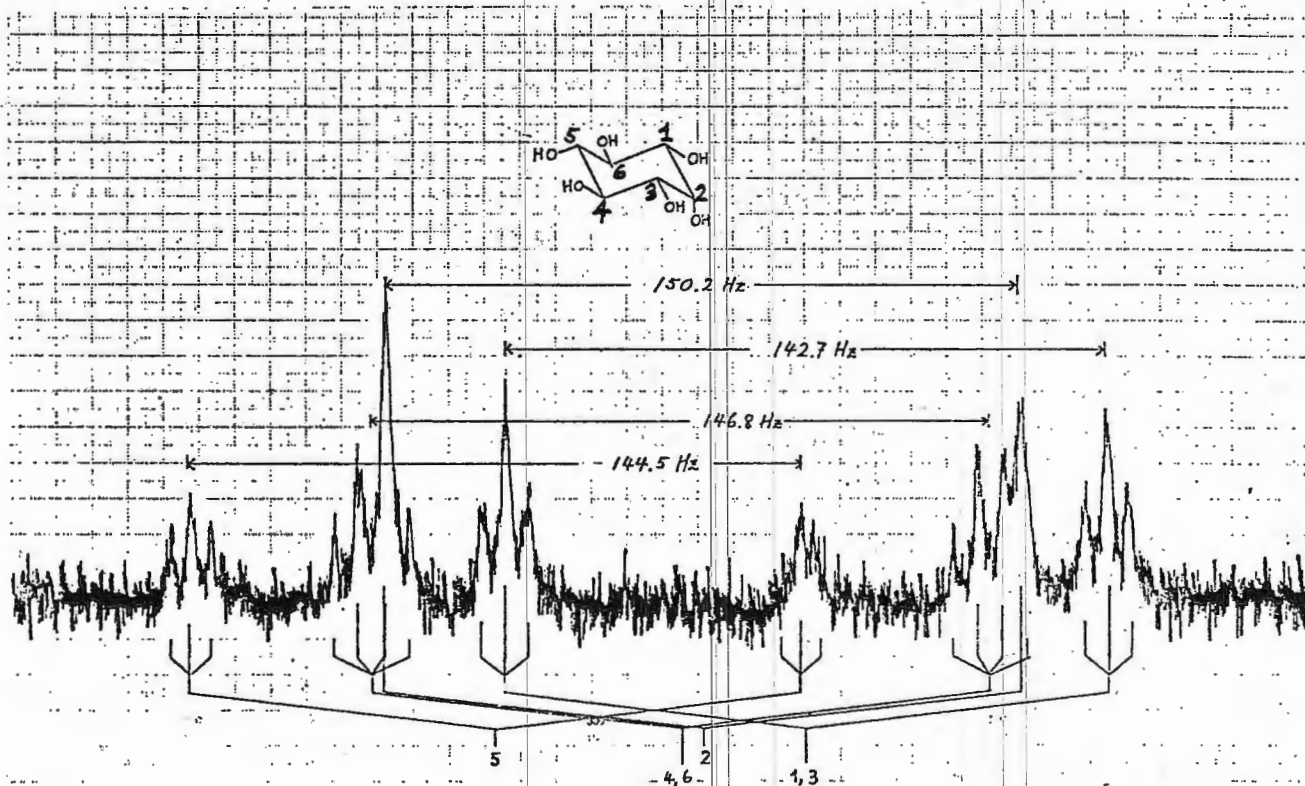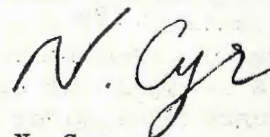
The ^1H coupled ^{13}C spectrum with assignments is shown above. The
chemical shift results agree with the general observation,[2,3] that the carbon
nuclei next to axial OH groups (C1,3) appear at higher field than those next

Dr. Barry Shapiro   August 6, 1975

to equatorial ones, and that cis arrangements of vicinal OH groups also shift the carbon resonances involved to high field. This assignment for C1,3 and C4,6 is the reverse of that given in ref. 1.

1. D.E. Dorman, S.J. Angyl and J.D. Roberts, J. Amer. Chem. Soc., 92, 1351(1970).

2. N. Cyr, R.G.S. Ritchie, N.K. Richtmyer and A.S. Perlin, 58th C.I.C. Meeting, Toronto, May 1975.

3. A.S. Perlin, B. Casu and H.J. Koch, Can. J. Chem., 48, 2596(1970).

Yours sincerely,

N. Cyr

N. Cyr
G. Ritchie
A.S. Perlin

/ce

THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.

DEPARTMENT OF ORGANIC CHEMISTRY.

7th August, 1975.

NVR.RC

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

Dear Professor Shapiro,

Title: A Trinuclear Varian HA60-IL Hybrid
Subtitle: Teaching an Old Dog New Ways to Perform His Tricks
or
Resuscitation for Machines (or Persons) in extremis

We have already described[1] how our aging (born, 1966) Varian HA60-IL spectrometer was converted for ^{13}C n.m.r. measurements in c.w. mode at 15.09 MHz. The appropriate proton-decoupling frequency near 60.0 MHz was generated by mixing a variable frequency near 3.6 MHz with a crystal-controlled frequency near 56.4 MHz, the ^{19}F resonance frequency at the designated field (14092G) for the ^{13}C and ^{1}H resonance frequencies mentioned. This method was chosen because we proposed to instal an external ^{19}F field-frequency lock. The frequency source for the latter must however be coherent with the ^{13}C exciting frequency and, in these days of financial stringency, we must achieve coherency through use of a General Radio Model 1170 Frequency Synthesizer (FS 1170) (obtained in a relatively affluent yesteryear) and such devices as we can construct with the much smaller funds now available to us.

The FS 1170 provides one dial-selectable and several fixed output frequencies all derived coherently from the 5 MHz internal (or, if desired, external) master crystal. We chose, as the simplest course, to multiply the fixed 1 MHz output to 14.000 MHz (actually in two stages, X7 followed by a doubler) which, in order to avoid possible complications of field modulation on ^{13}C spectra measured in PFT mode, is phase modulated (by a stable a.f. in the range, 1-3 kHz; the manual oscillator of the standard "lock box" is adequate), passed through a limiting amplifier (to become in effect frequency modulated), and fed to the (retuned) V4311 r.f. unit in place of the standard 14.111 MHz crystal source for ^{19}F resonance; the V4311 standard i.f. of 5 MHz is generated by using a 51.000 MHz crystal in the local oscillator. With use of the standard lock-box circuits, the field (ca 13980G) now locks strongly to the ^{19}F resonance of C_6F_6 in a non-spinning 5mm sample tube. The appropriate proton-decoupling carrier frequency (near 59.5 MHz) may now be obtained by mixing a variable frequency near 3.5 MHz with the 56.0 MHz. The corresponding ^{13}C exciting frequency (near 14.97 MHz) is obtained by dialing one-half the required value on the front panel of the FS 1170 and feeding the output to our pulse system (where the frequency is doubled) but, because of delays in completing construction, we have not yet recorded any ^{13}C spectra in PFT mode.

Alternatively, by changing a few BNC connections we can apply field modulation in both analytical and lock channels, and use the standard V4333 5mm probe for $^{1}H/^{19}F$ work to record ^{19}F spectra (not proton-decoupled) in homopolar-internally locked c.w. mode at 56.000 MHz; suitably high audiofrequencies to avoid

Professor B.L. Shapiro, Texas A&M University.   7th August, 1975.

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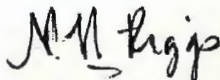
overlap of chosen sideband and other-band spectra, and the convenience of computer control, are provided by the system (apart from the probe) and program used[1] for ^{13}C spectra in c.w. mode.

We now possess an EM-360 for routine, ambient-temperature p.m.r. spectra, but at times shall have to use the (modified) HA60-IL system for higher-resolution and/or variable-temperature p.m.r. spectra. We abhor retuning the V4311 r.f. unit (several retunings have proved deleterious to the tuning slugs) and cannot afford a new, separate 60 MHz unit (if they are still available!). Our approach has been to construct a module containing a 4 MHz crystal-controlled oscillator whose output is fed to two low-noise mixer circuits (6AK5 tubes, as used in the probe preamplifier), one between transmitter and probe, the other between probe and receiver, each with appropriately tuned output stages and levels being matched to those in the original (unmixed) system by tuned low-noise amplifiers. The module is connected or disconnected by changing four BNC connections. The mixer naturally introduces additional noise into p.m.r. signals, but adequate tests of the complete system have been prevented by recent breakdowns in other components. In retrospect, additional noise would probably be more readily tolerable in the ^{19}F lock signal or (infrequently required) ^{19}F spectra, and we intend to retune the system so that the V4311 unit operates at a synthesizer-based frequency of 60.000 MHz and the 4 MHz mix-in frequency for ^{19}F lock must of course be coherent with it.

The system is unquestionably a hybrid and it is at least trinuclear; other nuclei could be added by appropriate trickery, but you will agree that we are approaching, if not already in, extremis.

Dr. D.M. Doddrell was heavily involved in the earlier design stages and Dr. A. Moritz gave valuable advice on phase modulation. Mr. F.B. Hanson and Mr. R.J. Kenny have designed some of the circuits and done all the construction work.

Yours sincerely,

N.V. RIGGS.

---

[1] Doddrell, D.M., Hanson, F.B., Kenny, R.J., Marker, A., and Riggs, N.V., Aust.J.Chem., 1974, 27, 2175-90.

04-17

Department of Trade and Industry
Laboratory of the Government Chemist
Cornwall House Stamford Street London SE1 9NQ

Telephone 01-928 7900 ext 649.

Dr Bernard L Shapiro Dept. of Chemistry Texas A and M University College Station TEXAS 77843 USA	**Your reference** **Our reference** **Date** 11 August 1975

Dear Dr Shapiro

QUANTITATIVE C-13 FT-NMR?

Recently we have been studying the application of FT-NMR to quantitative
analysis. One possible area of application is the analysis of sugar
mixtures. As yet we have only studied aqueous sucrose in detail, and
have been able to obtain results within 3.0% of the true values for
concentrations in the range 0.34 - 1.47 M using 1,2-dihydroxybenzene
as a standard. The results are summarised in Table 1. The peak area
for C-3, C-6, at 117.3 ppm and C-4, C-5 at 122.1 ppm of 1,2-dihydroxybenzene
and C-2' at 104.4 ppm of sucrose were measured (Chemical shifts in ppm
downfield from TMS).

Our procedure has been to make up the solutions in 0.1 M potassium
hexacyanochromate in order both to eliminate NOE's and to reduce the
T_1's of the nuclei being studied to less than 0.3 sec. at 32°C.
The sucrose concentration changes the solutions viscosity markedly
and affects the T_1 values as would be expected from the dependence of
T_1 on the rate of molecular motion. Measurements have been made
using 90 pulses with pulse delay times of 7-10 times the longest T_1's.
Gated decoupling was used to eliminate NOE's not removed by the
presence of the relaxation agent.

By chance, in each solution that we examined, the T_1's for all nuclei
specified above were approximately the same. However we have also worked
with maltose using the same concentrations and procedure, but where the T_1
for maltose C-1 at 101.1 ppm was approximately half the value for the carbon
nuclei of 1,2-dihydroxybenzene.

Initial measurements indicate that the determinations are only within
10-15% of the true concentrations. The integrated peak area ratios for
C-1 (maltose) : C-3 + C-6 (1,2-dihydroxybenzene) were found to vary
with acquisition time and also the exponential filter used for
apodization; the peak areas of the nuclei with long T_1's increase with
increasing acquisition time and smaller apodization functions. It
appears that for quantitative determinations by C-13 FT-NMR, it may
be necessary for the T_1's of the nuclei being studied to be essentially
equal, or for the data acquisition process to be taken into account.
These conditions did not appear to be necessary for quantative P-31
FT-NMR determinations of phosphorylcolamine$(H_2NCH_2CH_2OPO_3H)$ using

$P_2O_7^{4-}$ as an internal standard.

Our experience has been that NOE is not a difficult problem in FT-NMR quantitation (note that we compare protonated and non-protonated carbons), but is lengthy because of the necessary gated decoupling. We note that there is a dearth of quantitative as opposed to semi-quantitative work in the literature and would like to know of other people's experience in this area.

We acknowledge the Government Chemist for authorisation to release these details. Please credit this communication to I K O'Neill.

Yours sincerely

I.K. O'Neill

I K O'NEILL

H. J. Prosser

H J PROSSER

C. P. Richards.

C P RICHARDS

Table 1

Quantitative determination of sucrose by C-13 FT-NMR

Sucrose in solution	Sucrose determined	% error
1.466 M	1.519 M	+ 3.6
1.231 M	1.201 M	− 2.4
0.953 M	0.954 M	+ 0.10
0.706 M	0.713 M	+ 1.0
0.344 M	0.357 M	+ 3.8
0.480 M	0.477 M	− 0.6

StonyBrook

August 12, 1975

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

Dear Barry:

"A Tritium NMR Facility"

We are in the early stages of setting up a tritium NMR facility centered
around a Varian XL-100-12 FT spectrometer and an adjacent hot lab. Our goals
include the study of biochemical mechanisms and biosynthetic pathways and the
investigation of very complex biological systems in which the high sensitivity
and freedom from background signals of ^{3}H NMR spectroscopy may make possible
experiments that cannot be done with other nuclei. The unusual and highly
specialized nature of such a laboratory suggests to us that it should be made
widely available to the scientific community, and that its operation might be
partially funded by a national agency as a special research resource.

Suggestions, comments, and project proposals are hereby solicited. The
pace and scope of our planning will depend upon the amount of use that might
be made of such a laboratory, and upon the kinds of experiments proposed and
the requirements they place upon the spectrometer and upon other laboratory
apparatus and facilities. For those of you who have not previously considered
the properties of tritium resonances, the main features may be summed up rather
simply. The triton behaves like a better proton (except for its instability -
a half-life of 12.5 years). The spin is 1/2 and the magnetic moment slightly
larger than that of the proton, so that our XL-100 sees tritium at nearly 107
MHz. One can therefore expect a slightly better sensitivity for ^{3}H than for
^{1}H signals, with chemical shifts and coupling constants almost the same, and
relaxation times usually not tremendously different. From the activity of
32 Ci/mole, it can be estimated that practical FT measurements on narrow lines
will typically employ a few millicuries to a few tens of millicuries of activity
in the sample. The soft beta radiation will not penetrate the wall of an NMR
tube, making the handling of sealed samples quite safe as long as the tubes
remain intact. Reservations about the practicality of ^{3}H NMR may be at least
partially laid to rest by the recent papers from Surrey listed below, as well
as by some preliminary work done here.

The results of one of our first experiments are shown below. A sample of
50 mCi of "uracil-5-^{3}H" in 200 μl of 10% D_2O/EtOH was examined. The undecoupled
spectrum on the left and the proton noise decoupled spectrum on the right were
found. The only reasonable explanation seems to be the radiation induced hydra-
tion:

Professor B. L. Shapiro   August 12, 1975
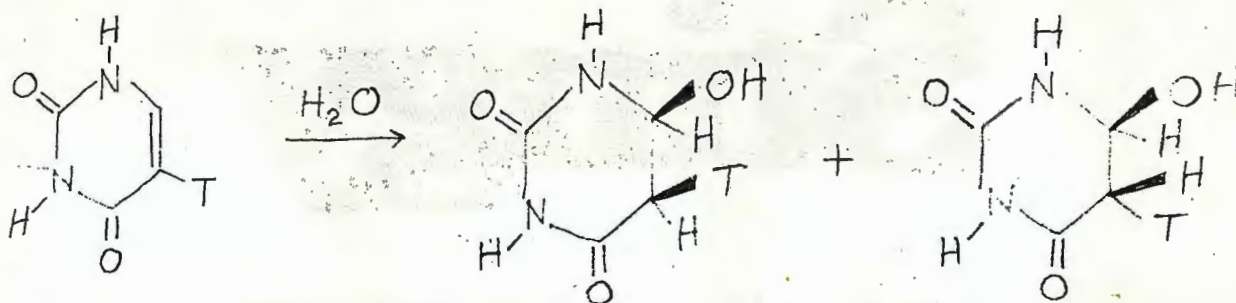
The usefulness of proton decoupling is obvious in this example, which could otherwise have been rather misleading, and should make possible a number of interesting experiments.
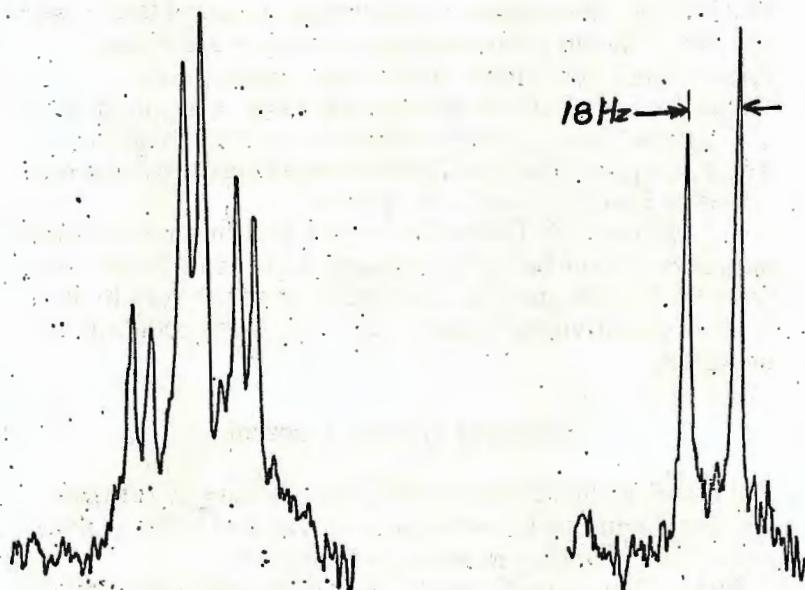
Studies by NMR spectroscopy of stable nuclei in samples containing various other radioactive isotopes might also be safely accommodated, and we would be interested in learning of any needs for such experiments that might exist.

Yours truly,

Paul C. Lauterbur
Professor of Chemistry

Lawrence J. Altman
Assoc. Prof. of Chemistry

1. J. Bloxsidge, J. A. Elvidge, J. R. Jones, and E. A. Evans, Org. Magn. Res. 3, 127 (1971).

2. J. M. A. Al-Rawi, J. A. Elvidge, D. K. Jaiswal, J. R. Jones and R. Thomas, J. C. S. Chem. Comm. 220 (1974).

UNIVERSITY OF SOUTHERN CALIFORNIA

UNIVERSITY PARK

LOS ANGELES, CALIFORNIA 90007

DEPARTMENT OF CHEMISTRY
(213) 746-2780

August 7, 1975

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

Dear Barry:

Title: $^{29}Si-\{^{19}F\}$ NOE and T_1 for Hexafluorodisilane

We have determined what we believe to be the first observed NOE for $^{29}Si-\{^{19}F\}$. A neat sample of Si_2F_6 (b.p. -18°) in a 9 mm medium wall tube was placed inside a standard 12 mm tube containing C_6D_6 and 19.9 MHz spectra were recorded in the F.T. mode on an XL-100 (probe temperature 35°). Spectra were obtained using gated decoupling (NOE mode) of the ^{19}F decoupling frequency. The value we obtained for η is -0.34. We have also determined the T_1 for ^{29}Si in the same sample to be 33 sec using the standard inversion-recovery sequence.

The theoretical maximum for the NOE (assuming 100% dipole-dipole relaxation) is -2.37. These data allow a calculation of the contributions to T_1 as follows:

$$T_1^{DD} = 230 \text{ sec.}$$

$$T_1^{other} = 39 \text{ sec.}$$

We assume that T_1^{other} is dominated by contributions from spin-rotation, which should be quite effective for a molecule possessing the high symmetry and volatility of Si_2F_6. Theoretical reckoning of the value for T_1^{DD} may be rather difficult since the Si-F bond distance in Si_2F_6 is not precisely known and may be significantly different from that in SiF_4.

Sincerely yours,

Kenneth G. Sharp

Kenneth L. Servis

KLS:KGS:cab

Stony Brook

August 12, 1975

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

Dear Barry:

"Zeugmatographic Spectroscopy"

It seems not unlikely that knowledge of the locations within complex objects of various chemical species may at times be of some interest and utility. If their chemical shifts may be distinguished in any NMR experiment in a homogeneous applied magnetic field, their individual distributions within the object may be discovered by combining zeugmatographic spatial discrimination with spectroscopic frequency discrimination. One of the several possible schemes for achieving such a combination may be described with the aid of the diagram below.
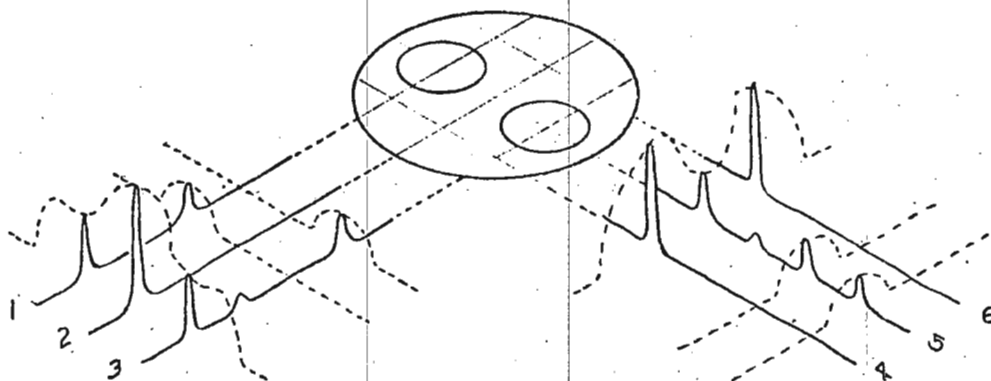
It represents a view along the axis of a set of tubes containing three different compounds in three compartments. In the presence of a field gradient, a long rf pulse may excite only a thin slice of the sample. If the gradient is then switched off, the free induction decay of this selectively excited signal may be observed in a homogeneous field, as in a normal high resolution pulsed NMR experiment. The Fourier transform of the FID is composed only of the peaks of those compounds in the excited region, as sketched, for example, along line 1 in the diagram. Excitation in another plane with the same gradient

Professor B. L. Shapiro   August 12, 1975

direction may give the spectrum shown as <u>2</u>, and so on. Separate projections
of the intensities of each observable line may be constructed, as shown by
the dashed lines. Repetition of the whole procedure for other gradient
directions can give other projections, as shown on the right of the diagram.

Finally, by the image reconstruction techniques used in earlier zeugma-
tographic experiments, the separate distributions of the three compounds may
be found. The actual test sample used by Dave Kramer in these experiments
had sulfuric acid in the outer tube, water in one of the inner tubes, and
$(CH_3)_3C$ —⟨   ⟩— NO_2 in the other. The images are shown below, and clearly
demonstrate that the objective has been achieved.
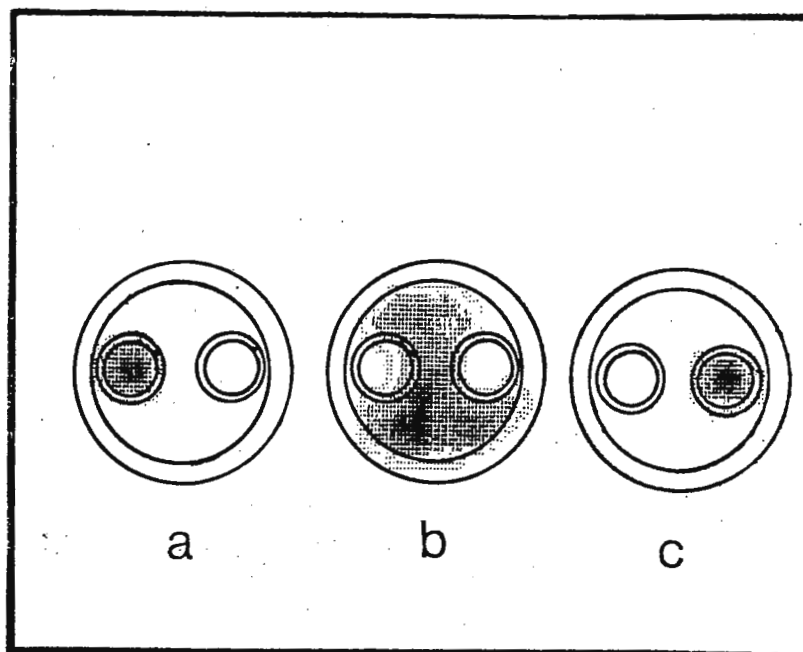
Until we get the whole process under computer control, such an experiment,
which required special modifications and additions to our Seimco pulsed NMR
system by Waylon House, and computer programming and processing by Ching-Nien
Chen, is tedious in the extreme. Nevertheless, it may eventually find use with
various objects of technological or biological significance from which narrow
liquid lines may be obtained, or whose solid resonances may be narrowed by
multiple pulse or double resonance methods.

Yours truly,

Paul C. Lauterbur
Professor of Chemistry

PCL:eg

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

August 12, 1975

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

Dear Dr. Shapiro:

NMR Study of the Mechanism of Isomerization
of a Series of Aldimines

Recently we have developed a method for enhancing the normally low concentrations of less stable syn isomer in aldimines.[1] The ability to produce the less stable isomer under conditions where its lifetime was much longer than kinetic measurements of its decay has allowed us to study the mechanism of the syn to anti isomerization.

Our preliminary results (see Table) of a series of aldimines as a function of substituents and the medium (solvent effects) are interesting and strongly suggest that isomerization about the C=N bond in these compounds occurs by more than one mechanism. For a rotation mechanism initial bond rupture is heterolytic and therefore the transition state should be more stable in a polar solvent, i. e. rate should be faster in methanol than in benzene (or toluene). In the case of a lateral shift mechanism some redistribution of charged density on the carbon and nitrogen is expected, however the magnitudes should be less. As one can see for compound 1 the rate increased by a factor of 160 in going from toluene to methanol, however, the activation energies remains about the same (7-10 kcal) in both solvents. The result suggests that 1 isomerizes predominently via rotation mechanism in both solvents. The largest increase in rate about 10^3 occured for 3, however the activation energies for isomerization in benzene and in methanol differed appreciably indicating a probable change in mechanism (from lateral shift to rotation) in going from a nonpolar to a polar solvent. The rate of isomerization in 4 which has a large activation energy in both solvents actually decreases in going from benzene to methanol, suggesting that 4 proceeds predominently via a lateral shift mechanism. Compound 2 probably isomerizes by both mechanisms in toluene and methanol.

A complete discussion of these results will be reported shortly.

Sincerely yours,
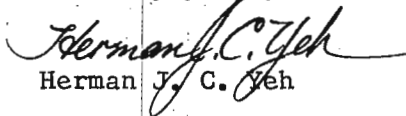
Herman J. C. Yeh

Table. Rates and Activation Energies for the syn → anti Isomerization in Aldimines.
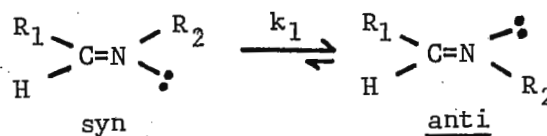
	Compound	Solvent	k_1, sec^{-1} at 30°	Ea kcal/mole
1	R_1 = 1-naphthyl R_2 = methyl	Toluene-d_8 Methanol-d_4	5.5×10^{-5} 9.0×10^{-3}	7.0 10.2
2	R_1 = 1-naphythyl R_2 = tert-butyl	Toluene-d_8 Methanol-d_4	4.0×10^{-3} 2.0×10^{-2}	17.0 12.8
3	R_1 = 9-anthryl R_2 = methyl	Benzene-d_6 Methanol-d_4	6.0×10^{-8} 6.0×10^{-5}	26.2 10.7
4	R_1 = 9-anthryl R_2 = tert-butyl	Benzene-d_6 Methanol-d_4	3.2×10^{-4} 8.0×10^{-5}	29.5 21.3

1. H. J. C. Yeh, H. Ziffer, D. M. Jerina and D. R. Boyd, J Amer. Chem. Soc., 95, 2741 (1973)

CALIFORNIA INSTITUTE OF TECHNOLOGY

August 13, 1975

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

JOHN D. ROBERTS
INSTITUTE PROFESSOR OF CHEMISTRY

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

<u>Natural-Abundance ^{15}N Nmr</u>
<u>with the WH-180</u>

Dear Barry,

Many of your readers heard the account by Devens Gust at the ENC meeting in April of the good works possible with the WH-180 of natural-abundance ^{15}N nmr spectra of rather large molecules. This does not mean there are no problems; in fact, there are several, the most important being the rather difficultly predictable NOE of ^{15}N and the very long relaxation times associated with tertiary amines, as in ordinary tertiary amines.

Six years ago, we had real difficulty observing ^{13}C at 0.15 M concentrations and, because ^{15}N at natural abundance is expected to take about a 6×10^{11} longer observation period for a comparable signal-to-noise ratio, we were not optimistic about getting useful ^{15}N at similar concentrations. We still find it hard to believe that even with the larger tubes (25 mm), higher field (45 kgauss), and quadrature detection of the WH-180, combined with the shorter relaxation times arising from longer correlation times with large molecules, have permitted us to take spectra down to 0.015 M or less with natural-abundance ^{15}N. An excellent example is provided by spectra taken here by Richard Moon and Devens Gust of yeast tRNA as shown below. To be sure, an outlandish quantity of tRNA was required— but information is there, and in reasonable amount. The differences between the helical structure and the "melted" form coming with a temperature differences of about 50° are quite striking. The resonances of tRNA at 80° could be assigned to nitrogens of guanosine, cytidine, adenosine and uridine by comparison with the chemical shifts of the 5'-monophosphates measured here by Volker Markowski.

With all good wishes,

Very truly yours,

Jack

JDR:k

204-28
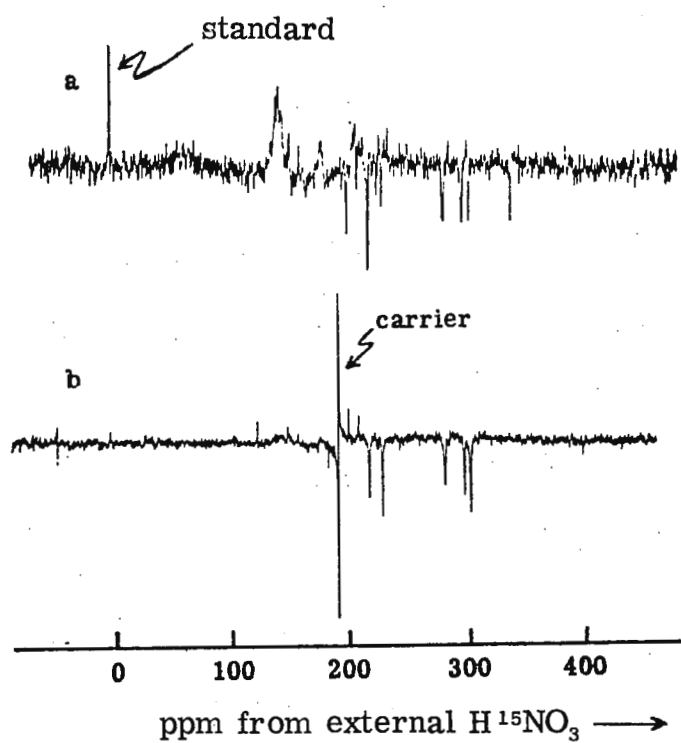
Proton decoupled spectra of yeast tRNA (5 g/15 ml solution, about 11 mM) in 0.15 M sodium chloride solution. Spectrum (a) was obtained on a sample at pH 5.6 at about 30° with a 90° pulse, a 0.409 sec repetition rate, and 301.802 transients. Spectrum (b) was obtained at about 80° on a sample at pH 5.4 using a 0.819 sec repetition rate and 82,810 transients.

UNIVERSITY OF CALIFORNIA, DAVIS

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DEPARTMENT OF CHEMISTRY   DAVIS, CALIFORNIA 95616

August 15, 1975

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

Shift-Reagent-Induced Relaxation

Dear Barry,

We have been interested for some time in the use of lanthanide-induced paramagnetic relaxation in organic substrates as a solution structural probe to complement shift reagent studies. Although relative linewidths have been used to estimate relative values of r^{-6}, there are several reasons why such T_2 data cannot be simply interpreted in terms of substrate structure. In addition to the fact that the relaxation rates in a magnetically anisotropic system depend on the structure in a more complicated manner than just r^{-6}, (Texas A & M Newsletter #183, p. 6) sizable contributions from chemical exchange effects can and do occur.

The relative induced linewidths for a substrate, (S), proton have generally been taken as indicative of the inherent relaxation rates induced by different lanthanide complexes, (SR). Such linewidth, δ, as well as shift, ΔH, data, for o-H of 3,5-lutidine coordinated to some SR's in CCl_4, ($[SR]/[S] = 0.1$), are given in the Table. A better indication of the inherent spin-lattice relaxation rates due to different SR's, however, can be obtained from the protons on the SR-complexes, (i.e. methine proton, β-H, in $Ln(dpm)_3$. These β-H linewidths (as well as shifts), are insensitive to the $[SR]/[S]$ ratio as long as S is in large excess. These β-H shift and linewidths are also listed in the Table.

Some conclusions indicated by the data in the Table are: 1) the β-H shift is primarily dipolar, since $\Delta H(o\text{-}H)/\Delta H(\beta\text{-}H)$ is essentially invariant with Ln; 2) the inherent relaxation rates indicated by the different lanthanides do not differ very much and tend to parallel the relative values of μ_{eff}^2; 3) the o-H linewidths exhibit large exchange broadening contribu-

Professor B. L. Shapiro

August 15, 1975

tions for some Ln since the relative δ(o-H) do not parallel δ(β-H), but correlate better with the magnitude of the induced shifts. Some current T_1 measurements should provide more definitive answers to this problem.

Sincerely,

Gerd N. La Mar
Professor of Chemistry

GNL:gmh

TABLE

Ln(dpm)₃	3,5-Lutidine[a]		dpm		
	ΔH(o-H)[b]	δ(o-H)[e]	ΔH(β-H)[b]	δ(β-H)[c]	ΔH(o-H)/ΔH(β-H)
Tb(dpm)₃	+ 41	180	- 135	102	- 0.30
Dy(dpm)₃	+ 53	270	- 159	112	- 0.33
Ho(dpm)₃	+ 24	160	- 79	92	- 0.30
Er(dpm)₃	- 11	70	+ 37	54	- 0.30
Tm(dpm)₃	- 25	150	+ 83	26	- 0.30

a) [3,5-Lutidine]/[Ln(dpm)₃] = 0.10, in CCl_4 solution at 35°C.

b) Shift, in ppm, from same solution containing La(dpm)₃.

c) Linewidth, in Hz at 100 MHz.

UNIVERSITY OF SOUTH FLORIDA

TAMPA • ST. PETERSBURG

DEPARTMENT OF CHEMISTRY
TAMPA, FLORIDA 33620

813: 974-2571

August 16, 1975

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

Dear Barry:

It is now well established that interactions between lanthanide shift reagents (LSR) and organic Lewis bases can be quite well accounted for by the simultaneous presence of two complexed species: LS and LS_2. The possible implications of the presence of two complexes on structure assessments have, however, been ignored by many workers. In this short letter we show a case in which different bond lengths between the LSR metal atom and the substrate basic substituent atom are obtained when different measures of the lanthanide-induced shift (LIS) are used.

The substrate in this case is 1-adamantanecarbonitrile (1-cyano-adamantane) and the LSR is $Eu(fod)_3$. Similar behavior has been observed by us for $Pr(fod)_3$ and for several other nitriles. The shift parameters investigated are the bound shifts of the LS and LS_2 species (Δ_1 and Δ_2), the initial slopes of the LIS dilution curves (λ), and isolated observed shifts at ρ = 0.5, 1.0, 1.5, and 2.0. These LIS values were fit to the simplest form of the pseudocontact equation:

$$S_i = \frac{k(3\cos^2\Theta_i - 1)}{r_i^3} .$$

Here, S_i simply represents the particular shift parameter under consideration. Since r_i and Θ_i are not independent variables for any particular (or rigid) structure, only two parameters enter into the fits: k and the N-Eu bond distance (R_{LN}).

The results are presented in the accompanying table. It is immediately apparent that the values derived for k and the bond length are very much dependent on the particular LIS parameters used. Of course, many more sets of data must be gathered and correlated before a definitive set of conclusions can be reached. For instance, here we are fitting two parameters to only four different protons in a single substrate. Nevertheless, it now appears that the simultaneous presence of LS and LS_2 necessitates the use of bound shifts.

For the sake of brevity, many numbers are not included in the table. Only the results, not the data from which they were derived, are reported. Anyone wishing a closer look at these latter items

is certainly welcome to write to one of us.

Sincerely yours,

Milt

Milton D. Johnston, Jr.
Assistant Professor

Doug

Douglas J. Raber
Associate Professor

TABLE

STRUCTURE FIT RESULTS FOR 1-ADAMANTANECARBONITRILE*

Parameter	R_{LN} (Å)	$10^{-2}k$	R
Δ_1	1.98	8.28	0.995
Δ_2	1.71	3.58	0.996
λ	1.67	7.34	0.996
$\rho = 0.5$	1.79	3.62	0.999
$\rho = 1.0$	1.96	6.08	0.997
$\rho = 1.5$	1.94	6.85	0.996
$\rho = 2.0$	1.93	7.19	0.996

---

*Data were obtained by methods described elsewhere (B. L. Shapiro and
M. D. Johnston, Jr., J. Amer. Chem. Soc. 94, 8185 (1972); M. D. Johnston, Jr.,
B. L. Shapiro, et al., J. Amer. Chem. Soc. 97, 542 (1975)). The
k values have units of ppm. The "R" in the last column is the correlation
coefficient (subtract it from unity and you get the so-called "agreement
factor."); differences in "R" from result to result are not statistically
significant. Note that all these parameters afford "good" fits to
the structure--at least under the criterion of the correlation
coefficient--but clearly only one value of R_{LN} can be correct. Of
all the criteria one can use for goodness-of-fit, it can be plainly
seen here that the correlation coefficient can be quite insensitive.

CENTRAL RESEARCH

PFIZER INC , EASTERN POINT ROAD, GROTON, CONNECTICUT 06340

203-445-5611

August 8, 1975

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

Title: Random Noise Stirring

Dear Barry:

Having also rediscovered Ernst's noise modulation experiment at inter-
mediate RF power levels, we were very interested in Hall's recent letter
on the subject (202-24). Since the conditions are rather analogous to
those described by Baldeschweiler (for coherent radiation) as "stirring",
and mnemonics are in vogue these days, we refer to the experiment as
"random noise stirring" (RNS). As an alternative, "agitation" might
be an equally appropriate term. We could then distinguish between
spatially coherent, decoupler noise (DNA) and truly random (RNA) processes,
and confuse readers to the same extent we do with off-resonance decoupling
(ORD) experiments.

The experiment has been applied by Schaffer (Macromolecules 5, 590 (1970))
to distinguish methylene from methine and methyl carbons, and it is in
this direction that our own interest lies. This is prompted by the fact
that the experiment is quite sensitive to intersystem crossing between the
singlet and triplet states of the methylene protons, and less to other
complications than alternative ways (ORD) of looking for methylene non-
equivalences. Hence, it is useful in distinguishing methylene carbons
bearing equivalent and nonequivalent protons in the assignment of CMR
spectra. As an example, the proton nonequivalence in acetaldehyde diethyl
acetal can be detected by the broadening of the methylene carbon line.

We haven't been able to distinguish magnetic   equivalence (commutation
of F^2) from symmetric equivalence yet, although this would be fun to do.
One complication is that proton relaxation can give intersystem crossing
and a T_2 effect on the CMR of the singlet, which is not apparent when the
system is completely decoupled.

Another fun experiment is to look at the T_1 and NOE of the singlet and
triplet combinations separately in magnetically eqivalent cases. To
play, one should try to guess the outcome before doing the experiment.

Sincerely yours,

E. B. Whipple

/kce

National Research Council   Conseil national de recherches
Canada   Canada

Division of Biological   Division des sciences
Sciences   biologiques

File   Référence

12 August 1975

A CONVENIENT MEANS TO REMOVE THE INFLUENCE OF RESIDUAL PARAMAGNETIC METAL IONS IN DEUTERIUM OXIDE ON ^{13}C SPIN-LATTICE RELAXATION TIMES

Dear Barry,

     Roberts and coworkers[1] recently reported the effect of traces of metal ions, present as impurity in commercially available D_2O, on the carbon-13 spin-lattice relaxation time (T_1) of the carbonyl carbon of glycine. According to these authors the presence of paramagnetic ions causes a severe shortening of the experimentally determined T_1 values; the effect of these ions can be eliminated by extensive treatment of glassware and sample with EDTA.

     We have tried to achieve similar results in a more simple fashion by adding hydrogen sulfide and/or EDTA directly to the sample. Both of these reagents are known to remove metal ions from solutions very efficiently and direct addition to the sample could prove to be a fast and convenient method for removing metallic impurities from commercially available D_2O. Hydrogen sulfide is a particularly attractive reagent as products are easily removed from the sample. Glycine-1-^{13}C (Merck, Sharpe and Dohme, Canada) was dissolved in commercial D_2O, the major source of which is the U.S. Atomic Energy Commission. Hydrogen sulfide was bubbled through the solution for about 10 minutes and the T_1 values were determined before and after bubbling. Different samples of glycine were prepared with added paramagnetic ions and T_1 values were measured before and after the addition of hydrogen sulfide or EDTA solution. A Varian CFT-20 spectrometer was used to determine T_1 values via a $(180-\tau-90-T)_n$ sequence.

     The data in Table I show that the common impurities in the commercially available D_2O are effectively removed by hydrogen sulfide. After separation from the precipitate, residual H_2S can be removed from the sample by warming under reduced pressure. The T_1 values obtained by this procedure are very close to those reported by Roberts and coworkers[1]. This indicates that the method is rapid, convenient, and effective for removing the paramagnetic ions which might affect the spin-lattice relaxation times in D_2O. No extensive treatment of glassware or sample is necessary.

Ottawa, Canada
K1A 0R6

In order to check whether the observed increase in the spin-lattice relaxation time caused by bubbling hydrogen sulfide is due to the partial removal of dissolved oxygen, nitrogen was bubbled through the sample for about 10 minutes before determining the value of T_1. In a subsequent experiment the nitrogen-saturated sample was subjected to several freeze-pump-thaw cycles and the T_1 values measured. The results in Table I indicate that the increase observed on saturation with H_2S is entirely due to removal of the metal ions from the solution.

To get an idea of the efficacy of the method for particular metal ions, the experiments were repeated with known concentrations of Mn^{2+}, Fe^{3+}, Cr^{3+}, and Cu^{2+}. From Table I it is apparent that cupric ions are completely removed by hydrogen sulfide, ferric ions are removed to a large extent, and manganous and chromic ions are removed only partially by this method. This is in agreement with the solubility products and the solubilities of the corresponding sulfides in slightly acidic solution[2,3]. Cupric sulfide, having a very low solubility product (4×10^{-38}) at room temperature, is completely precipitated. The sulfides of the other ions, being more soluble in acid, are not fully precipitated. In this case addition of 0.001M EDTA is sufficient to remove the influence of the metal ions.

Best regards,

Fariza Hasan, Roxanne Deslauriers and Ian C. P. Smith

1. H. Pearson, G. Gust, I.M. Armitage, H. Huber, J.D. Roberts, R.E. Stark, R.R. Vold and R.L. Vold, Proc. Natl. Acad. Sci. U.S., 72, 1599 (1975).

2. E.B. Kelsey and H.G. Dietrich in "Fundamentals of Semimicro Qualitative Analysis", The MacMillan Co., New York, 1956.

3. "Handbook of Chemistry and Physics", The Chemical Rubber Co., 50th ed., 1969-70.

Effects of paramagnetic ions on ^{13}C-spin-lattice relaxation times for the carboxyl carbon of 0.34 M glycine in D_2O.

Added Ions		pD	T_1(sec)
−		6.9	19.9
	with H_2S	5.4(6.4)[a]	83.5
	with N_2	6.9	17.9
	after degassing	6.9	17.7
Mn^{2+}, 9×10^{-6} M		6.9	7.9
	with H_2S	5.5(6.5)[a]	42.0
	with EDTA	6.8	75.7
Fe^{3+}, 9.6×10^{-5} M		6.8	6.5
	with H_2S	5.5(6.5)[a]	62.7
Cr^{3+}, 1×10^{-4} M		6.9	41.8
	with H_2S	5.5(6.5)[a]	47.6
Fe^{3+}, 9.6×10^{-5} M + Cr^{3+}, 1×10^{-4} M			
	with EDTA	6.7	75.0
Cu^{2+}, 2.5×10^{-5} M		6.9	9.7
	with H_2S	5.4(6.5)[a]	82.5

[a] pH of the sample after removing hydrogen sulfide.

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DEPARTMENT OF CHEMISTRY
SANTA BARBARA, CALIFORNIA   93106

August 18, 1975

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

"Surplus Tubes for Sale"

Dear Barry:

Our venerable HA-100 retired from service gracefully about two
months ago, leaving us with a number of surplus electronic tubes
on hand. We are willing to sell the following at our cost:
Three GE 304 TL ($80 each) and seven RCA 872-A mercury rectifiers
($12 each). All are new but have been on our shelf 1.0-1.5 yrs.
A check of current prices will reveal that the above prices re-
present a substantial saving.

Sincerely yours,

J. Thomas Gerig
Associate Professor

JTG:jh

THE UNIVERSITY OF WINNIPEG

WINNIPEG, CANADA   R3B 2E9

Department of Chemistry

18 August, 1975

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

Dear Barry:

^{1}H-T$_1$'s in condensed ring hydrocarbons

We have been interested in examining the potential of ^{1}H nmr spin-lattice relaxation rates in studying condensed ring hydrocarbons. Our results indicate that proton T$_1$'s may be helpful in confirming the assignment of ^{1}H nmr spectra and in some cases may also allow <u>crude</u> estimates of internuclear proton-proton separations.

For phenanthracene (I) we find $T_1(H_a) \simeq 5.7$ sec and $T_1(H_b) \simeq 11.6$ sec. Since $T_{1,d-d}^{-1}$ depends upon r^{-6} the two
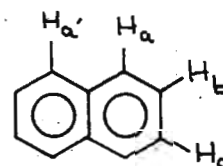

I
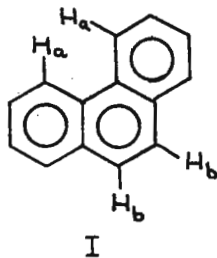
equivalent H$_a$ protons have the shorter T$_1$ because of their relatively small internuclear separation. In this particular example proton-proton NOE experiments would not be helpful in allowing distinction of the H$_a$ resonances from other proton resonances.

Similar results have been obtained for perylene (II) where
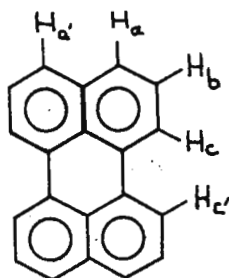
II   III

$T_1(H_a) = 9.2 \pm 1.0$ sec and $T_1(H_c) = 4.2 \pm 0.5$ sec. It is possible
to estimate $r(H_c-H_{c'})$ in II if one makes a number of assumptions,
including: (1) the $H_a-H_{a'}$, H_a-H_b, and H_b-H_c separations in II
are the same as those in napthalene (III): approximately 2.45 Å,
2.50 Å, and 2.45 Å, respectively, (2) intramolecular dipole-
dipole relaxation completely dominates the spin-lattice relax-
ation of H_a and H_c, and (3) T_1^{-1} is given by an expression similar
to that of Gutowsky and Holm [1], $T_1^{-1} = 3/2 \, \gamma_H^4 \hbar^2 \gamma_c \sum r^{-6}$. We
calculate approximately 2.0 Å for $r(H_c-H_{c'})$ which is in fair
agreement with the value estimated from X-ray crystallographic
data [2].

Sincerely,

Rod Wasylishen

Roderick Wasylishen

[1]   H.S. Gutowsky and D.E. Woessner. Phys. Rev. 104, 843 (1956).

[2]   A. Camerman and J. Trotter. Proc. Roy. Soc. (London),
      279A, 129 (1964).

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casella postale 3698 . 20100 Milano

destinatario:

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

nostro riferimento Department of Physical Chemistry data: August, 28, 1975

Subject: ^{13}C Spin lattice relaxation times of the antibiotic rifampin

Dear Prof. Shapiro,

in the framework of our studies on ansamycin antibiotics, we have
run the ^{13}C NMR spectrum of rifampin and performed an almost complete
assignment of its 43 C atoms. To try to understand about molecular
motion, we have recently measured the ^{13}C T_1's by the PRFT technique,
using our new Bruker WP-60 instrument. The preliminary results repor
ted in the Table seem to indicate that the whole molecule has a fairly
slow rotational reorientation.

The CH_3 groups of the ansa chain, which show longer T_1's than the back
bone carbons, my have shorter effective correlation times, as observed
for the angular CH_3 groups of steroids [1].

We intend to obtain new T_1 data in different solvents and on the two
separated mojeties of the molecule, i.e., the naphthoquinone chromophore
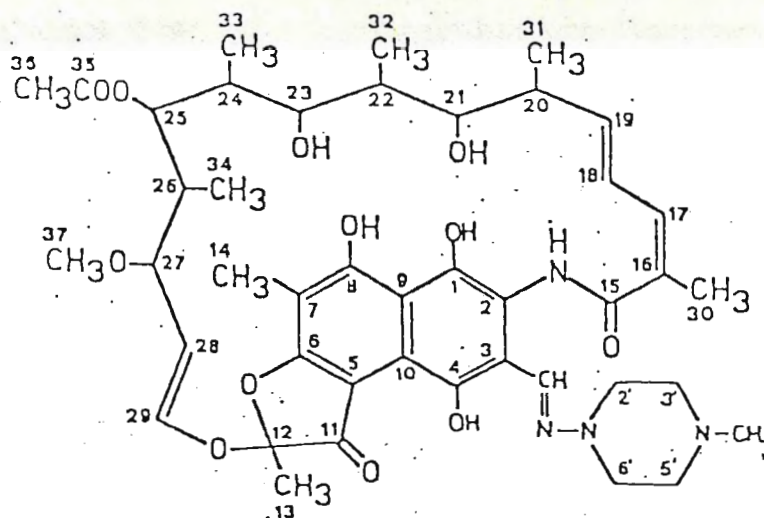and the ansa chain, to substantiate this hypothesis.

Yours sincerely,

(Edoardo Martinelli)   (Ambrogio Ripamonti)

1) A.Allerhand, D.Doddrell and R.Komoroski, J.Chem.Phys., 55, 189 (1971)

RIFAMPIN

TABLE – ^{13}C Chemical shifts (δ, ppm) and T_1's (sec) of rifampin

(conc. ~0.3 M in $CDCl_3$)

C	δ	T_1	C	δ	T_1
1	138.6	3.5	23	76.7	2.1
2	110.8 *	3.5	24	37.6	0.8
3	105.9 *	5.0	25	74.4	0.6
4	147.8	3.3	26	39.5	1.6
5	117.8 *	2.6	27	76.7	2.1
6	174.3	5.5	28	118.7	0.5
7	120.3 *	6.5	29	142.6	1.3
8	169.3	3.2	30	20.7	1.5
9	104.4 *	5.5	31	17.8	1.1
10	112.8 *	6.4	32	10.9	1.2
11	195.3	4.1	33	8.5	0.7
12	108.7	5.2	34	8.8	0.7
13	21.5	1.2	35	171.9	5.3
14	7.6	1.1	36	20.7	1.5
15	169.6	3.2	37	57.0	1.6
16	129.4	3.3	CH=N	134.4	0.4
17	135.0	0.4	2'	50.2	0.6
18	123.2	1.1	3'	53.9	0.6
19	142.6	1.3	5'	53.9	0.6
20	38.6	1.4	6'	50.2	0.6
21	70.7	1.6	$N-CH_3$	45.8	1.1
22	33.4	0.7			

THE UNIVERSITY OF BRITISH COLUMBIA
2075 WESBROOK PLACE
VANCOUVER, B.C., CANADA
V6T 1W5

DEPARTMENT OF CHEMISTRY

August 13th, 1975.

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

Dear Professor Shapiro:

COMPUTATIONALLY OFFSETTING THE FREQUENCY IN NMR SPECTRA AND OTHER NMR SIGNALS

It is interesting (and in very limited cases useful) to note that the phase shift routine in fourier transform magnetic resonance spectrometers can be used to computationally offset the frequency. Suppose, for example, that one has obtained an fid with the bad fortune of having one line on exact resonance. Therefore, one would like to shift the entire spectrum by a small number of Hz. The fid is multiplied by $\cos(\omega_s t)$ using the technique described below and then fourier transformed. The line that was on resonance now appears shifted to higher frequencies by ω_s but all lines that were not at zero frequency now appear as doublets at $\omega + \omega_s$ and $\omega - \omega_s$. This is because the process of multiplying by a cosine modulation is identical to mixing the signal with a carrier at ω_s, in an ideal mixer. Owing to folding about zero frequency, the line at zero frequency does not have two sidebands. In order to make the technique useful, one has to remove all lines at $\omega - \omega_s$. This can be done simply: The original fid is multiplied by $\sin(\omega_s t)$ and fourier transformed. The resulting sine transform is identical to the cosine transform in the original shifted spectrum except that now the lower sidebands appear inverted. The sine transform of the second manipulation is then added to the cosine transform from the first manipulation to yield the original spectrum shifted by ω_s. The line originally at zero frequency becomes twice as large in this procedure. Also, ω_s should be chosen so that there were no lines between the zero frequency line and ω_s.

The above procedure is an exact analog of a commonly used electronic scheme for generating variable frequency single-sideband, suppressed-carrier rf in transmitters. The block diagram of a circuit which performs the above procedure is shown.

The procedure for multiplying by a sine or a cosine employs the first-order phase shift routine. As the phase correct routine was developed to operate on spectra after an fid had been fourier transformed, with the cosine (real) transform in the first block and the sine (imaginary) transform in the second block, this routine mixes appropriately data from both blocks in performing the phase correction.

$$\chi'_{REAL} = \chi_{REAL} \cos\phi + \chi_{IMAGINARY} \sin\phi$$

$$\chi'_{IMAGINARY} = \chi_{REAL} \sin\phi + \chi_{IMAGINARY} \cos\phi$$

August 13, 1975.

For our purposes, the fid occupies the region "χ_{real}", and $\chi_{IMAGINARY}$ is zeroed. After "phase correction", the original fid multiplied by $\cos\phi$ is then in the first block and that multiplied by sine ϕ is in the second block. Most first-order phase correction routines cause the last point (the Nyquist frequency point) to be corrected a number of degrees designated by a constant (PB), and the first point left unchanged. All points inbetween are corrected proportionately. The value for PB was determined by taking the acquisition time for the block of data and determining how many cycles of oscillation in that time duration gives rise to the desired frequency offset. This number of cycles x 360°/cycle gives the appropriate value of PB.

This technique is of limited utility for shifting ordinary spectra; it might find use in those cases where one must gather the data on resonance and then wishes to fourier transform afterwards (e.g. the Jeener echo experiment).

Sincerely,

STEPHEN B.W. ROEDER and
TIMOTHY P. HIGGS.

/ds
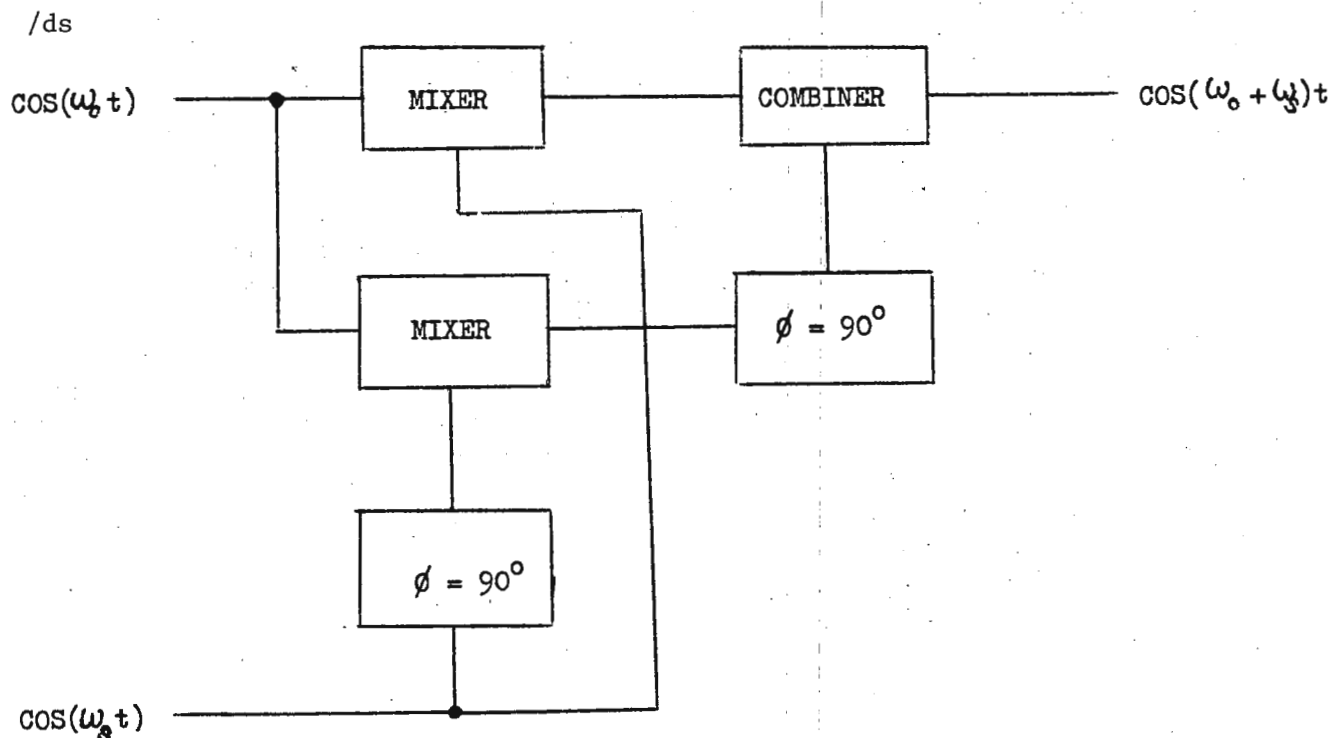
Block diagram of circuit used to generate carrier-suppressed, single-sideband modulation

Top to bottom: (a)Real and imaginary parts of spectrum with one line on exact resonance; (b) Result of modulation of fid by a cosine modulation at frequency w_s and fourier transformation; (c) Result of modulation of fid by a sine modulation and fourier transformation; (d) Real part of original spectrum; (e) Real part of final spectrum resulting from addition of the right hand side of c to the left hand side of b.
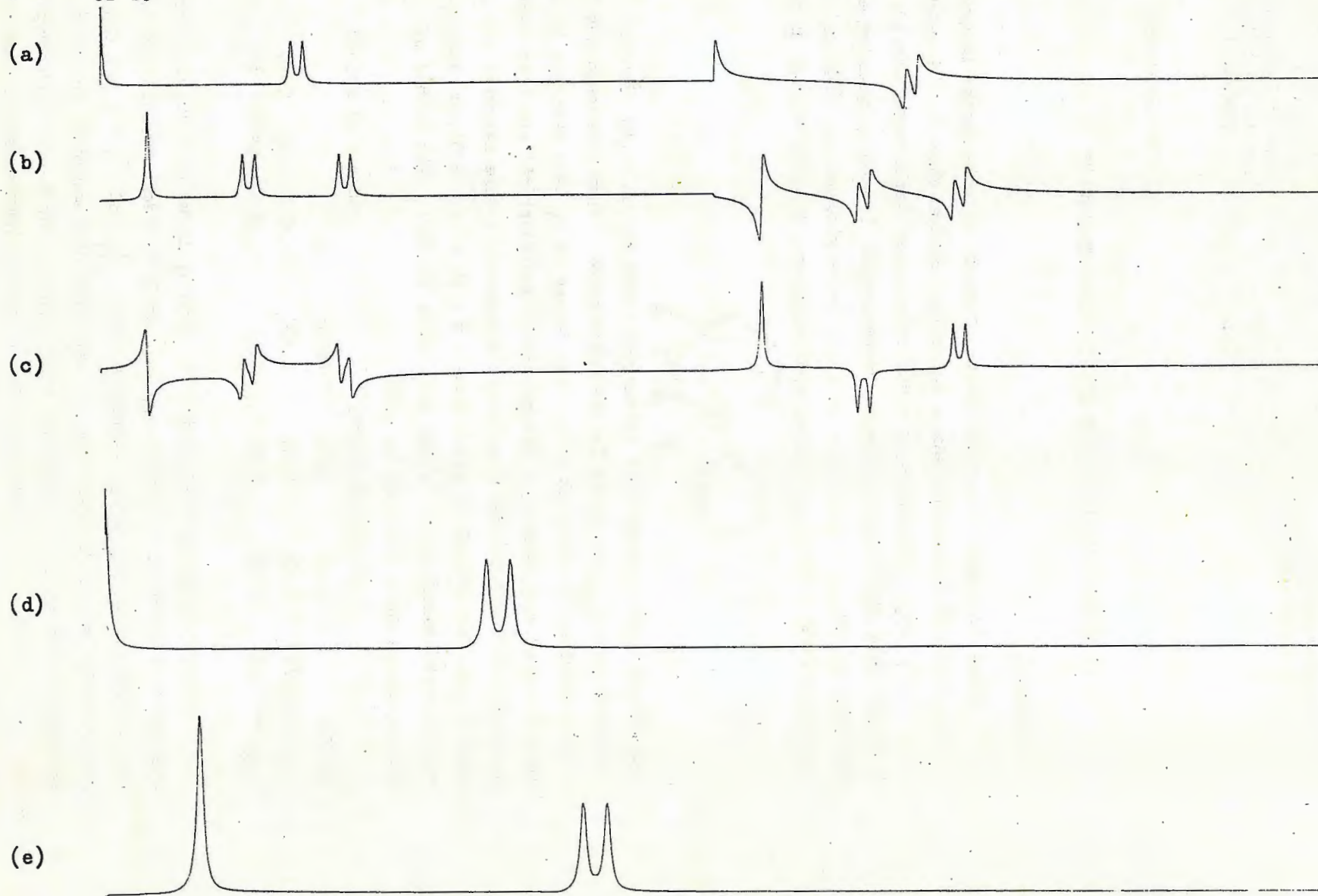
(a)

(b)

(c)

(d)

(e)

1st September, 1975

^{13}C SPIN-LATTICE RELAXATION FOR 1-PHENYLADAMANTANE

Dear Barry,

Along with many other NMR spectroscopists we have become interested
in the detailed information about molecular motion which can be obtained
from ^{13}C T_1 data. We wished to study relatively simple cases involving
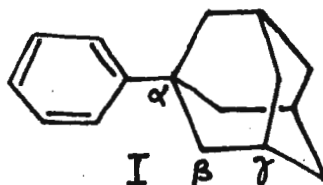a single axis of internal molecular motion which is also a symmetry axis
for each moiety. As an example we chose 1-phenyladamantane (I), which
has six different types of carbon atom which are directly bonded to protons.

The experimental spin-lattice relaxation times due to (C,H) dipolar
interactions, T_{1dd}, are given in the Table below. They were obtained for
a 1.0M solution in $CDCl_3$ at 32°C. The values of T_1 were measured by the
inversion-recovery technique (Freeman-Hill modification) and were reproducible
to within 3%. The nuclear Overhauser enhancements were measured using gated
decoupling; they ranged in value from $\eta = 1.89$ to $\eta = 2.01$, and were mostly
within experimental error of the full value (1.988). The values of T_{1dd}
are estimated to be accurate to $\pm$ 4%.

Carbon	phenyl moiety			adamantyl moiety		
	para	meta	ortho	β	γ	δ
T_{1dd}(expt)/s	2.89	6.28	6.50	4.32	7.35	2.30
T_{1dd}(calc)/s	2.84	6.32	6.44	4.23	7.43	2.38

We have attempted to describe the data in terms of a single correlation
time for end-over-end rotation, $\tau_\perp$, and two independent correlation times
for rotation about the unique molecular axis, $\tau_{//}^p$ and $\tau_{//}^a$ for the phenyl
and adamantyl moieties respectively, using standard geometry information.
We have not attempted to correlate the motion of one moiety with respect to
the other. We have, in effect, used Woessner's equation for anisotropic
rotation ^{1} of a single rigid molecule, and applied it to each moiety of I

independently. The best fit for the six items of experimental information
is given when the correlation time parameters have the following values:

$$\tau_\perp = 15.6 \text{ ps} \qquad \tau_{//}^p = 2.7 \text{ ps} \qquad \tau_{//}^a = 2.3 \text{ ps}$$

As expected $\tau_\perp$ is considerably longer than $\tau_{//}^p$ or $\tau_{//}^a$. Somewhat more surprising
is the fact that the bulkier adamantyl portion appears to rotate somewhat faster
about the internal rotation axis than does the phenyl moiety.

The values of T_{1dd} calculated from the above three parameters are given
in the Table. It can be seen that they agree with the observed values to
within experimental error, thus showing that the three-parameter model is
adequate in practice, at least in this case. In the calculations all non-bonded
protons on the same moiety as the carbon in question have been taken into account.
If only directly-bonded protons had been considered, the ratio $T_{1dd}^\gamma/T_{1dd}^\beta$
(adamantyl portion) would have been 1.98; inclusion of non-bonded protons reduced
this ratio to 1.75, compared to the experimental ratio of 1.70. Of course,
interactions between protons on one moiety and carbons in the other would require
a further motional parameter, but it looks as though the data obtained would
not justify inclusion of this extra complication, and we have reason to believe
that it can be neglected in the present case.

We hope this report is of interest to some TAMUNMR readers, but in any
event we trust it suffices to keep RKH on the TAMUNMR mailing list.

Best wishes,

R. K. Harris   R. H. Newman

[1] D. E. Woessner, J. Chem. Phys. 37, 647 (1962).

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

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

Ihr Zeichen	Ihre Nachricht vom	Unser Zeichen VW/DNL/uh	Tel. Durchwahl: 7008 ·362/·363	Datum September 3rd, 1975

Measuring acurate line positions on CFT-20

Dear Barry,

We have previously reported[1] an improved way to measure line positions
on our XL-100, using an interpolation routine. Recently we needed to perform
high-resolution work on our CFT-20 and found that the current version of the
software FT-16/T$_1$ (Varian part No. 994114-07 Rev. E) gave larger r.m.s. errors,
at small spectral widths, than we had expected from the Hz/channel ratio.

Perusal of the software showed that in the routine CFIT the frequency
correction for point interpolation is being properly calculated, i.e. in channel
units, but not in the form that it is used later in the program, i.e. in Hz.
Also, the correction is added, at the point of application, to the frequency
of the highest-intensity point, instead of being subtracted.

We have cured this problem with a patch to CFIT (see below) that returns
a correction in Hz, which is added at the appropriate point in the program.
At present this patch overwrites part of the Sykes cassette routine.

We have checked out the patch by recording the proton-coupled ^{13}C spectrum
of pyrazine, which shows a small coupling of 2.11 + 0.03 Hz (XL 100) that appears
six times in the spectrum. The reproducibility under various conditions is shown
in the table.

Yours sincerely,

(Dr.D.N. Lincoln)   (Dr. V. Wray)

1. TAMU 189, 31

PATCH TO CENTROID FOR CFT-20 PROGRAM (REV.E.)

(11630)	12177		PATCH		
(12177)	0	PATCH	ENTR		
(12200)	64015		STB	CORR	
(12201)	5001		TZA		
(12202)	21041		LDB	SWP	WIDTH IN Hz
(12203)	30271		LDX	DTOX	REAL DATA PTS
(12204)	2000		CALL	GDIV	Hz/CHAN
(12205)	1735				
(12206)	5014		TAX		
(12207)	5001		TZA		
(12210)	164005		MUL	CORR	
(12211)	5042		TXB		
(12212)	164003		MUL	CORR	CORR * Hz/CHAN
(12213)	1000		RETU*	PATCH	
(12214)	112177				
(12215)	0	CORR	DATA	0	

PATCH FOR TWO DECIMAL-PLACE FREQUENCY PRINTOUT

(11713)	140300
(11770)	150402

Table

Coupling	rms error	Hz/channel
* 1.83	0.51	0.073
2.13	0.03	0.073
2.17	0.17	0.292

* without correction

DEPARTMENT OF CHEMISTRY

THE UNIVERSITY OF GEORGIA   ATHENS, GEORGIA 30602

August 21, 1975

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

N-Nitroso-N-methylaniline, An Error

Dear Barry:

We have spent some time trying to reproduce the ^{13}C NMR spectrum of N-nitroso-N-methylaniline as reported previously! It had been reported that the ortho and meta carbons were nonequivalent as a result of slow rotation about the carbon-nitrogen bond. In each of our spectra, the ortho and meta carbons remained equivalent. Finally, I contacted Professor Randall concerning this problem. In his reply, he stated that the reported nonequivalence was spurious and due to an error in data handling and suggested that I use TAUMU NMR to alert others to this error. It is my understanding that Professor Stothers has also tried to reproduce the non-equivalence.

The chemical shifts one obtained for neat N-nitroso-N-methylaniline (5000 Hz, d_6-acetone lock) with respect to TMS are: CH_3 -30.82, C_{ortho} -118.57, C_{para} -126.58, C_{meta} -128.91, and C_{sub} -141.77 ppm.

Sincerely yours,

Dick

Richard H. Cox
Associate Professor

1. P. S. Pregosin and E. W. Randall, Chem. Commun., 399 (1971).

RHC:mjd

UNIVERSITY of PENNSYLVANIA

PHILADELPHIA 19174

The School of Medicine

JOHNSON RESEARCH FOUNDATION G4
DEPARTMENT OF
BIOPHYSICS AND PHYSICAL BIOCHEMISTRY

3 September 1975

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

Dear Dr. Shapiro:

Rotameric Preference of β-Alanine

In relation to recent studies on the time-averaged conformation of biological molecules, we have had occasion to study β-alanine. The 60 MHz spectrum in D_2O gave rise to the 14 line AA'BB' pattern shown in Figure 1. The upfield multiplet was assigned to the methylene protons adjacent to the carboxyl group by virtue of the $\overset{+}{N}$-C-C-H coupling. The 220 MHz spectrum consisted of two triplets with an average peak separation of 6.65 Hz.

The chemical shifts and coupling constants for the 60 MHz spectrum were obtained by computer assisted analysis using LAOCN III as previously described.[1] This procedure provided vicinal coupling constants of 6.29 and 7.26 Hz, with geminal coupling constants of -12.19 and -14.39 Hz and an rms error of 0.08. These values were used to calculate the 220 MHz spectrum, and a good fit was obtained.

The vicinal coupling constants were used to establish the rotameric preference using the relationship between the electronegativities of substituents and the average coupling constant:[2]

$$17.97 - 0.8 \sum_{i=1}^{6} E_i = 1/3 \ (3/2 \ N + 1/2 \ L)$$

The value of ΣE_i calculated with L negative, 14.37, agrees more closely with that obtained using Huggins electronegativities, 14.45, than does that calculated with L positive, 13.57. Based upon the usual arguments, the trans rotamer is thus favored. Using model coupling constants J_t and J_g we calculate the trans:gauche:gauche rotamer ratio to be $\sim$ 2:1:1.

The pattern of triplets at 220 MHz arises because $\frac{L^2}{2|M|} < \Delta\nu_{1/2}$, where L and M are the difference between the vicinal and geminal coupling constants and $\Delta\nu_{1/2}$ is the observed width of a single line, and does not indicate that $J = J'$ with rotamer populations identical. This represents but another example of an old caveat.
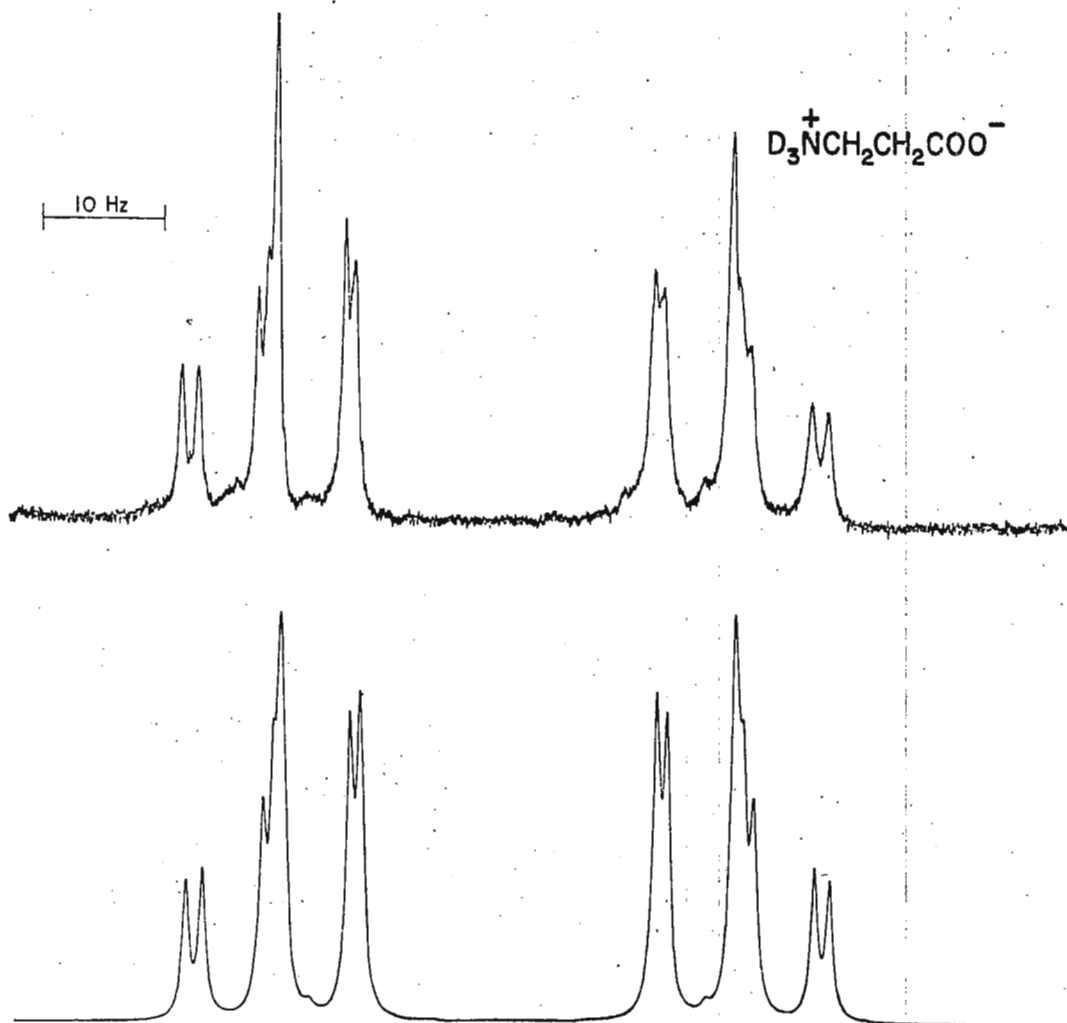
A more detailed report of this work will appear in a forthcoming publication.

1. G.E. WIlson, Jr. and T. J. Bazzone, J. Amer. Chem. Soc., 96, 1465 (1974).
2. R. J. Abraham and K. G. R. Pachler, Mol. Phys., 7, 165 (1963).

Sincerely,

G. Edwin Wilson, Jr.
Visiting Associate Professor

$D_3\overset{+}{N}CH_2CH_2COO^-$

10 Hz

Varian's Special Offer: Over 30 Additional Nuclei

If you own an XL-100 NMR Spectrometer, Varian now offers you an opportunity to add a list of more than 30 nuclei to your experimental repertoire. The new GyroCode™ Observe Accessory makes it possible to observe ^{15}N, ^{17}O, ^{2}H, ^{29}Si, ^{13}C, and ^{11}B and many other nuclei in the XL-100's frequency range of 9.65 to 32.5 MHz — most of them at little or no extra cost per nucleus.

The GyroCode Observe Accessory expands the capabilities of the XL-100 significantly. And it is the first time this

degree of experimental freedom is offered for an NMR Spectrometer that combines state-of-the-art performance and ease of operation. At present, we cannot begin to assess the impact the new-found experimental scope might have on the direction of future investigations. But we expect that a lot of new ground will be broken.

The inorganic chemist, for example, will be able to work with unexplored nuclei whose usefulness as NMR probes or ability to solve real chemical problems is still a matter of speculation. The list of nuclei he will be working with will include ^{23}Na, ^{27}Al, ^{59}Co, ^{77}Se, ^{113}Cd, ^{199}Hg, and ^{195}Pt. And he will enjoy this opportunity without having to commit large sums of research monies.

Let us send you our brochure on the GyroCode Observe Accessory. If, on the other hand, you do not own an XL-100 — this may be the time to reconsider. Write Varian Instrument Division, Box D-070, 611 Hansen Way, Palo Alto, California 94303.

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

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

varian instrument division