CT

Texas A & M University N-M-R Newsletter

No. 202

July, 1975

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Deadline Dates: No. 203: 4 August 1975
No. 204: 1 September 1975

All Newsletter Correspondence, Etc. Should Be Addressed To:

Dr. Bernard L. Shapiro
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TEXAS A&M UNIVERSITY
COLLEGE OF SCIENCE
COLLEGE STATION, TEXAS 77843

7 July 1975

Department of
CHEMISTRY

TAMU NMR Newsletter Business

1. Subscription Renewals

Once again it is time for subscription renewals, and invoices together with a covering letter will be sent out later this week. All Newsletter recipients should have received a renewal notice and invoice by the time they read this notice. If anyone has not received his notice, please contact me without delay.

As indicated in the covering letter with the invoices, financial necessity required us to raise the subscription rates a modest amount - for the first time in several years. The economic facts of life also force us to send the October and subsequent issues of the Newsletter only to those from whom payment has been received or from whom firm notice has been received that payment is coming. It will save all of us much work if everyone processes his invoice for payment without delay. Remember - no October Newsletter will be mailed (approximately Oct. 25) unless we have your money in hand or know it is coming.

2. Newsletter Finances

The Newsletter, being a non-profit, "break even" enterprise, is even more than usually susceptible to inflationary pressures. Somehow we have managed to survive from year to year, but we can never seem to get even a little bit ahead of a condition best described as that of a null balance. Accordingly, I once again invite and request your earnest consideration of the possibility of your company or institution becoming a Sponsor or Contributor (please consult your copy of the "Statement of Policies and Practical Considerations" - next month's issue will contain a copy of the new version of this statement). Even better would be for your company to become an Advertiser. A monthly ad in the Newsletter costs an amount which is truly trivial to a company of any size, and the cost would in fact be measured in ppm compared to the advertising budget of any substantial business corporation. Please think about the Newsletter financial problems, and do what you can.

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B. L. Shapiro

THE EPPLEY INSTITUTE
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May 5, 1975

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

Dear Dr. Shapiro:

Subject: Modified Tuning Procedure for Varian HA-100

While the Varian HA-100 spectrometer system manual recommends adjusting the homogeneity of the system in the HR mode, many individuals prefer adjusting the system in the HA (field/frequency lock) mode. The latter procedure is faster and avoids the use of the V-4352A linear sweep unit, a source of trouble in older systems. The homogeneity controls are adjusted while observing the amplitude of the lock signal on the oscilloscope or by using the shim control on the V-4354 and the recorder pen. Unfortunately both of these techniques have disadvantages. The oscilloscope is relatively insensitive and the shim/recorder combination produces slow pen response.

A 50 microammeter and a 100Kohm SPST potentiometer were wired in series between pin p of the AC amplifier and phase detector card in the V-4354 through switch S1101 (V-4391) to ground. Switch S1101 is wired into the circuit such that the circuit is only completed when the instrument is in the "mon lock" mode. The meter therefore can effectively monitor the lock signal with greater sensitivity than is possible using the scope and with a much faster response to the homogeneity controls than is possible using the shim/recorder combination.

Our procedure involves (1) adjusting the lock signal to 1.5 volts; (2) maximizing the Y and curvature using the lock meter; (3) stop spinning; (4) re-adjusting the lock signal to 1.5 volts; (5) maximizing the X and Z using the lock meter; (6) resume spinning; (7) re-adjusting the lock signal for 1.5 volts; (8) maximizing the Y and curvature. We find this procedure produces the optimum resolution on our instrument.

The lock meter circuit was suggested by N.S. Morales, Iowa State University, private communication.

Sincerely,

D.L. Nagel, Ph.D.

DLN:an

University of Nebraska Medical Center, 42nd and Dewey Avenue, Omaha, Nebraska 68105

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June 4, 1975

Prof. Dr. P. Diehl
Dr. A.S. Tracey

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

Zeise's salt ordered in a nematic soap solution, a problem of insensitive dipolar coupling.

Dear Barry,

We have been interested in determining the structure of Zeise's salt in aqueous solution. However we found rather unexpected difficulties. The proton spectra are insensitive to the platinum-hydrogen dipole coupling and although we observe a $|2D+J|_{PtH}$ splitting, this sum is near zero and the transitions overlap with those from the ethylene complex with zero spin of platinum. Only very inaccurate values were obtained. In an attempt to solve this problem spectra were run from other solutions. Although we could vary the magnitude of the interproton-axes orientation by about 35% still $|2D+J|_{PtH}$ was practically invariant. The figure shows the reason why. It gives a plot of D_{PtH} vs r_{PtH} using the order obtained from one particular spectrum. The true r_{PtH} corresponds to a D_{PtH} near the top of this curve. With changing S-values we are shifting the curve but not affecting D much. It is interesting to note that from this curve a change in r_{PtH} from 1.95 Å to 2.50 Å affects D by less than 3 Hz.

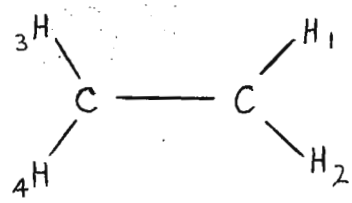
We have obtained the structure of the ethylene moity quite accurately. It is given below with other molecules for comparison.

Yours sincerely

Peter A Tracey.

P.Diehl A.S.Tracey

COMPOUND	r_{13}/r_{12}*	r_{14}/r_{12}*	Ref.
ethylene	1.316	1.653	1
zeise's salt	1.340	1.672	-
ethylene sulphide	1.346	1.677	2
ethylene oxide	1.353	1.682	2



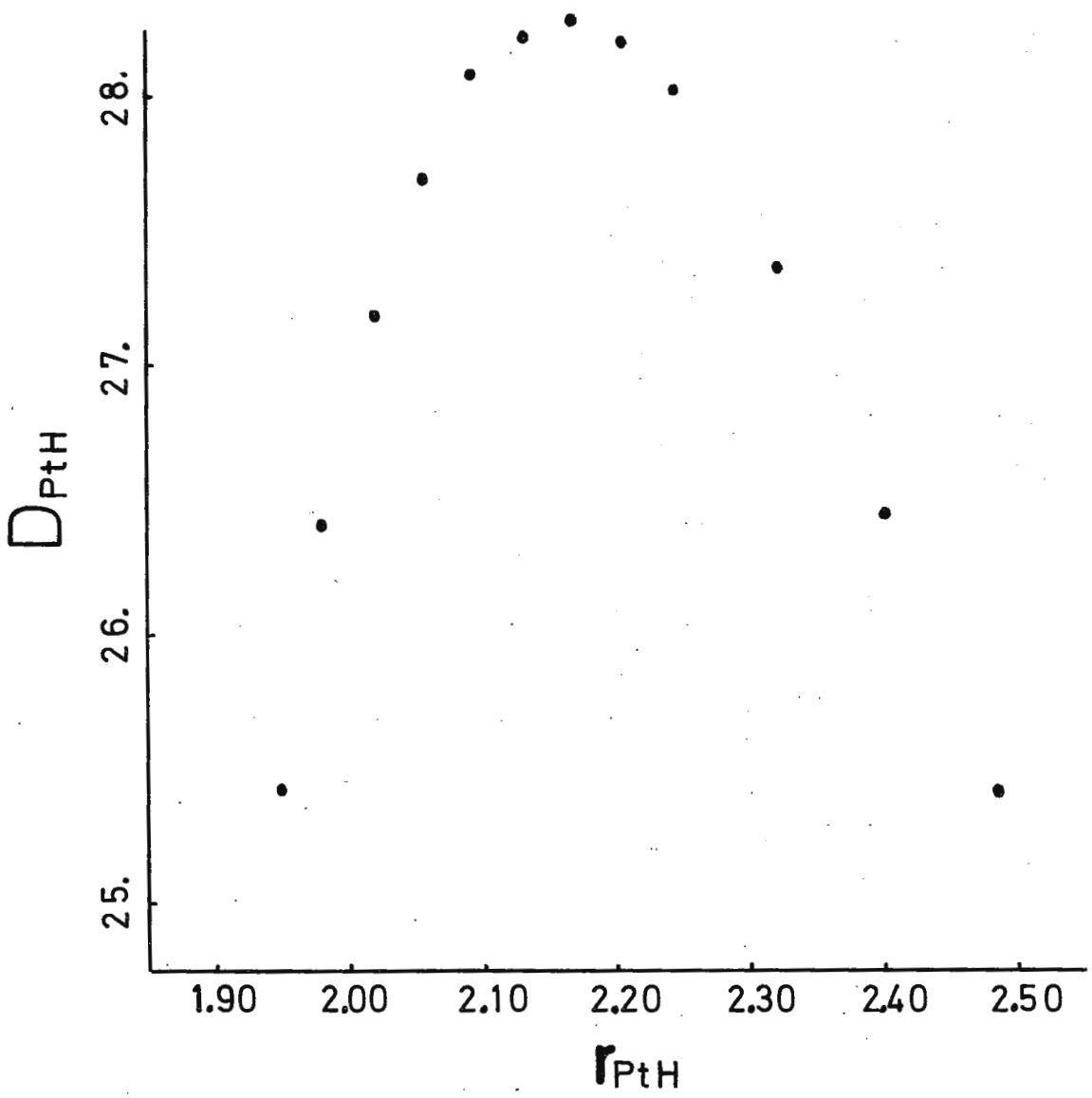
*errors in distance ratios are less than 0.002

References:

1 P. Diehl and W. Niederberger, J. Mag. Res. 9 495 (1973)

2 E. Haloui and D. Canet, J. Mol. Struct. 24, 85 (1975)

J_{PtH} in isotropic micellar soap solution is 66.22 ± 0.06 Hz



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Onderwerp

Dear Professor Shapiro,

As a result of your reminder Dr. Bovée, who does the HR-NMR work in our group, has written the following note about

Relaxation measurements on AB systems

Our previous contribution (13th August 1974) to the TAMU NMR newsletter dealt with preliminary relaxation measurements on AB systems. In the meantime the measurements on the AB systems of figure 1 (10 mole % solutions in acetone) have been finished. The results are interpreted using the theory for intra- and intermolecular relaxation of AB systems by Khazanovich e.a.[1]; due to the inaccuracy in the experimental relaxation rates (about 3%), not all the information is obtained that might in principle be extracted from them. However, the following conclusions can be drawn: From the four conformations in compounds A and B, formed by rotations of π radians about the C_8-C_9 and C_9-R bond, only two occur, namely those in which the CH_3 group is as far as possible from protons A and B. Moreover there is an angle of 20-45° between the aromatic and the ethylenic planes. In compound C the conformer in which the C_7-C_8 and C_9-O double bonds are trans to the C_8-C_9 bond has an energy which is at least 0.7 kcal/mol lower than the corresponding cis conformer. The correlation time for molecular reorientation in compound D is found to be $(1.28 \pm 0.20) \times 10^{-11}$ s. Using the longitudinal, as well as the transverse relaxation rates in D, for the ^{14}N-H coupling constants in this molecule is found:

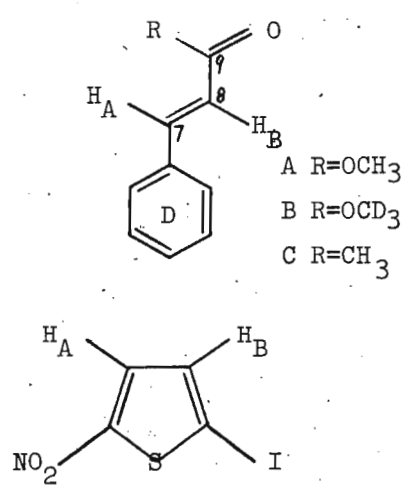

fig. 1

$$J_{NA} = |0.95| \pm 0.07 \text{ Hz}$$

$$J_{NA} = |0.47| \pm 0.09 \text{ Hz}$$

In the moment the full results are made suitable for publication.*)

Yours sincerely,

Dr. W.M.M.J. Bovée

*) See also the thesis "Structure and motions of molecules in liquids as determined by selective proton relaxation time measurements", Delft, June 1975 by W.M.M.J. Bovée.

Prof.Dr.Ir. J. Smidt

1) T.N. Khazanovich and V. Yu. Zitserman, Molec. Phys. 21, 65 (1971)

Dr. Stefan Berger
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Professor
B. Shapiro
TAMU NMR
College of Science
Texas A + M University
College Station, Texas, 77843

Dear Dr. Shapiro:

The t.-Butyl-Group as Sensor Group

Forced by your blue reminder we would like to present some preliminary results of C^{13} measurements of a series of substituted t.-butyl-benzenes[1].
We define the chemical shift difference between the quarternary carbon atom and the methyl carbon atoms of the t.-butyl group as a probe for the electronic and other effects of a substituent. First we had to establish that the system works: in the table the chemical shift difference within the t.-butyl group is given for a large number of para substituted t.-butyl benzenes[2]. Least squares analysis shows a very good Hammett type correlation of these data, which is not too common for aliphatic carbon atoms[3]. The few points for the ortho compounds, however, deviate significantly from the order of the para series. After obtaining more points (currently at a rate of 2 per week[4]) within the ortho and meta series, we hope to establish a theory which explains the difference in the bond polarization of the ortho compounds.

Sincerely yours

Stefan Berger

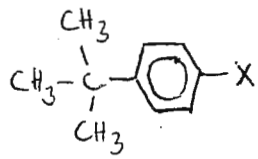
Stefan Berger

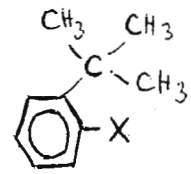
1) VARIAN CFT-20, 1-molar $CDCl_3$ solutions.

2) Some of the compounds have been already reported, cf. J.B.Stothers, C^{13} NMR Spectroscopy, Academic Press 1972 and C.D.Schaeffer, J.J.Zuckermann and C.H.Yoder, J.Organomet.Chem. 80, 29 (1974)

3) G.J.Martin, M.L.Martin and S.Odiot, Org.Magn.Res. 7,2 (1975)

4) I am indebted to Michael Marsch for his valuable synthetic help.





X	$\Delta\delta$ [ppm]	$\Delta\delta$ [ppm]
$N\equiv N^{\oplus}$ a)	6.88	
NO_2	4.35	4.99
$C\equiv N$	4.30	
COOH	4.06	
$COCH_3$	3.98	
COOEt	3.89	
J	3.38	6.73
COO^- b)	3.38	
H	3.21	3.21
Br	3.26	
Cl	3.17	
Phenyl	3.13	
$OCOCH_3$	3.02	4.21
F	2.84	
CH_3	2.83	
t.-Butyl	2.71	
OH	2.52	4.85
OCH_3	2.46	5.02
NH_2	2.28	4.59
$N(CH_3)_2$	2.18	
$O^{\ominus}$ c)	1.04	4.64

a) in CD_3OD as $R\text{-}N\equiv N^{\oplus}\ BF_4^{\ominus}$

b) in D_2O

c) in DMSO-d_6

GRIFFITH UNIVERSITY
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School of Science

Ref: D.D./Lc

Prof B.L. Shapiro,
Department of Chemistry,
Texas Aand M University,
College Station, TEXAS...778843,
U.S.A.

19th June, 1975.

T_1 Errors on a Bruker HX-90 with a 1083 Computer.

Dear Prof Shapiro,

We have started an extensive programme of ^1H, ^{15}N and ^{13}C T_1, studies on a variety of compounds and at an early stage in these investigation it became apparent that the measured values of the T_1 appeared in our experience, to be about 25% too short. This error remained even though great care was taken in setting the 90° pulse widths (17.5 μsec 90° pulse for ^{13}C) and other instrument parameters.

The error was finally tracked to a software fault. We have the NIC 1083 computer (cycle time 2 μsec) whereas we had been given software for use on the BNC-12 computer (cycle tme 1.76 μsec). This meant the τ values typed in on the TTY were 0.8 of the values used by the instrument, giving the observed error. The fault is easily corrected location 01520_8 is reset from 0144_8 to 0120_8. The τ values typed in now corresponds to those actually used.

We would recommend other Bruker users to check this point out before doing any T_1 studies.

Yours sincerely,

D. Doddrell R. Bendall

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202-10

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

RÉFÉRENCE A RAPPELER : G/ COP-75-347/mjc

VOTRE RÉF

VOTRE LETTRE DU

GRENOBLE LE 30 mai 1975

Dear Dr. Shapiro,

^{31}P n m r of cyclopolyphosphines in nematic phases

Partial orientation of solutes in nematic liquid crystals is widely used to study molecular structure and chemical shielding anisotropy. As part of our stereochemical studies of phosphorus compounds, we have been investigating the ^{31}P n m r spectra of the cyclotetraphosphines ($(CF_3P)_4$ and $(tBuP)_4$ dissolved in liquid crystals.

The experimental and theoretical spectra of $(tBuP)_4$ are shown in the Figure.

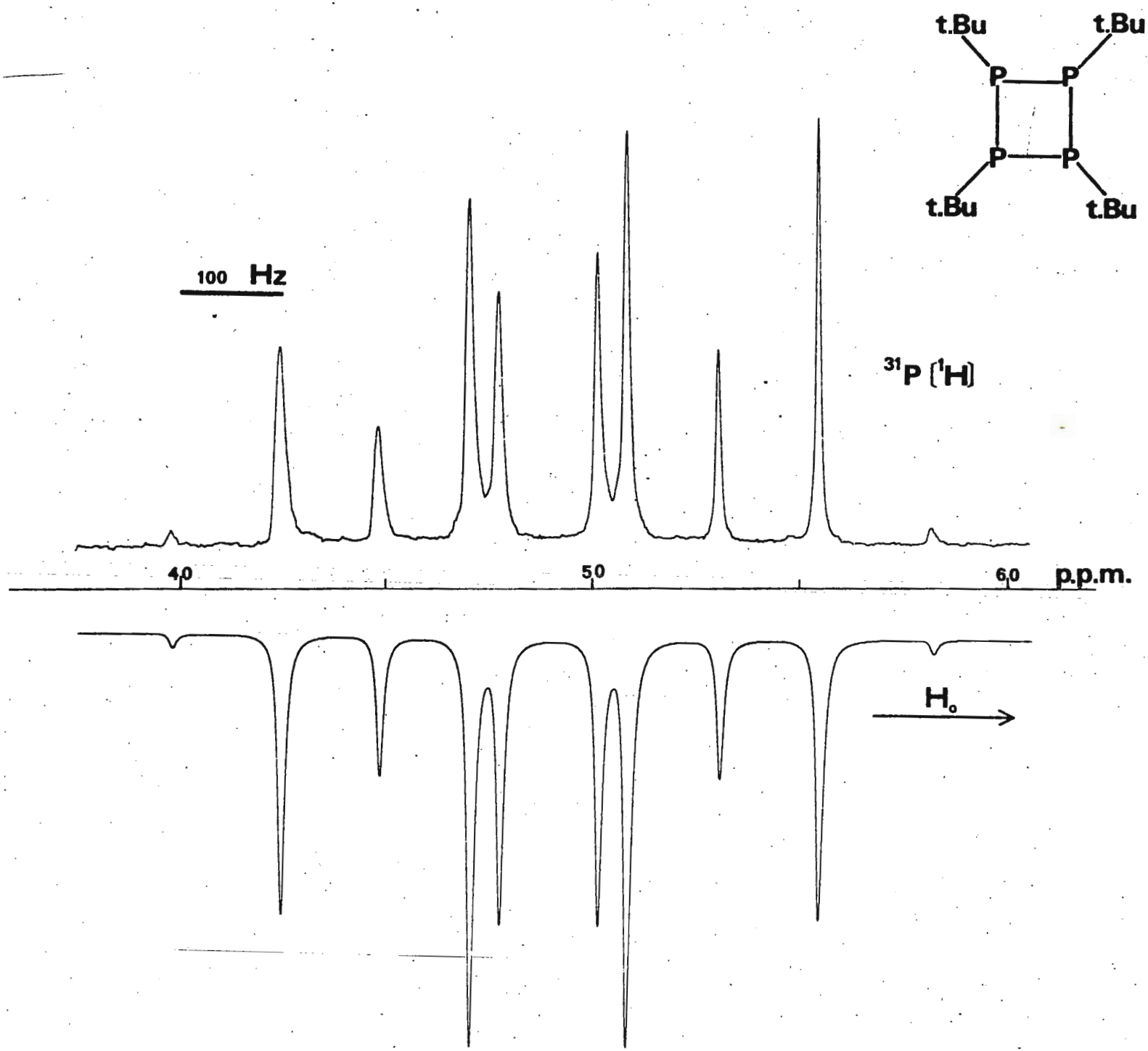
Three kinds of information can be obtained from such a study :

- The amplitude of the folding of the four membered ring (18° for $(tBuP)_4$ and 24° for $(CF_3P)_4$). For this latter molecule, the result is in good agreement with X-ray data (PALENIK and DONOHUE, Acta Cryst., 15, 564, 1962).
- The chemical shift anisotropy $\Delta\sigma = \sigma_{zz} - \frac{\sigma_{xx} + \sigma_{yy}}{2}$ which are equal to +167 ppm and +141 ppm respectively for $(tBuP)_4$ and $(CF_3P)_4$.
- And finally the $^1J(PP)$ n m r coupling which was not accessible from n m r spectra in isotropic liquid. One obtains 148.4 Hz for $(tBuP)_4$ and 100.6 Hz for $(CF_3P)_4$. These small values as compared with the one measured in other cyclopolyphosphines of diphosphines suggest as previously noticed (ALBRAND and ROBERT, Chem. Comm., 1974, p. 644, and references cited therein), that a trans relationship of the phosphorus lone pair will cause a decrease in $|^1J(PP)|$.

Sincerely yours,

J.P. ALBRAND A. COGNE J.B. ROBERT

C.E.N.G. IMP. N° 1-C - 1-74


t.Bu
t.Bu
P
P
P
P
t.Bu
t.Bu
100 Hz
$^{31}P\{^1H\}$
4.0
5.0
6.0
p.p.m.
H_o

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	40L	1-240 MHz	40
	30LA	1-110 MHz	30
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	60LA	4-150 MHz	60
	100LA	1-110 MHz	100
	100L	10 kHz-220 MHz	100
	100LM8	1-220 MHz	100
	100LM9	1-200 MHz	100
	500L	10 kHz-220 MHz	500
	500LM8	1-220 MHz	500
	500LM9	1-200 MHz	500
	1000L	10 kHz-220 MHz	1000
	1000LM8	1-220 MHz	1000
	1000LM9	1-200 MHz	1000
	1500LA	1-150 MHz	1500
	5000LA	1-100 MHz	5000
H	10HA	225-410 MHz	10
	10HB	300-500 MHz	10
	6 HC	400-700 MHz	6
A	1A70	100 Hz–70 MHz	1
	4A15	20 KHz – 15 MHz	4
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	50A15	20 KHz – 15 MHz	50
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Department of Chemistry

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10th June, 1975.

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

Report on FT Instrument; selective ^{1}H decoupling in ^{13}C NMR

Dear Dr. Shapiro,

Our JEOL-PS-100-PFT spectrometer, interfaced with a NICOLET 1085 computer, has been operating for 2½ years. Originally chosen on performance and ease of use, the system has also proved reliable (downtime 4%; total spent on servicing and modifications: £240). Apart from an early programme fault in T_1 plotting, problems have been few and minor.

The system is fully occupied with problems in Organic Chemistry, involving molecules of molecular weight 200-1200. Indeed, unless there is a chemical problem, users are discouraged from submitting series of compounds for determination of NMR parameters. Time-wise, 61% has been devoted to ^{13}C, 35% to ^{1}H and 4% to ^{2}D. Deuterium applications are limited by the low ratio of normal spectral width (10 p.p.m., 150 Hz) to line width (0.8 Hz, C_6D_6). ^{15}N work has only just got off the ground, thanks to pressure on ^{1}H and ^{13}C services.

The choice of sample tube size for the ^{13}C probe (8m.m., minimum volume 0.8 ml.) has proved fortunate. The majority of submitted samples are not available in quantities over 100 mg and solubility is rarely a problem. Under these conditions, larger diameter sample tubes offer no benefit.

Hitherto, carbon T_1 values have proved of little value, as the information deduced was nearly always available more simply (and in less time) from routine experiments of noise, off-resonance and selective decoupling. Selective ^1H decoupling has proved invaluable in the correlation of ^1H and ^{13}C spectra. When operating at a fixed lock (^2D) frequency, it is only necessary (for each deuterated solvent) to spend a couple of hours determining the ^1H frequency for complete de-coupling, at very low power, of the TMS ^{13}C signal in (say) a solution of Et benzene (40%) in $CDC\ell_3$ containing TMS. From many successful experiments, we know that the frequency thus determined can be relied upon as a reference point for selective decoupling of the vast majority of samples.

In the example, the α-carbon atom of a proline residue was identified in the ^{13}C spectrum of a peptide antibiotic containing over 60 carbon atoms and including 10 amino acids.

Yours sincerely,

Harold Booth

Harold Booth

NOISE DECOUPLED

RANGE 6024 Hz (HIGH FIELD PART PLOTTED)

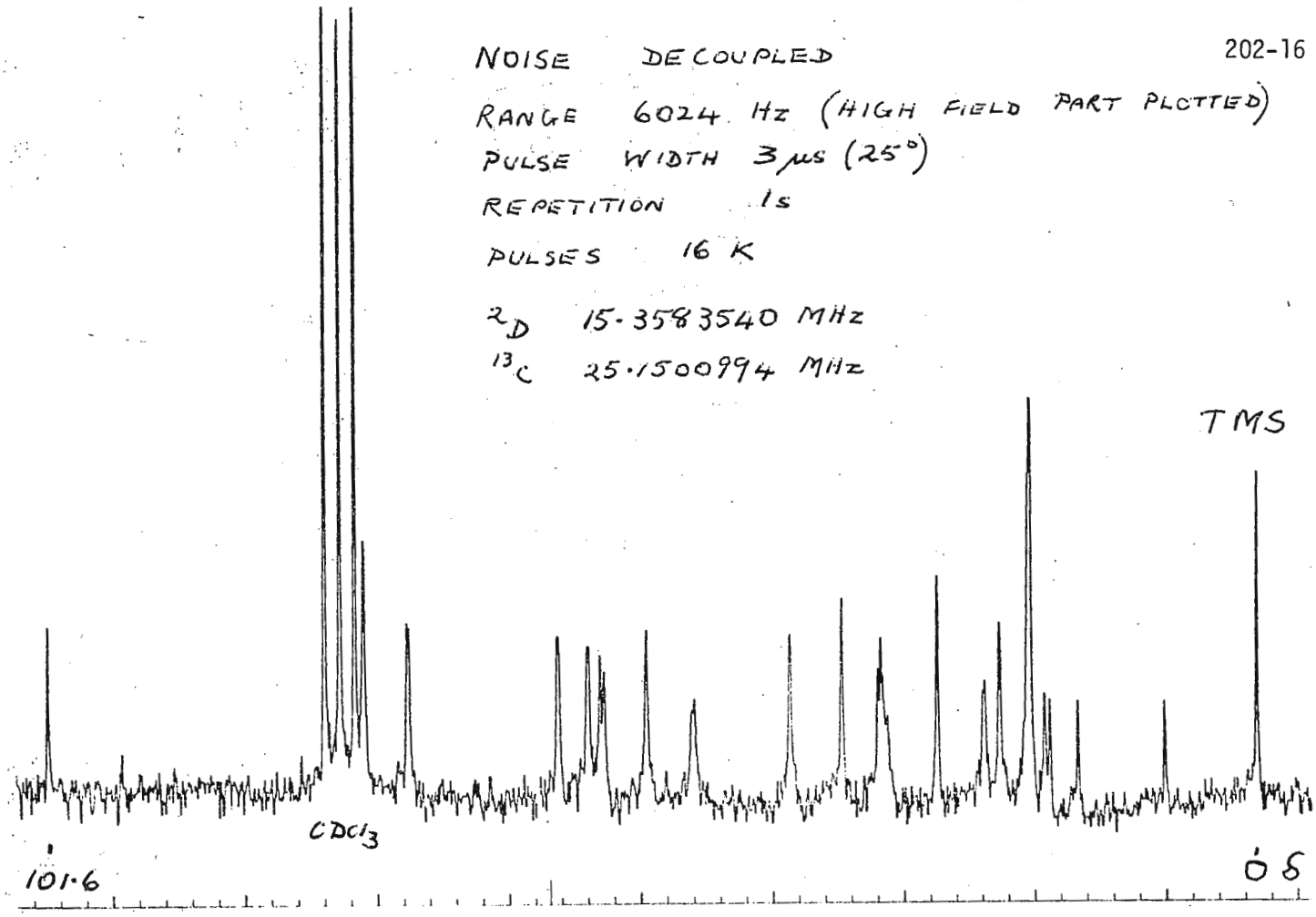
PULSE WIDTH 3 μs (25°)

REPETITION 1s

PULSES 16 K

^{2}D 15.3583540 MHz

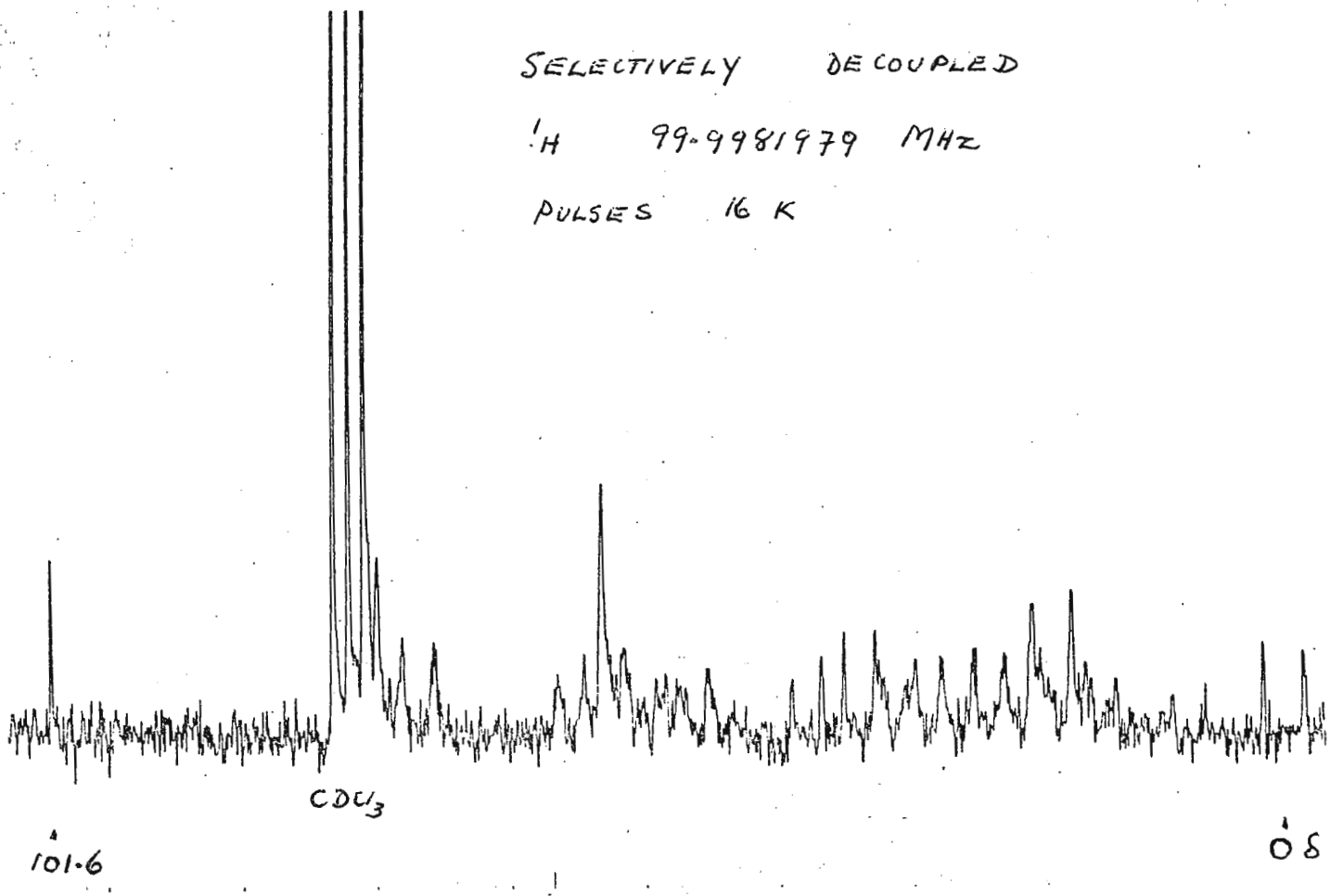
^{13}C 25.1500994 MHz



SELECTIVELY DECOUPLED

^{1}H 99.9981979 MHz

PULSES 16 K



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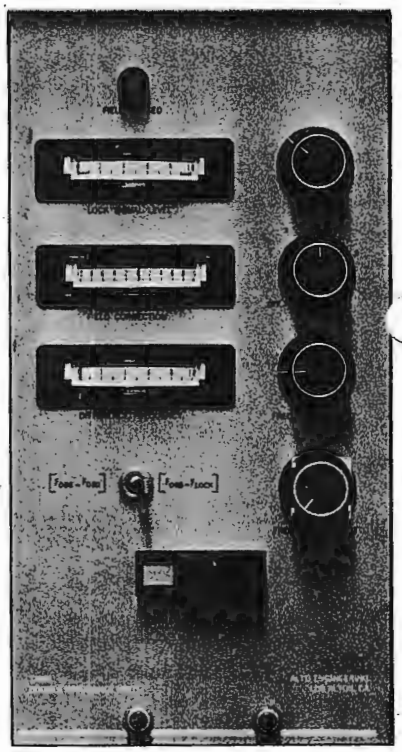

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ENGLAND

June 2, 1975

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

FLUX STABILISER PROBLEM ON HX-90 SPECTROMETER

Dear Professor Shapiro,

May we through the TAMU newsletter appeal to contributors for some assistance in overcoming an instrumental problem which neither we nor the manufacturer have been able to solve. It concerns the flux stabiliser on our HX-90 spectrometer which 'drops-out' on switching to field scan amplitudes greater than '50' on the sweep control. The fault is intermittent but at its worst can make the instrument 'setting-up' procedure an exceedingly tedious and lengthy business. Needless to say we have tried all the obvious remedies suggested by an examination of the circuit diagrams. Perhaps one of the TAMU newsletter readers has experienced the same problem and perchance has found a solution to it. If they could write to us concerning the solution of this problem we should be most grateful.

Yours sincerely,

S. Knight

S.A. KNIGHT
Analytical Branch

202-19
TELEPHONE: 660 0522.

Department of Organic Chemistry
The University of Sydney
N.S.W. 2006

June 4, 1975.

IN REPLY PLEASE QUOTE:

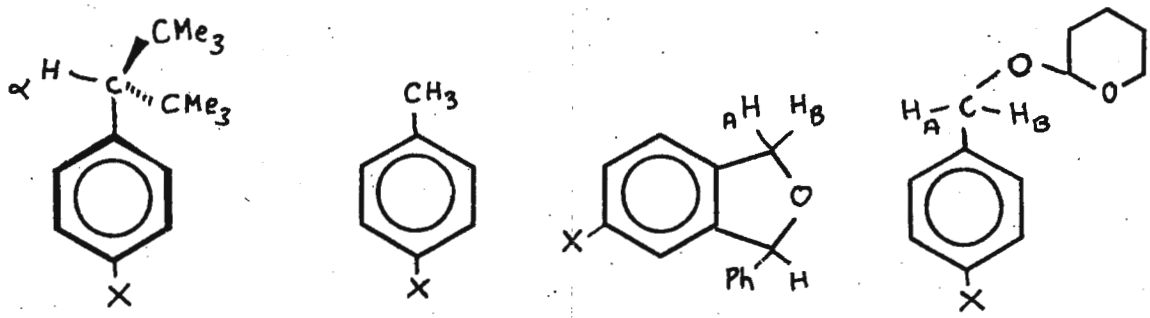
Prof. B.L. Shapiro
Department of Chemistry
Texas A and M University
College Station
Texas 77843, U.S.A.

CONFORMATIONAL DEPENDENCE OF SUBSTITUENT EFFECTS ON THE CHEMICAL SHIFTS OF BENZYLIC PROTONS

Dear Barry,

In connection with another project, Mr. C.J. Fallick a graduate student in this Department, prepared a series of para-substituted di-tert. butylphenylmethanes (I) and showed that they adopt the conformation indicated in the ground state, i.e., that the benzylic proton H_α is always essentially in the plane of the benzene ring.

The transmission of electronic effects from the para position to benzylic protons has been studied by a number of authors and, in particular, Marcus, Reynolds and Miller[1] dealt with p-substituted toluenes (II), while Fraser and co workers[2] investigated, inter alia the dependence of substituent effects on the chemical shifts of benzylic protons in systems (III) and (IV) and found a small but significant conformational effect, i.e., the chemical shifts of H_A and H_B in (III) and (IV) are not necessarily equally susceptible to the changes of substituent X. Some calculations relevant to these data were also reported.[3]



(I) (II) (III) (IV)

The plot of the chemical shifts of H_α in (I) against the chemical shifts of the identically substituted toluene (II) is shown in Fig. 1 : it is a straight line with a correlation coefficient better than 0.99 and slope of 1.05. We conclude therefore that conformational effects are undetectably small or, in other terms, that the charge density at the benzylic proton does not depend on the orientation of the benzylic C-H bond towards the benzene ring.

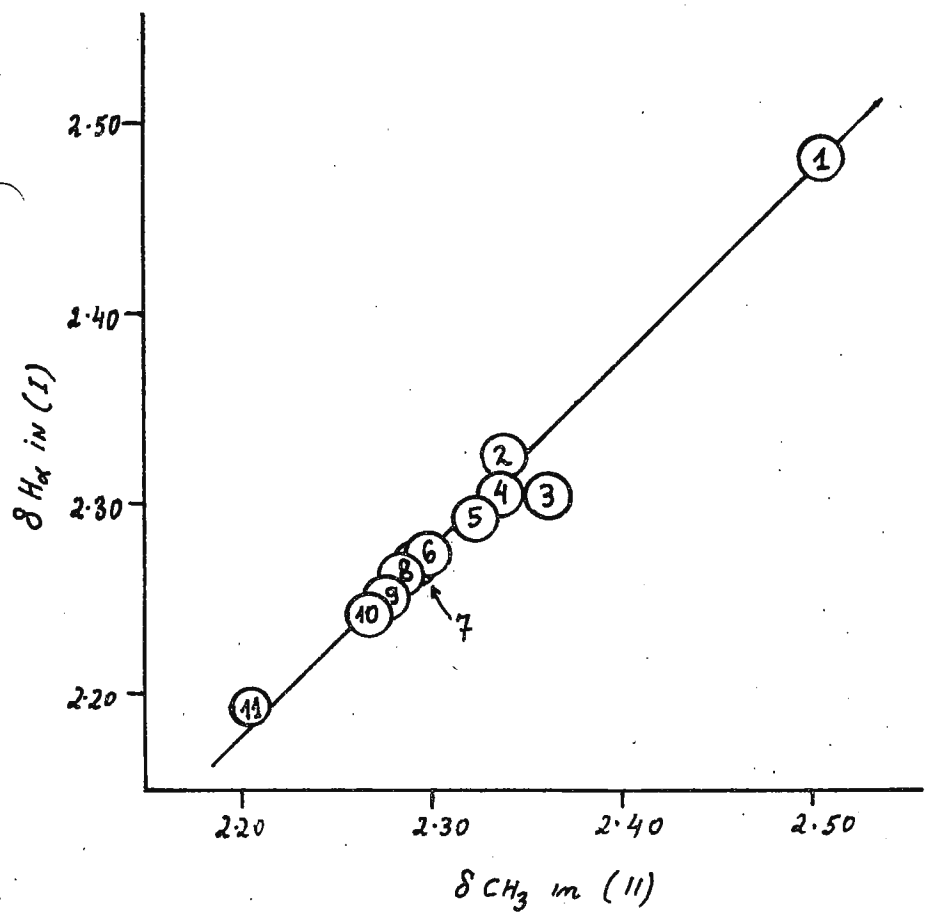
It is possible that the more significant effects observed by Fraser[2] are connected with the presence of oxygen atoms at the benzylic carbon, i.e., they may be due to relative orientation of the benzylic C-H bonds with respect to the lone pairs.

With best regards,

Yours sincerely

S. Sternhell

(1) Marcus, Reynolds and Miller, J. Org. Chem., 31, 1872(1966). (2) Fraser Gurudata, Reyes-Zamora and Swingle, Canad. J. Chem., 46, 1595(1968); Fraser and Renaud, ibid., 49, 800(1971). (3) Dawson, Hamer and Reynolds, Canad. J. Chem., 52, 39 (1974).



1 = NO_2
2 = OAc
3 = H
4 = Cl
5 = Br
6 = NHAc
7 = I
8 = Me
9 = OMe
10 = OH
11 = NH_2

Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

June 5, 1975

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

Title: (1) Request for new ^{13}C material, suggestions; (2) Intra versus Intermolecular Hydrogen Bonding in ortho-Chlorophenols

Dear Barry:

(1) The time has come to update the monograph "Carbon-13 Nuclear Magnetic Resonance For Organic Chemists (Wiley-Interscience, 1972). I plan to re-write some of the text completely for the second edition, which should appear late in 1976. I am currently assembling materials for this second edition and would appreciate receiving preprints or good quality copies of new ^{13}C spectra for inclusion in the book. Our goal is once again to be as up-to-date as possible!

Also, if any of the TAMU-NMR readers have suggestions as to content, corrections, etc. I'd be happy to see them. Although we want the 2nd edition to remain as a low level approach we do plan to introduce some new topics.

(2) We have recently examined several ortho and meta halogen substituted phenols as concentrated solutes (in CCl_4) in the presence and absence of the paramagnetic relaxation reagent, $Cr(acac)_3$. In these systems ^{13}C T_1 data obtained in the diamagnetic solutions probe intramolecular rotational diffusion while the T_1 data from the solutions containing $Cr(acac)_3$ monitor intermolecular hydrogen bonding from the phenolic OH to the chelate. Both types of data are functions of the level of association of the phenol molecules.

The study has shown us that meta chlorination of phenols increases somewhat their tendency to associate (presumably with stronger H-bonds, a not unexpected result). Ortho chlorination, on the other hand, reduces the ability of a phenol to aggregate with other phenol molecules or to hydrogen bond to basic sites on $Cr(acac)_3$. Two mechanisms might account for this effect: (1) steric inhibition of intermolecular association or (2) competition from intramolecular hydrogen bonding between the phenolic hydrogen and the ortho chlorine.

On the basis of experiments performed-to-date mechanism (2) appears to dominate, however, mechanism (1) is clearly significant. For example comparisons among o-cresol, o-bromophenol, and o-chlorophenol indicate that the o-chlorophenol is least associated followed by the bromo-compound and then o-cresol.

A preprint describing this work in detail will be forwarded on request.

My best regards.

Yours sincerely,

George

George C. Levy
Associate Professor

GCL/dlh

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DEPARTMENT OF CHEMISTRY

June 16, 1975

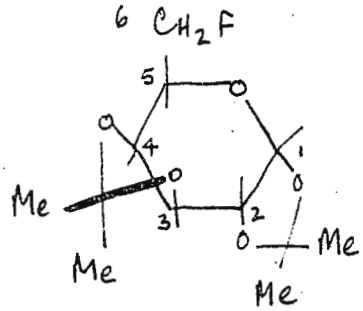
Professor Barry L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
College Station,
Texas 77843

Noise Modulated Heteronuclear Decoupling

Dear Barry,

As you know we have made extensive use of both c.w., and noise-modulated, heteronuclear decoupling. Last year we "rediscovered" yet another of the several variants on the "noise-modulated" theme - again this variant was described in Richard Ernst's original, prescient paper (J. Chem. Phys., 45, 3845 (1966)), but we had not previously appreciated its diagnostic utility. Basically it depends upon the introduction of a time dependent perturbation, from the noise modulated decoupler, into the transitions associated with the irradiated spins, which causes those transitions to behave as if they were "exchange broadened".

It is easiest to illustrate this experiment with reference to the attached figure, which shows ^{1}H n.m.r. spectra (HA-100) of 6-deoxy-6-fluoro-1,2,3,4-di-O-isopropylidine-α-D-galactopyranose.



The spectrum in [B] shows the normal spectrum and that in [A] the spectrum obtained with simultaneous irradiation at the ^{19}F frequency using a modest (ca. 200Hz) noise modulation bandwidth. A careful comparison of the transition frequencies can lead to an assignment of both spectra, but even so the spectrum in A has some degeneracy. The spectrum in [C] was obtained by increasing the noise bandwidth to ca. 2KHz and decreasing the R.F. intensity by ca. 20 dB. Note that the transition of the protons which have a spin-coupling with the fluoring (H-6, H-5) are now substantially broadened - with the H-6 transitions essentially eliminated from the spectrum - whereas the other resonance have their normal line-widths.

Professor B.L. Shapiro June 16, 1975

We find this approach greatly facilitates the assignment of the proton spectra of organic molecules containing magnetic heteronuclei, and shall eventually be submitting several papers using it. We find that these experiments are easily obtained by reducing the intensity of the decoupling field and/or by increasing the noise modulation bandwidth.

With all best regards,

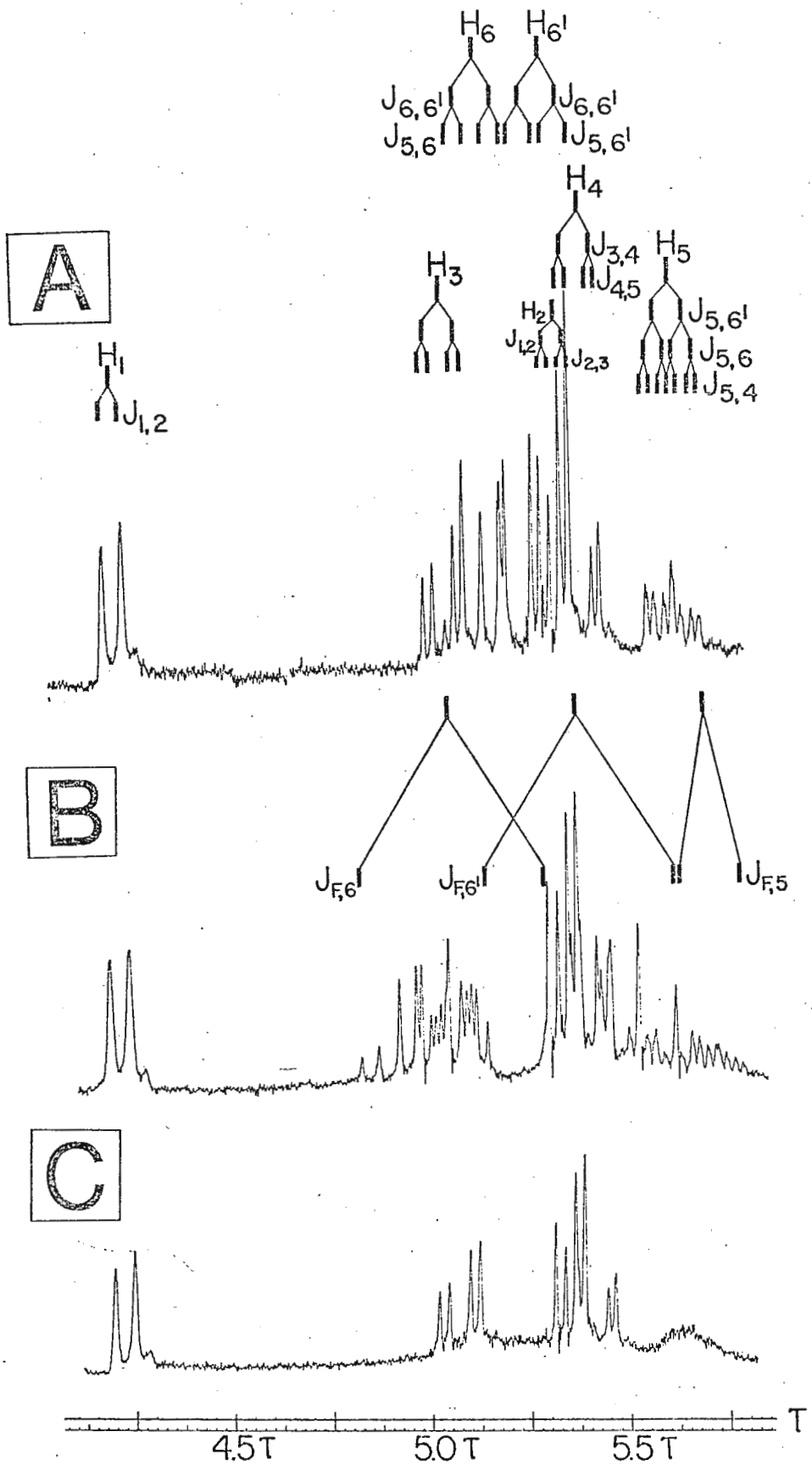
Yours sincerely,

Laurie Hall.

L.D. Hall

Leone Evelyn

L. Evelyn


A
B
C
H6
H6'
J6,6'
J5,6
J6,6'
J5,6'
H4
J3,4
J4,5
H5
J5,6'
J5,6
J5,4
H3
H2
J1,2
J2,3
H1
J1,2
JF,6
JF,6'
JF,5
4.5 T
5.0 T
5.5 T
T

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF GEORGIA ATHENS, GEORGIA 30602

June 6, 1975

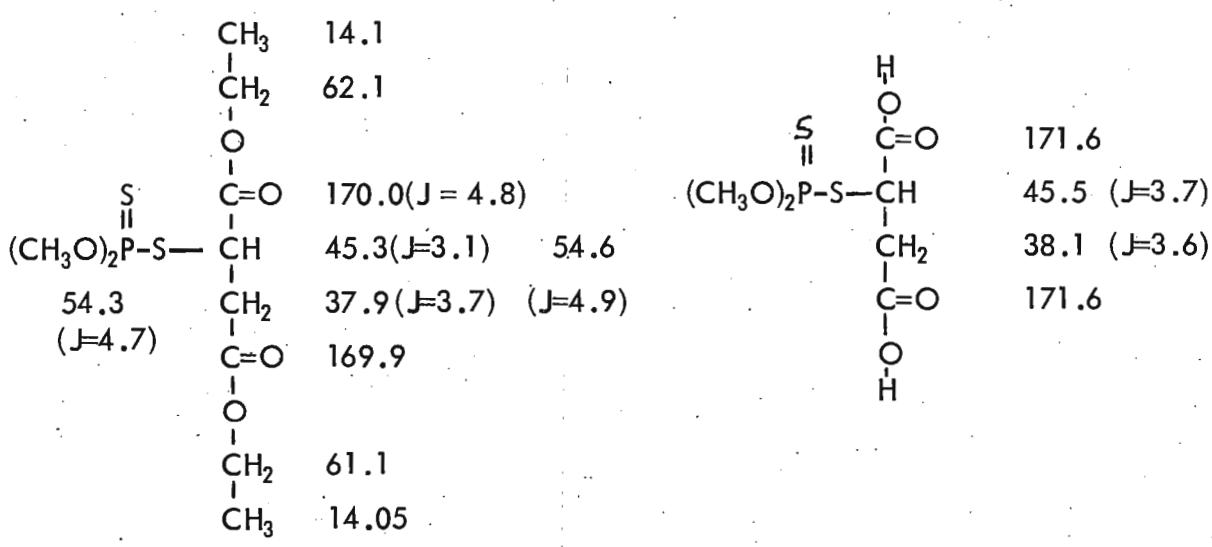
Professor B. L. Shapiro
Department of Chemistry
Texas A and M University
College Station, Texas 77843

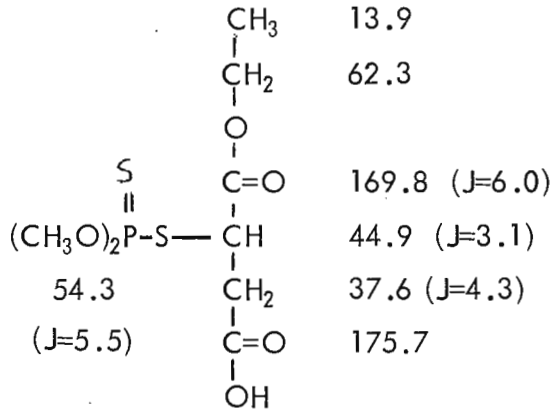
Dear Barry:

Malathion Mono-Acids

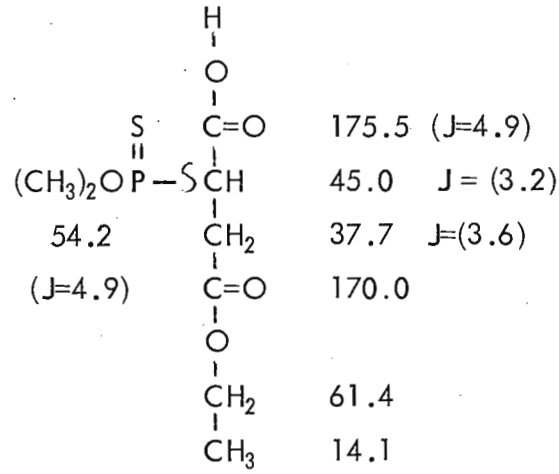
During a recent investigation of the hydrolysis products of malathion(I), we needed to uniquely determine the structures of the two possible mono-acids (II and III). The mono-acids have been previously determined using proton NMR spectra. (1) However, the assignment was based on very small differences in chemical shifts. The use of ^{13}C spectra allows a relatively straightforward assignment of the two isomers using two basic assumptions: (a) a carboxylic acid carbonyl carbon is further downfield than a corresponding ester carbonyl carbon; and (b) the coupling constant ^{3}J C-C-S-P is larger than ^{4}J C-C-C-S-P. Both of these assumptions appear to be reasonable based on previous data. (2)

The ^{13}C spectra of II and III are similar with the following exceptions. With one isomer, the low-field carbonyl is a singlet whereas the high-field carbonyl is a doublet and with the other isomer, the low-field carbonyl is a doublet and the high-field carbonyl a singlet. Using off-resonance decoupling, known shift correlations and the above assumptions, the assignment of the isomers is as follows:





II β -isomer



III α -isomer

Coupling constants are ± 1.2 Hz. This assignment is consistent with the previous assignment based on proton spectra. (1)

Sincerely yours,

Dick

Richard H. Cox
Associate Professor

1. P. R. Chen, W. P. Tucker and W. C. Dauterman, J. Agr. Food Chem., 17, 86 (1969).

2. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, 1972.

202-29 Institut für Organische Chemie
Laboratorium Niederrad
Universität Frankfurt am Main
Prof. Dr. H. Kessler

D-6 Frankfurt/M., June 6, 1975
Sandhofstr.
Telefon: (0611) 6301 - 6033

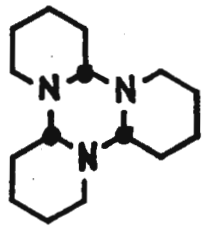
Postanschrift:
Theodor-Stern-Kai 7

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

Dear Dr. Shapiro:

<u>^{13}C-NMR-Line Shape Studies as Proof of Mechanism of Exchange Between Three Sites.</u>

α-Tripiperideine 1 shows a fluxional behaviour in its ^{13}C-NMR spectra caused by nitrogen inversion/ring inversion[1]. The apparent



1

C_3-symmetry (5 lines) at room temperature changes to C_1-symmetry below about -40°C (15 lines). Two mechanisms can be taken into account for the observed rate process:

1. A symmetric (C_3-symmetry) intermediate is involved. The probability to interconvert conformation A into conformation C is equal to the interconversion of A into B. The most probable intermediate for such a process is the conformation with three axial lone pairs (X), (Scheme 1).

2. The rearrangement is asymmetric (A interconverts faster into one of the other two conformations). This mechanism fits with the interconversion without any intermediate (retention of C_1-symmetry) or more probable through an intermediate conformation with only one axial lone pair.

The line shape studies of the tert. α-carbon (figure 1) show that only the random exchange (mechanism 1) fits the results.

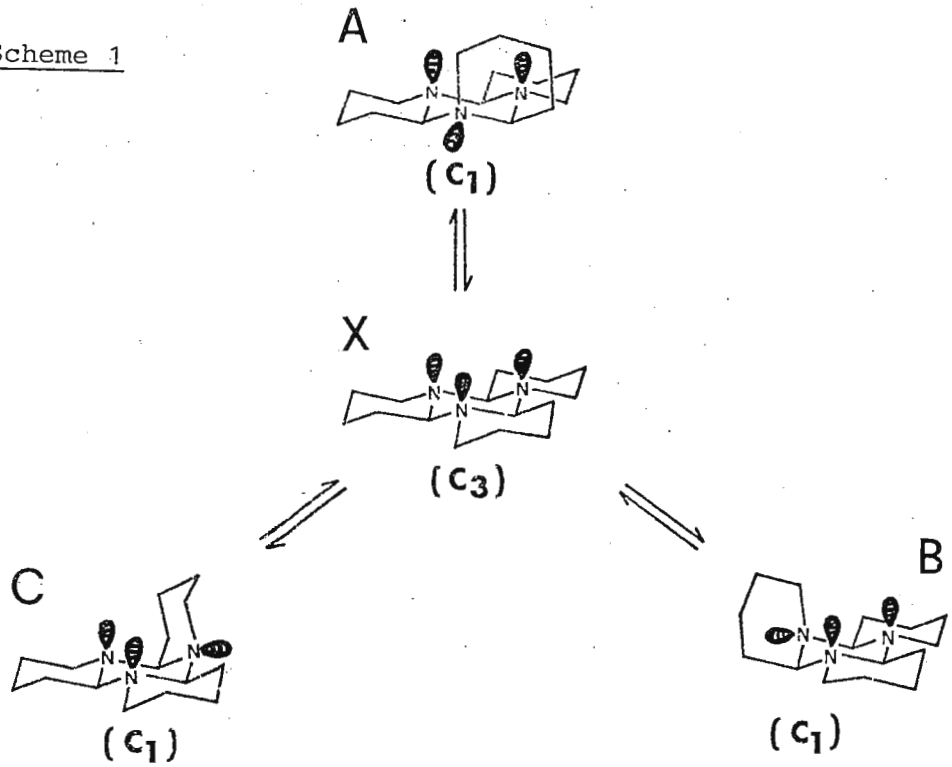
Yours sincerely,

H. Kessler G. Zimmermann

G. Zimmermann

1) H. Kessler, H. Möhrle and G. Zimmermann, to be published. Details will be given in the paper.

Scheme 1



Conformational Exchange of α-Tripiperideine.

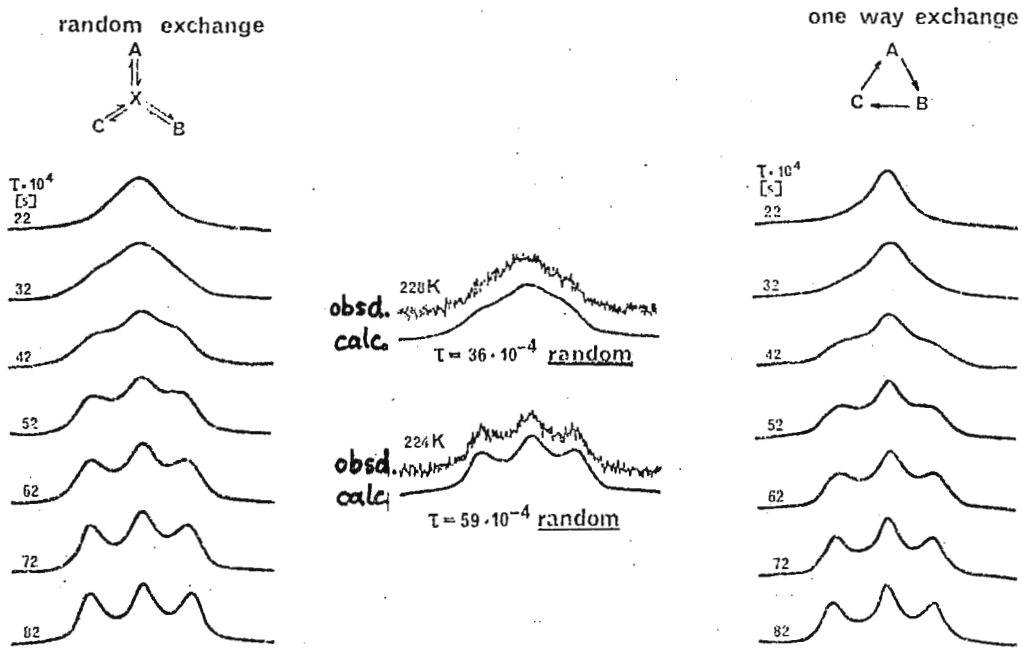


Figure 1: ^{13}C-DNMR-Spectra of α-Tripiperideine (α-Carbons).

Transform your T-60 for ^{13}C spectra with a Nicolet TT-7 pulsed FT system.

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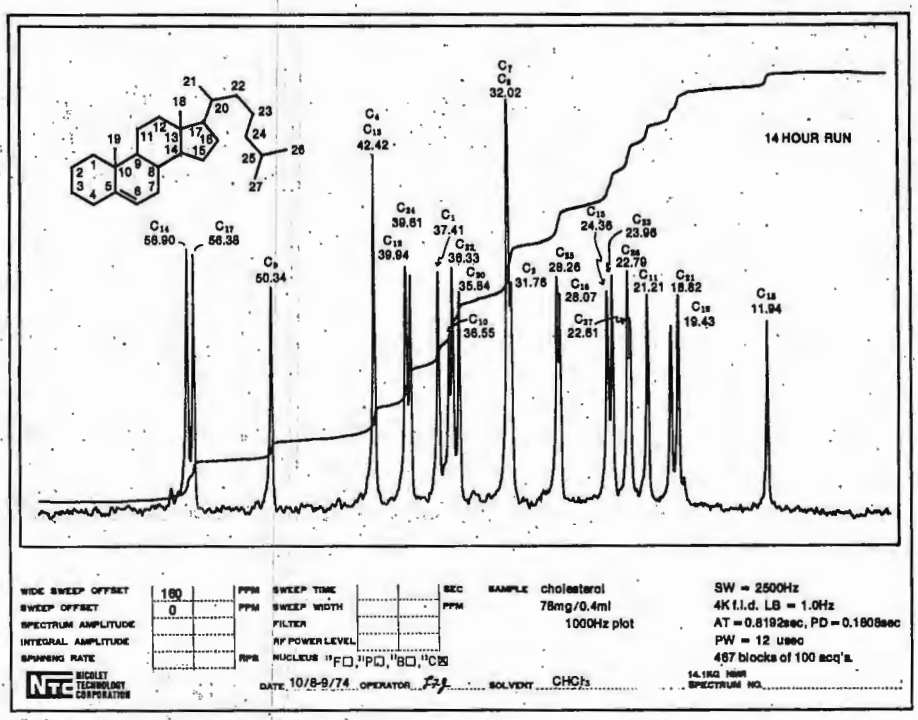

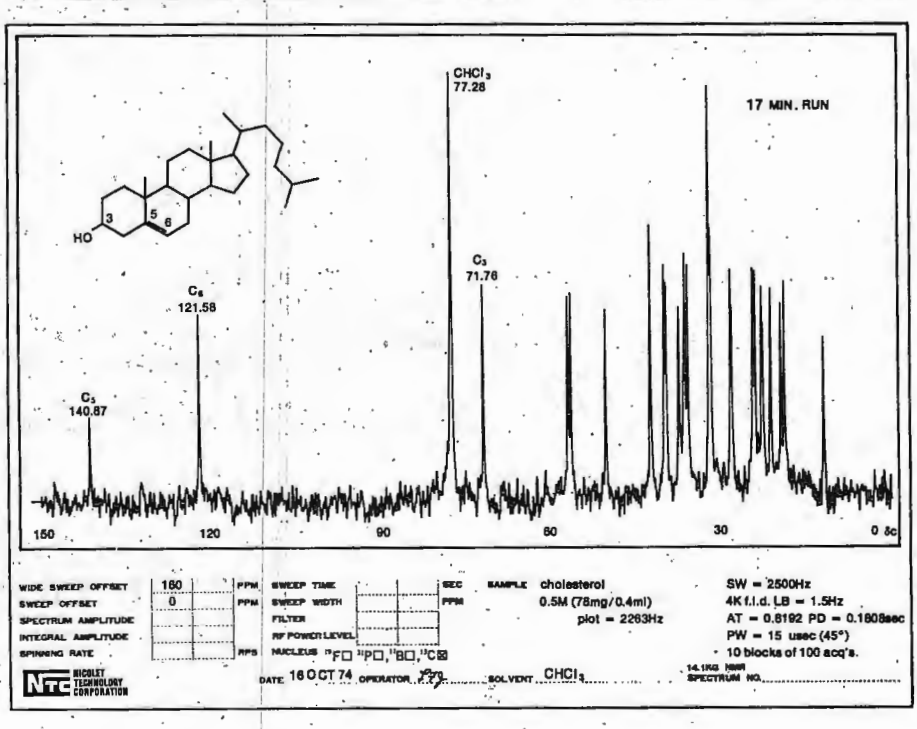

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EVANSTON, ILLINOIS 60201

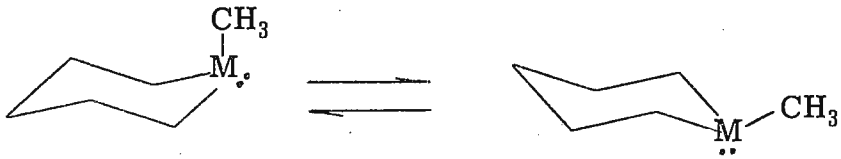
DEPARTMENT OF CHEMISTRY

June 11, 1975

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

Dear Barry:

The axial/equatorial ratio for molecules of the type:



where M is a Group V element, has been of interest for some time. When M = N, the equilibrium is far on the equatorial side ($-\Delta G^\circ > 1.4$ kcal/mol, i.e., >90% equatorial at room temperature), as has only recently been demonstrated conclusively (Eliel, Robinson). Thus the earlier dipole moment results appear to be in error. For M = P, Quin and Featherman found that $-\Delta G^\circ = 0.12$ (2/1 equatorial preference) at -110° and -0.35 kcal/mol (axial preference) at room temperature.

We have now looked at the next member of the series (M = As) and have found that there is no conformational preference ($\Delta G^\circ = 0$, K = 1.0) at -140°. Ring reversal is slow on the nmr time scale ($T_c = -140°$), $\Delta G^{\ddagger} = 6.8$ kcal/mol), and separate resonances can be observed for both isomers below -140° at 270 MHz, using a β-deuterated derivative. A complete lineshape analysis is in progress.

Theory has not yet produced a clearcut explanation for the decreased equatorial preference by methyl in the series N, P, As. Possible reasons include increased attractive 1,3 axial-axial interactions and greater ease of bending away from the ring in the axial conformation. It is noteworthy that the As system does not exhibit a net enthalpic preference for the axial conformation. The series N, P, As has a $-\Delta G^\circ$ that dwindles to nothing. This result suggests that attractive interactions may not be the critical phenomenon. In this context, the series $CHCH_3$, $SiHCH_3$, $GeHCH_3$ (for $M-CH_3$ above) would be of interest.

Sincerely,

Joseph B. Lambert

Hsiang-ning Sun

JBL/kp

Title: 1-Methylarsenane

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

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SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

June 9, 1975

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

Title: Creatine Kinase ADP NOE/Polyamine Self-Diffusion Coefficients

Dear Barry:

Our initial work showing the utility of nuclear Overhauser effect measurement for the study of enzyme structure-function relationships, in particular exposing the mechanistic role of a lysine at the active site of creatine kinase (1), have been continued on the HXS-360 at Stanford. Whereas the previous studies involved measurement of the NOE of formate in the transition state analog complex with creatine kinase, the present investigation entails NOE measurements of the H2 and H8 protons of ADP in various creatine kinase complexes. As shown in the figure on the next page, an NOE is obtained for the H2 proton of ADP in the abortive complex, CK-ADP-Mg (II)-creatine, implying that protons from the enzyme which resonate in the "methyl" region are in close proximity to the ADP H2 proton in the complex. The H8 proton of ADP does not exhibit an NOE.

We have also found a medical science application for our pulsed gradient FT measurement of self-diffusion coefficients (2). Vic Levin of the Neurology Department here at UCSF is interested in studying the rate of diffusion and capillary transport of certain polyamines which show up in the cerebrospinal fluid of patients with brain tumors. For his work, it was necessary to have values for the self-diffusion coefficients for the polyamines. Through the kind cooperation of George McDonald at the University of Pennsylvania who ran the spectra for us, we were able to calculate D for some compounds. For example, D for putrescine and spermidine in aqueous solution at 37°C are $3.3 \pm 0.8 \times 10^{-5}$ and $2.2 \pm 0.4 \times 10^{-5}$ cm^2/sec, respectively.

We hope that our next communication to the TAMUNMR newsletter will emanate from work on "our own" FT NMR instrument which was just funded by NIH.

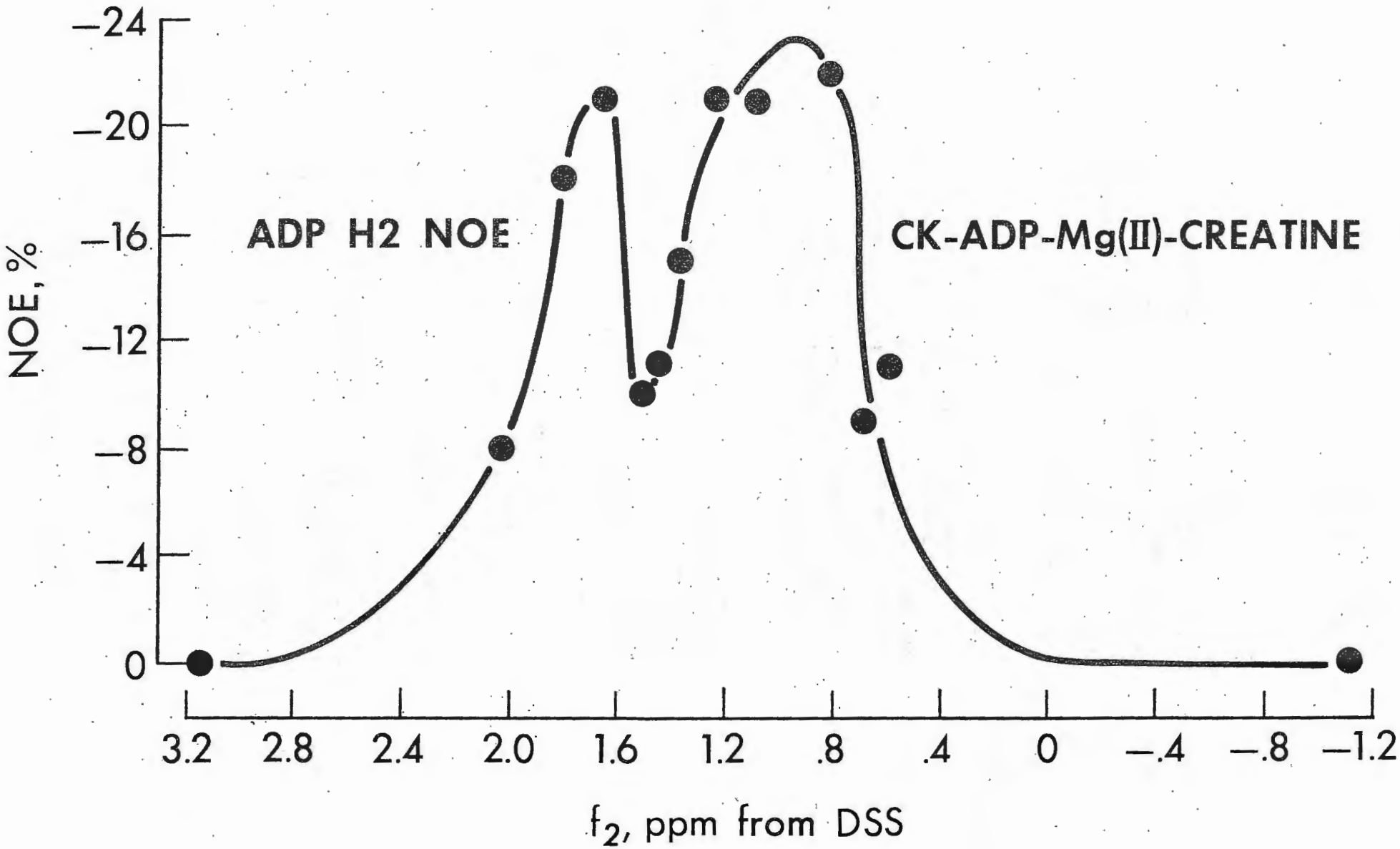
Sincerely yours,

Tom

Thomas L. James
Assistant Professor of Chemistry
and Pharmaceutical Chemistry

(1) T.L. James and M. Cohn, J. Biol. Chem., 249, 2599 (1974).
(2) T.L. James and G.G. McDonald, J. Mag. Reson., 11, 58 (1973)

TLJ:dc


ADP H2 NOE
CK-ADP-Mg(II)-CREATINE
NOE, %
−24
−20
−16
−12
−8
−4
0
3.2
2.8
2.4
2.0
1.6
1.2
.8
.4
0
−.4
−.8
−1.2
f2, ppm from DSS

202-34

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

10th June 1975

University of Salford

Salford M5 4WT

Department of Chemistry
and Applied Chemistry

Telephone 061-736 5843
Telex 668680 (Univ Salford)

Dear Dr. Shapiro,

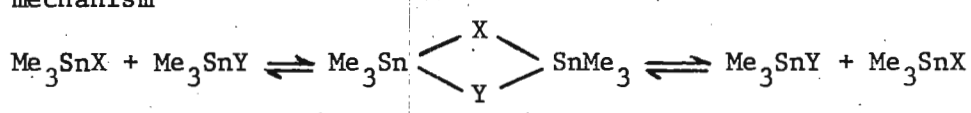
Exchange between trimethyltin halides in solution

The pmr spectra of binary mixtures of trimethyltin halides in solution clearly show that facile halogen exchange takes place on the nmr time-scale. The rate of exchange is too fast to observe decoalescence of the single resonance for Cl^-/Br^- mixtures but this is accessible for Cl^-/I^- and Br^-/I^- mixtures by dilution of the sample or by lowering the temperature.

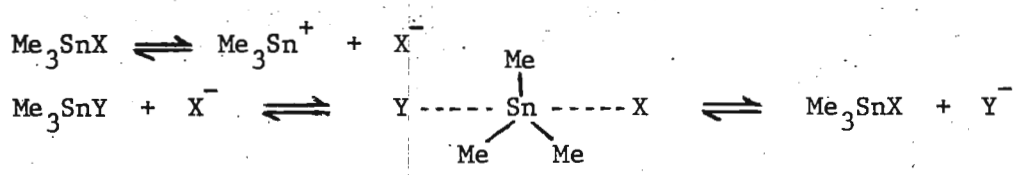
Recently Chan and Reeves[1] concluded that ionization of the methyltin halide was an essential prerequisite for halogen exchange but in another study of the same system in the same solvent, Peregudov et al.[2] argued that such an ionization was untenable in an aprotic solvent like toluene and proposed that the exchange mechanism was an associative one involving a 5- coordinate bridged intermediate.

Meanwhile, Brian Glasberg was looking at these exchange systems in $CDCl_3$ and CH_2Cl_2 solution so we hoped that the change in solvent would solve the problem. He determined the activation parameters shown in the Table using a total line-shape analysis.

The large negative values for $\Delta S^{\neq}$ explain why no transition state species is observable but this $\Delta S^{\neq}$ is consistent with the associative mechanism



and with the dissociative mechanism



if the latter process is the rate determining step.

The influence of the solvent on the rate is not expected to be very marked for the associative mechanism but the concentration of halide ion in solution is expected to increase with the permittivity of the medium thus increasing the rate in the dissociative case.

Our results tend to support the latter mechanism and are now in press in J. Chem. Soc. Dalton.

Yours sincerely,

J. A. Ladd

J. A. LADD

1. Chan & Reeves, Inorg. Chem., 12 (1973) 1704.
2. Peregudov et al., Zh. Obshchei Khimii, 42 (1972) 2194.

Table 1. Arrhenius and Eyring Activation Parameters for the Exchanges[a]

System	Solvent	Total halide concentration mol l^{-1}	Temperature range K	Ea kJ mol^{-1} l	A	$\Delta H^{\neq}$ kJ mol^{-1} l	$\Delta S^{\neq}$ J mol^{-1} l	$\Delta G^{\neq}$ kJ mol^{-1} l
Cl/I	toluene[b]	0.3	203.2-303.2	9.5 ± 0.4	8.54×10^{3}	7.5 ± 0.4	-171 ± 2	58.3 ± 0.2
Cl/I	methylene dichloride	0.2146	215.0-305.5	17.1 ± 0.3	4.05×10^{6}	14.9 ± 0.3	-120 ± 1	50.5 ± 0.2
Cl/I	chlrorform-d	0.2502	199.0-300.9	12.03 ± 0.4	2.87×10^{5}	10.11 ± 0.08	-141 ± 1	52.12 ± 0.04
Br/I	methylene dichloride	0.2500	207.0-303.0	16.0 ± 0.3	1.11×10^{6}	15.97 ± 0.04	-121 ± 1	51.96 ± 0.03
Br/I	chloroform-d	0.3100	214.5-300.0	10.5 ± 0.8	4.77×10^{4}	11.04 ± 0.04	-143 ± 1	53.80 ± 0.02

(a) Errors quoted are least squares errors.

(b) Values computed from data of ref. 3.

MRC
Medical Research Council

National Institute for Medical Research
The Ridgeway, Mill Hill
London NW7 1AA

telegrams Natinmed LondonNW7
telex 922666(Natinmed London)
telephone 01-959 3666

reference

18th June, 1975.

NADPH and $NADP^+$ Binding to L.casei Dihydrofolate Reductase

Dear Barry,

We are involved in studies of ligand binding to dihydrofolate reductase (M.Wt.17,800) an enzyme which catalyses the NADPH-linked reduction of dihydrofolate to tetrahydrofolate. Recently we have been looking at the ^{31}P spectra of the tightly bound coenzyme-enzyme (1:1) complexes. To our surprise at 40.5 MHz we observed relatively narrow absorption bands which allowed us to measure, for the first time, coupling constants in a ligand strongly bound to an enzyme.

The 2'-phosphate signal is shifted downfield on binding and its bound shift is pH independent over the range pH 4.5 to 7.5. Its chemical shift is the same in both the $NADP^+$ and the NADPH complex and its low field value indicates that it is binding in its dianionic form to a positively charged group in the enzyme. For NADPH the two pyrophosphate nuclei have accidentally the same chemical shift in free solution but in the complex they show marked non-equivalence. Thus in the proton noise decoupled ^{31}P spectrum (Fig. 1b) they appear as an AB quartet ($J_{^{31}P-O-^{31}P}$ = 20.8 Hz). In the single resonance ^{31}P spectrum (Fig. 1c) it is obvious that the pyrophosphate phosphorus nuclei are coupling to different extents to their 5'CH_2 protons. From spectrum simulation studies we can estimate the ranges of $J_{^{31}P-O-C-^{1}H}$ vicinal coupling constants for the two phosphorus nuclei and thus obtain information about the C5'-O5' torsion angles in the complex. One of the torsion angles is found to change when the coenzyme binds to dihydrofolate reductase.

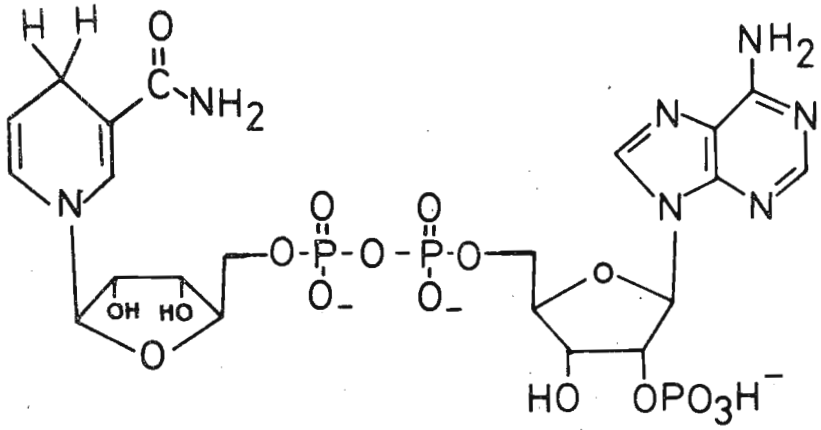
We are extending these studies to investigate the effects of inhibitor binding to dihydrofolate reductase on coenzyme conformation and also to examine coenzyme binding to other dehydrogenases.

We are grateful to Drs. D.G. Gadian and R.E. Richards (Oxford) and R.K. Harris (East Anglia) for allowing us to use their ^{31}P facilities.

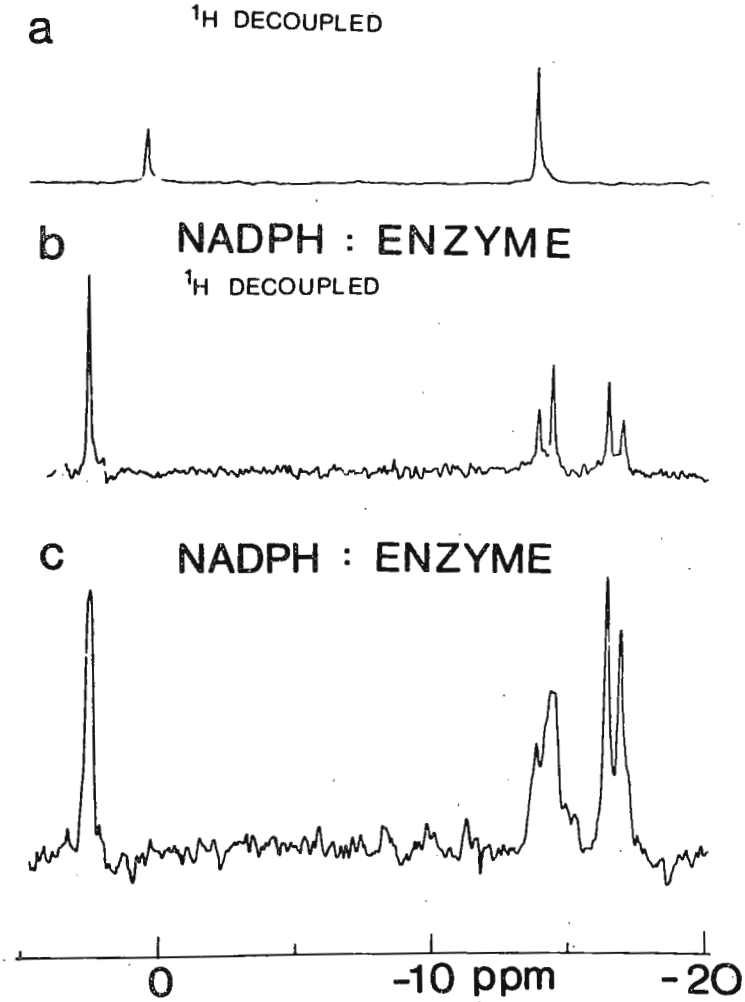
Yours sincerely,

Jim Feeney Berry Birdsall

J. Feeney, Berry Birdsall,
G.C.K. Roberts and A.S.V. Burgen.


H H
O
C NH2
N
O-P-O-P-O
O- O-
OH HO
O
NH2
N
N
N
N
O
HO OPO3H-

^{31}P Spectra


NADPH
a
1H DECOUPLED
b
NADPH : ENZYME
1H DECOUPLED
c
NADPH : ENZYME
0
-10 ppm
-20

UNITED STATES
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PITTSBURGH ENERGY RESEARCH CENTER
4800 FORBES AVENUE
PITTSBURGH, PENNSYLVANIA 15213

June 19, 1975

Dear Barry:

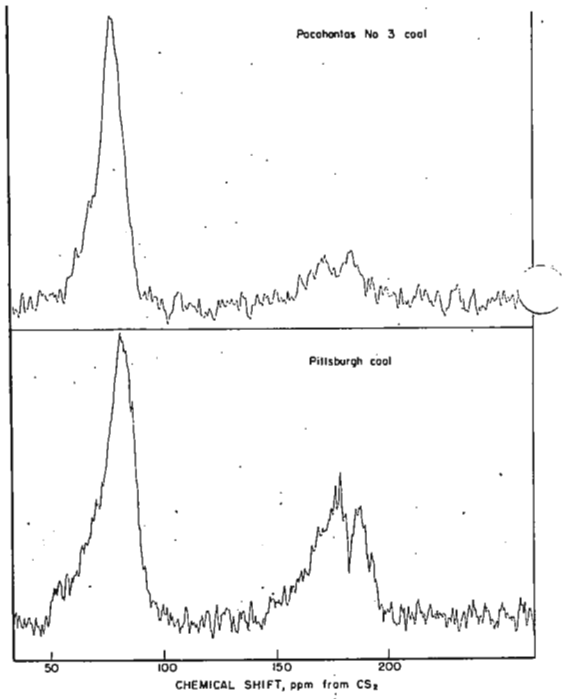
On January 19, 1975, the Pittsburgh Energy Research Center became part of the Energy Research and Development Administration (ERDA); thus, our new letterhead (Hopefully, the blue will reproduce!).

We have recently completed a

STUDY OF CARBON DISULFIDE EXTRACTS OF COAL BY ^{1}H and ^{13}C NMR SPECTROMETRY.

Representative ^{13}C spectra of two of the extracts are shown at the right. These are "coupled" spectra obtained on Joe Dadok's correlation spectrometer at Mellon Institute. NMR intensity data for the extracts investigated are given below:

Coal	Aromatic H / Total H	Aromatic C / Total C
Adaville	0.15	0.44
Pittsburgh	.27	.62
Powellton	.29	.61
Lower Banner	.29	.64
Pocahontas No. 3	.53	.81
Pocahontas No. 4	.50	.78



62.8 MHz ^{13}C nmr spectra of carbon disulfide extracts of coal.

Complementary use of intensity data from NMR of the two nuclei in conjunction with the elemental analysis of the extracts allowed estimates to be made for the average size of the condensed aromatic ring systems and the extent of substitution on the rings.

Two other items: (1) Tom Link, formerly of Mellon Institute recently joined our staff. (2) We have an XL-100 on order.

Sincerely yours,

Herb

H. L. Retcofsky (F. K. Schweighardt, Tom Link, and R. A. Friedel)

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

June 18, 1975

Building 2, Room B2-02

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

Subject: Varian T-1 Special

Dear Dr. Shapiro:

For some time people in our Lab have used the Varian Experimental T-1 program on our HR220, equipped with Varian FT. (30109-M T-1 Research Special)

Also, some of the users have complained about an occasional discrepancy in the result of a sequential T-1 run. Every now and then a spectrum would have a phase different from all the others, and even with the phase corrected the amplitude appeared off.

The problems reported seemed to be confined to relatively strong signals requiring few transients. (NT=5-50)

The reason for this problem turned out to be an occasional shift in the data table by one data point, due to an erroneous data point being picked up at the beginning of the data table. This occurred because the A/D converter is not stopped properly before it gets restarted for a new FID.

By running a short test program, we found that an EXC3 command should be issued to the A/D to stop any operation including the timer. Then the Buffer can be cleared, the timer restarted and the A/D set on its way for the new FID with the first data point conversion after the timer has run down the first time.

The present modification is a quick fix to get things going. We dropped the alfa-timer (Acquisition delay) to make room for the stop command.

At some later date we would like to make the alfa-timer a parameter that can be entered at will.

Location	Before		After	
2145	10230	LDA , ALFA	100360	EXC , ESTP
46	5311	DAR	10352	LDA , VTIM
47	1002	JAP , *-1	103160	OAR , TIMR
50	2146		5000	NOP
51	10352	LDA , VTIM	5000	NOP
52	103160	OAR , TIMR	5000	NOP
53	100260	EXC , EESA	100260	EXC , EESA
54	102560	CIA , VADC	102560	CIA , VADC
55	100261	EXC , MUXS	100261	EXC , MUXS
56	1000	JMP , REDY	1000	JMP , REDY
57	2172		2172	

Please credit this contribution to Dr. E. D. Becker's subscription.

Sincerely yours,

R. Tschudin

Rolf G. Tschudin

RGT:ell

Dr. A. Steigel
Institut für Organische Chemie
der Universität Düsseldorf
Direktor: Professor Dr. L. Birkofer

4 Düsseldorf, den June 20, 1975
Universitätsstraße 1
Fernsprecher 311-2298/99

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

Dear Dr. Shapiro:

SOLVATION AND HYDROGEN BONDING STUDIED BY ^{13}C-T_1 MEASUREMENTS

Setting up a new XL-100 with a VDM 620/L-100 computer I am not yet able to report on studies from my new location. The computer is giving me and the service men from Varian GmbH, Darmstadt, a hard time: although the maintenance test programs cannot detect any error, it happens regularly that, while in the sense loop of a program to wait for new commands, the instructions in the loop are suddenly changed. Sometimes the computer even refuses to store the instructions of the bootstrap.

For this reason I have to resort to a description of two studies, which I had the pleasure to perform together with Dr. George Levy and Dr. Tadeusz Holak at the Florida State University. Both of these investigations have been submitted for publication.

1) Carbon relaxation behaviour of aminobiphenyls in different solvents

As in the case of aniline (Levy, Cargioli, Anet JACS 95 1527 (1973)) the anisotropic overall motion of 4-aminobiphenyl - preferred rotation around the C_2 symmetry axis - is enhanced in acidic solvents. While in CCl_4 the ratio $T_1(2,3)/T_1(4')$ is similar to biphenyl (1.9), it is 2.6 and 3.2 in acetic and trifluoroacetic acid respectively. An interesting effect is revealed by comparing the T_1 values for C-2', 3' with C-2, 3: one generally observes ratios greater than one, the biggest ratio for CH_3CO_2H (1.45), the smallest one for CF_3CO_2H as solvent (1.03). For all other studied solvents (CCl_4, $Cl_2C{=}CCl_2$, CH_3OH) as well as for the trifluoroacetate dissolved in CH_3OH the ratio is between 1.1 and 1.2. We attribute this behaviour to an internal motion of the two phenyl rings around the C_2 axis, the motion of the substituted ring being more hindered by the solvent cage around the amine and ammonium group. In the case of CF_3CO_2H it seems reasonable to assume the unsubstituted ring to be also strongly solvated (hydrogen bonding).

For 3-aminobiphenyl the situation is more complex due to lack of symmetry. Nevertheless it is possible to simulate the T_1 data by assuming two preferred rotations, i.e. around the biphenyl axis and around an axis through C-3 and C-6 of the substituted ring.

2) Hydrogen bonding of chlorinated phenols

^{13}C-T_1 data can be used to distinguish between intra- and intermolecular hydrogen bonding because higher aggregation shortens T_1 values. Thus in the case of chlorinated phenols (2M in CCl_4) the T_1's for phenols without ortho-chlorines are about half as large as for o-chlorophenols which are undergoing intramolecular hydrogen bonding.

Addition of paramagnetic $Cr(acac)_3$, known to be a proton acceptor changes the situation. In this case electron-nuclear dipole-dipole interactions dominate the ^{13}C-T_1's. Using the T_1 values for the "inert" solvent CCl_4 and performing competition experiments (chlorinated phenols with phenol or 2 6-dimethylphenol) we have been able to obtain information about the different factors governing the hydrogen bonding.

Sincerely yours

Alois Steigel

(A Steigel)

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WP 60

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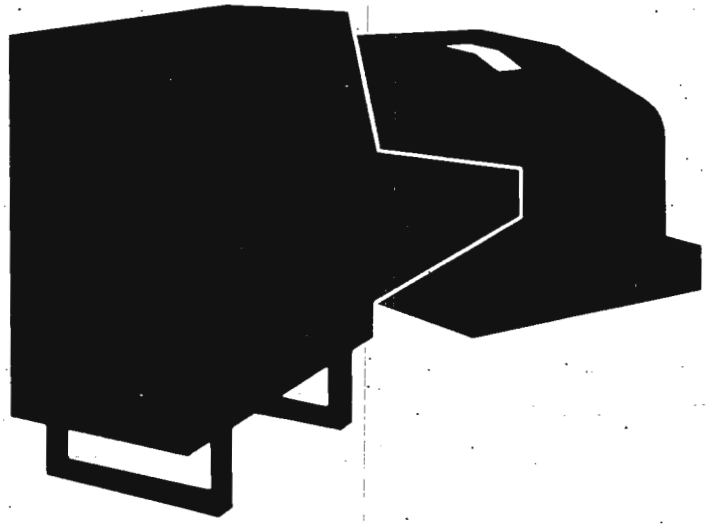

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DEPARTMENT OF PHYSICS

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

June 19, 1975.

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

Dear Barry;

Thank you for your blue reminder.

RADIATION FEEDBACK.

In our last contribution (195-12) we discussed a classification of radiation damping effects based on the value of the radiation-damping time-constant in relation to T_2 and to the electrical circuit time-constant. We showed some line narrowing effects resulting from weak negative "damping", and we now have some spectra taken with radiation feedback in phase-quadrature relative to the stimulating radiation.

Radiation "damping" originates from a feedback mechanism that returns to the sample part of the radiation emitted from the sample. In NMR, this mechanism normally operates via the tuned receiver coil: The voltage induced in this coil by the precessing magnetization causes a current to flow which generates a magnetic field acting back on the sample. There are several phase angles involved in this process: The x-y magnetization lags the stimulating H_1 by 90° on resonance and the induced voltage is in quadrature with the magnetization, but the current in the tuned receiver coil is in phase with the induced voltage. The reaction field is then 180° out of phase with the stimulating H_1 field, and this results in line broadening for strong resonances: H_1 is opposed most at the peak of a resonance, the peak height is reduced and the line appears broadened. Connecting the receiver coil through an electronic amplifier to the transmitter coil makes it possible to overcome this mechanism and to generate a feedback field in-phase with the stimulating H_1 field, and this gives the line narrowing reported earlier.

By the same electronic means, it is also possible to generate a feedback field in phase quadrature to the stimulating H_1 field at resonance. This scheme leaves the line width unchanged but it shifts the line frequency to higher or lower values depending on whether the phase angle is +90° or -90°. The amount of the frequency shift depends on the feedback gain as shown below in the upper row A-D of H^1 field-sweep spectra from a degassed sample of neat TMS. Spectrum A is without additional electronic feedback, the two satellites arise from coupling with the Si^{29} isotope of 4.7% abundance and spin 1/2 with J = 6.88 Hz

Prof. B. L. Shapiro

giving a frequency scale for the spectra. The main line is broadened by the normal radiation damping mechanism and, for this reason, neither peak heights nor areas correspond to the isotope ratio. Spectra B-D are from the same sample with increasing frequency shift of the main line by means of electronic radiation-feedback in quadrature-phase. The satellite lines are too weak to be affected directly by feedback of their own radiation, but they are strongly influenced by the main line especially when the main line is shifted on top of one of the satellites as in spectrum C. Trace D shows the main line shifted to just beyond the right hand satellite.

Turning now to the lower figure, trace B shows the main line (noisy) shifted still farther to the right with more feedback gain. On the left is the unperturbed spectrum, the feedback loop was closed near the middle of trace B where the transient appears, and the shifted line was traced in both directions. The line shapes for the two scan directions do not quite coincide because of the time delay in the recorder filter. Trace B (and also all traces in the upper row) was taken with a weak H_1 to avoid saturation of the resonance. Traces C, D, E in the lower part show what happens when H_1 is increased and saturation sets in: The two sweep directions no longer coincide because discontinuities appear in the line shape and a hysteresis effect becomes apparent. An explanation is offered in graph A. The line shape is slanted towards the unperturbed resonance frequency because saturation at the peak reduces the z-magnetization and decreases the feedback shift (as for a weaker resonance). The line shape curve is unstable in the "foldover" region, and the trace jumps where the slope is vertical as is indicated with the dashed lines. The upward jump occurs when the line is scanned from left to right, the downward jump for the opposite sweep direction, and this gives the hysteresis as in trace E. More details on these and other radiation feedback effects will be published in the Journal of Magnetic Resonance toward the end of the year.

POSTDOCTORAL POSITION

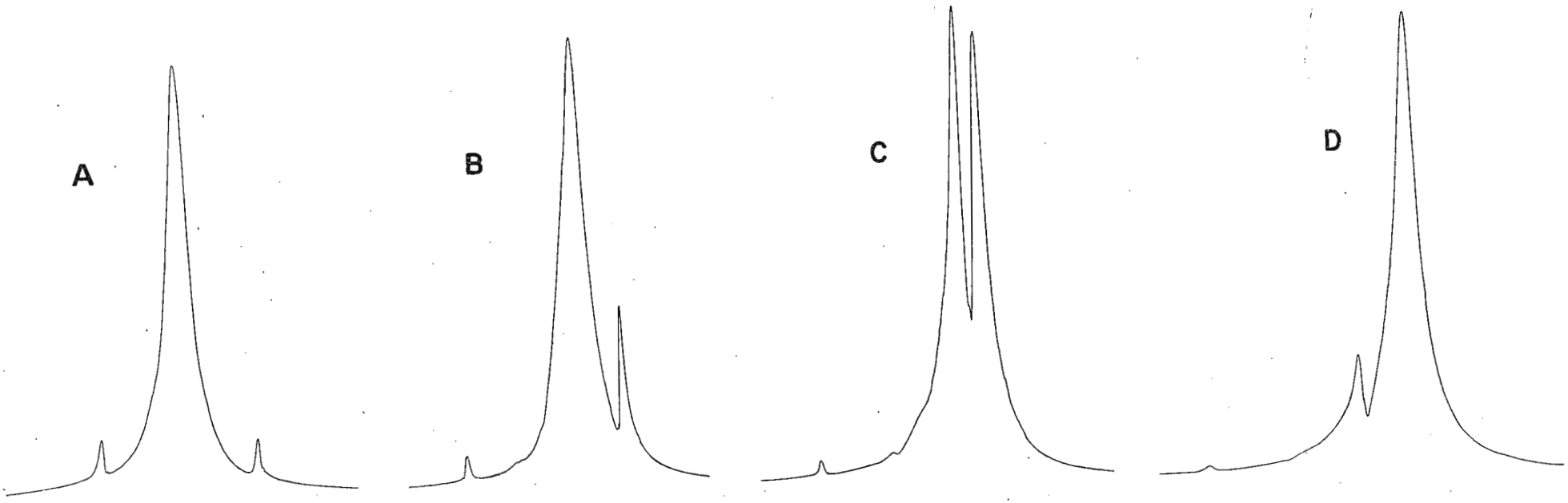
We expect to have a postdoctoral teaching position available for this year or next, and I would be pleased to hear from interested recent physics Ph.D.'s.

Sincerely yours,

Reinhold

R. Kaiser
Professor

RK/vmm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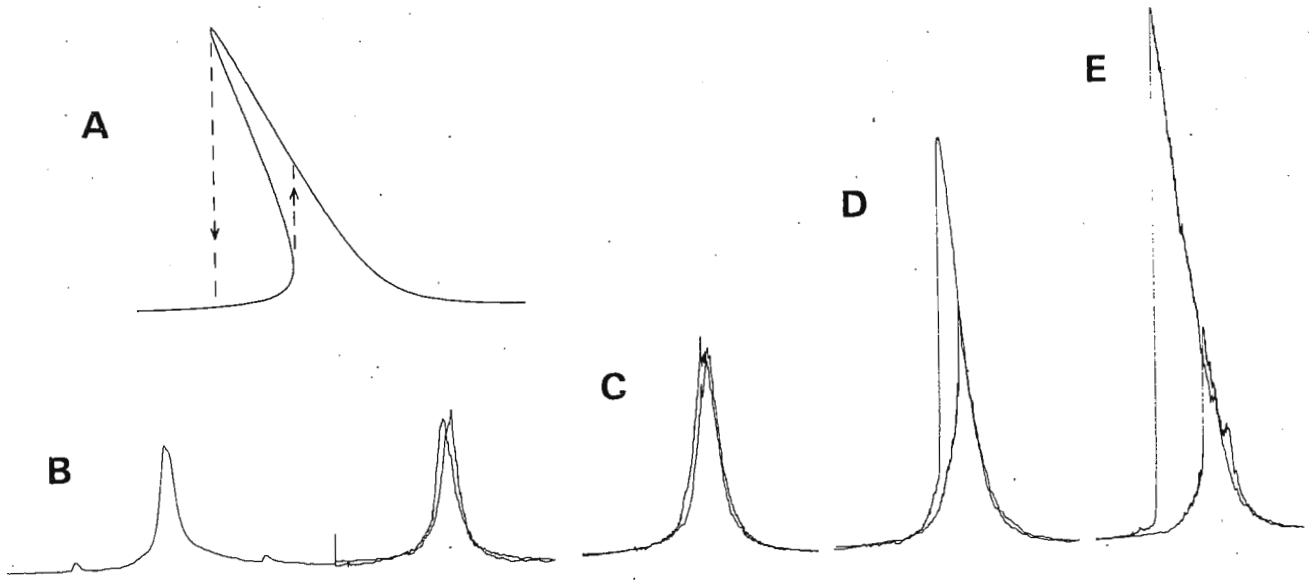
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Hunter College

OF THE CITY UNIVERSITY OF NEW YORK | 695 PARK AVENUE, NEW YORK, N.Y. 10021 | DEPARTMENT OF CHEMISTRY

(212) 360-2351

25 June 1975

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

Dear Barry:

Title(s): ^{13}C Spectra of Hordenine and Arecoline; Postdoctoral Positions Available; Research Associate Position Available.

While your pink slip is not as shattering as those some other New York City employees have been receiving, it's nonetheless serving its purpose. We hope our subscription will be maintained.

We have been looking at ^{15}N chemical shifts of several series of alkaloids and model compounds, and of course attempt to correlate results with other spectroscopic data. Our literature perusal revealed that the carbon spectra of a number of alkaloids, probably for good reason, have not been determined, so while our JEOL PS-100 was up on ^{13}C we looked at those which are of interest for our nitrogen studies. Here we report the shifts of the title compounds, given in the formulas below. Resonances were assigned on the basis of known substituent effects and single-frequency off-resonance decoupled spectra. Probably the main point of interest is the differentiation between C-2 and C-6 of arecoline. This was done by comparing the residual splitting of each of the resonances in the off-resonance spectra when the decoupler was set at ca. 10 ppm. Because the proton resonance of H-2 lies at lower field than that of H-6, the residual $^1J_{CH}$ should be smaller for C-2 than for C-6, assuming $^1J_{C_2H}$ is greater than or not much less than $^1J_{C_6H}$. The assignments were made on this basis. The shifts of the α and β carbons on protonation are consistent with previous observations on amines.

Item 2: I (i.e., R.L.L.) am looking for one or two postdoctoral fellows to continue in carrying out our natural-abundance ^{15}N studies of antibiotics, alkaloids, and related model compounds. The main qualifications are a good chemical background, some familiarity with nmr, and a willingness to live and work in New York. Salary will be no less than $9000 plus fringe benefits. Interested parties should send a resume and

at least two letters of recommendation .

Item 3: our department has a Research Associate position for an electronics engineer with a BSEE or equivalent. Responsibilities include maintenance of research and instructional equipment, and the design and construction of modifications or improvements to existing research equipment. Applicants should have a thorough knowledge of digital electronics and computer technology. The appointee could expect to collaborate extensively with about 7 of our 17-person department. Salary will be competitive and commensurate with experience. Applicants should send resumes and three letters of reference to Chairman, Department of Chemistry, at the address in the letterhead.

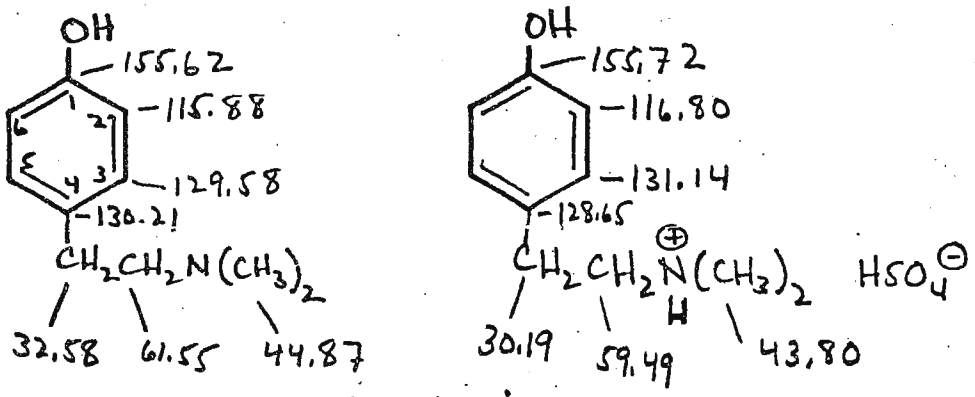
Have a good summer!

Sincerely,

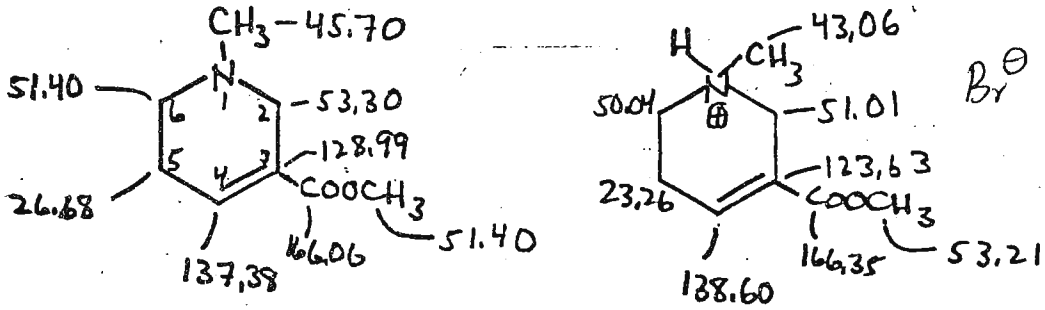
P.R. Srinivasan

Bob

Robert L. Lichter
Associate Professor



hordenine



arecoline

varian/611 hansen way/palo alto/california 94303/u.s.a./415/493-4000

July 1, 1975

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

Dear Barry:

Selective relaxation times and internuclear distances

We have been continuing our measurements of selective proton relaxation in rigid molecules (TAMU NMR 191, 55) and have been attempting to improve the accuracy of the experiments for determining the ratios of internuclear distances.

The experiments involve the measurement of relaxation following selective inversion of one or more protons in a multispin system. Let $R_1^A(\tilde{A})$ be the initial relaxation rate of proton A when it alone is inverted by a selective 180° pulse, and $R_1^A(NS)$ be its initial relaxation rate when all protons are inverted by a non-selective 180° pulse. If the only mechanism determining the relaxation of A is dipolar interaction with other protons, $R_1^A(NS)/R_1^A(\tilde{A}) = 1.5$. If two protons, A and B, are inverted by a selective pulse on each, the initial relaxation rate of A, $R_1^A(\tilde{A}, \tilde{B})$, will be greater than $R_1^A(\tilde{A})$ depending on the fraction, f_B^A, of the relaxation of A arising from the dipolar interaction between A and B:

$$f_B^A = \frac{2\left[R_1^A(\tilde{A},\tilde{B}) - R_1^A(\tilde{A})\right]}{R_1^A(\tilde{A})}$$

The fractional contributions from two nuclei, B and C, may be related to the internuclear distances, r_{AB} and r_{AC}, through the sixth power distance dependence of dipolar interactions:

$$\frac{f_B^A}{f_C^A} = \left(\frac{r_{AC}}{r_{AB}}\right)^6$$

The relaxation following a perturbation will only be exponential if
(a) the spin system is first order
(b) spins which are initially unperturbed maintain their equilibrium populations
(c) all spins which are perturbed relax at the same rate.

Requirement (a) is satisfied by a careful selection of the sample. Requirements (b) and (c) may be satisfied by even more careful selection of the sample! Often though, (b) is approximately observed in multispin systems, particularly when only one spin is inverted, since this represents a minor perturbation to the total system. We have found it possible to determine the selective relaxation rate $R_1^A(\tilde{A})$ with an accuracy of ~2%. If requirement (c) is also approximately satisfied, other relaxation rates may be determined to ~2% and the fractional dipolar interaction between a pair of protons to an absolute limit of about ± 0.05. The accuracy of internuclear distance ratios will vary with their magnitude and the best that we have observed is ~5%.

If requirement (c) alone is violated, the relaxation will be non-exponential but a simple numerical solution may be found using measured experimental parameters, with the fractional dipolar contribution as the free variable. In this case the error in the dipolar contribution is $\sim \pm 0.1$ and the best accuracy of distance ratios is ~10%.

We have recently tried to use a selective 90° pulse to perturb proton A and selective 180° pulses to perturb other protons. This doubles the disperson in relaxation rates but, since the absolute perturbation of proton A is lower, the signal to noise ratio of the experiment is reduced. Further experiments are needed to determine if this is a useful trade-off.

As a method of measuring internuclear distance ratios, selective relaxation experiments seem to offer promise as an alternative to static NOE measurements. The NOE experiment is complicated by multiple spin interactions--just the interactions which help to keep initially unperturbed spins at their equilibrium populations (condition (b) above).

Yours sincerely,

Howard.

H.D.W. Hill

CARLETON UNIVERSITY

OTTAWA, CANADA
K1S 5B6

DEPARTMENT OF CHEMISTRY

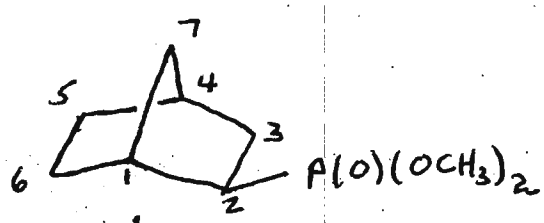
July 3, 1975

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

Title: "Substituent Effects on C-C-C-P Coupling In Phosphonates of Known Stereochemistry"

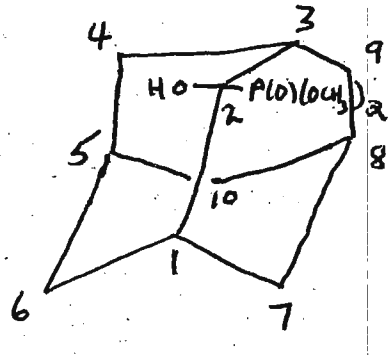
Dear Barry:

The angular dependence of vicinal C-P coupling has been reported for a number of systems including cyclic nucleotides[1] and phosphine oxides[2-4]. We wish to report some results for dimethyl phosphono compounds that suggest that considerable caution should be used in attempts to relate $^3J_{CP}$ with dihedral angle in these molecules. For 1, the coupling from C-6 to ^{31}P is 18.4 Hz for $\theta \simeq 180^0$. When $\theta \simeq 120^0$ (i.e. ^{4}C-C-C-P), J = 1.8 Hz and for $\theta \simeq 90^0$ (i.e. ^{7}C-C-C-P), J is not resolvable (less than 0.6 Hz).



1

For 2, however, the coupling from C-4,6 to ^{31}P is only 11.8 Hz for $\theta \simeq 180^0$. It is known for vicinal H-H coupling[5] that electronegative groups decrease ^3J, however, the maximum influence (lowest positive J) is observed when the electronegative group i.e. the OH in 2, is trans - coplanar to a terminus of the coupling path.[6]

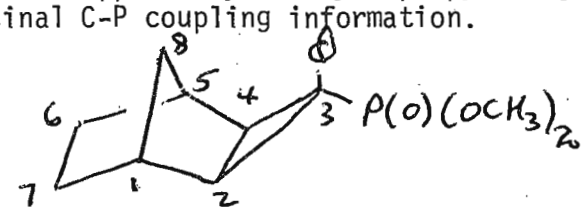


2

Prof. B.L. Shapiro July 3, 1975

This is perhaps the reason for the small $^{7,9}C-^{31}P$ coupling (0.7 Hz) for $\theta \simeq 60^0$ in 2. For the tricyclic case 3, $\theta \simeq 170^0$ for the path P-C-C-$^{1,5}C$, yet J is only 6.1 Hz. Apparently the cyclopropyl ring is a rather inefficient transmitter of vicinal C-P coupling information.

3



Some examples of this phenomenon for vicinal $^1H-^{31}P$ vicinal coupling are known.[7]

For compound 4, which is epimeric at C-3 to 3, J for the path $^{1,5}C$-C-C-P = 1.1 Hz, for $\theta \simeq 10^0$, indicating a highly asymmetric $|J|$ vs θ curve in phosphonates, by contrast to results for phosphine oxides.[2-4] Also, there appear to be some interesting "non W" long range P-C J's in these compounds.

Please credit this to John ApSimon's subscription.

Sincerely,

G. W. Buchanan
Associate Professor

GWB:lm

References

1. Lapper, et. al., JACS 94, 6243 (1972).
2. Gray, et. al., J.O.C. 37, 3458 (1972).
3. Wetzel et. al., JACS 94, 9330 (1972).
4. Wetzel et. al., Chem. Comm. 287 (1973).
5. Jackman and Sternhell, "Applications of NMR in Org. Chemistry".
6. Booth, Tet. Letters 411 (1965).
7. Benezra, JACS 95, 6890 (1973).

UNIVERSITY OF SASKATCHEWAN

DEPARTMENT OF CHEMISTRY
AND CHEMICAL ENGINEERING

SASKATOON, CANADA
S7N OWO

July 4, 1975

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

Dear Dr. Shapiro:

We have just started up a Bruker WP-60 Pulse NMR at the University of Saskatchewan. The instrument is equipped for ^{13}C and ^{1}H studies. We are looking for a postdoctoral fellow with pulse-FT NMR experience to work on this instrument starting in the fall. Preference will be given to candidates also having organometallic experience. Applicants should include the names of two referees with their curriculum vitae.

Yours truly,

Wilson Quail

J. Wilson Quail

JWQ/crm

THE UNIVERSITY OF TEXAS AT AUSTIN
AUSTIN, TEXAS 78712

Department of Chemistry

June 30, 1975

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

A Proper Chart Paper for ^{13}C Spectra

Dear Barry,

Our Bruker WH 90 arrived a few months ago and we have been running ^{13}C and ^{31}P spectra as fast as we can. We have had numerous small shake down problems, however they are much less frequent now. In general we have been pleased with the spectra we have been getting.

Bruker (as well as Varian and JEOL) has chosen to print its chart paper in a way that is very unhandy for ^{13}C spectra. The paper is printed to be used with an integral number of Hz and a nonintegral number of ppm. They have then put dotted lines for the principal marker of δc but have no small divisions. The paper is thus not readily useful for estimating chemical shifts in complex spectra. I have inquired and found that a proper chart paper could be printed, however, there will be a sizeable set-up charge. This charge would not be very much, however, if eight or ten laboratories could share the expense.

I have in mind a chart paper with 200 ppm full width. If anyone else is interested in sharing this set-up charge, please contact me.

Sincerely,

Ben A. Shoulders

Ben Shoulders

Please credit this contribution to the account of Dr. Charles Wade.

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POUL E. HANSEN and ARNE BERG

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Telefon (06) 12 46 33

June 30, 1975
/EL

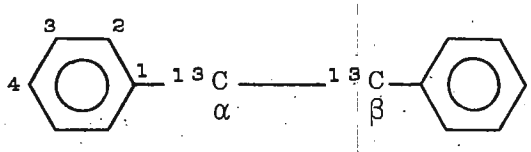
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
COLLEGE STATION, Texas 77843
USA

Relative Signs of ^{13}C-^{13}C Coupling Constants

Dear Prof. Shapiro,

Knowledge of signs of ^{13}C-^{13}C coupling constants may prove important in a number of cases: For evaluating the quality of theoretical calculations; in determining substituent effects; and in attempts to correlate ^{13}C-^{13}C coupling constants with other parameters.

We have succeeded in determining such signs in a very simple way by means of doubly labelled symmetric compounds, one type of which is shown:



If such a molecule is labelled in both positions marked α and β, a ring carbon, say C-1, may be the X-part of an AA'X system and thus showing a triplet with the separation $|J_{AX} + J_{A'X}|$ providing $|J_{AA'}|$ is sufficiently large. If the enrichment is not complete (50 or 75% is appropriate), molecules with a single label or no label at all will exist, giving rise to proton decoupled ^{13}C NMR signals of AX systems or non-coupled carbons, respectively. From the superimposed spectra of C-1 the quantities $|J_{AX} + J_{A'X}|$, $|J_{AX}|$ and $|J_{A'X}|$ can be measured. A comparison between these quantities will give the relative signs of J_{AX} and $J_{A'X}$.

The method described is attractive in more respects:

(i) Proton decoupling gives good S/N ratio and no auxiliary instrumental parts are needed.

(ii) The relative signs can be determined if only the splittings can be observed.

(iii) Synthesis of several doubly enriched symmetri-

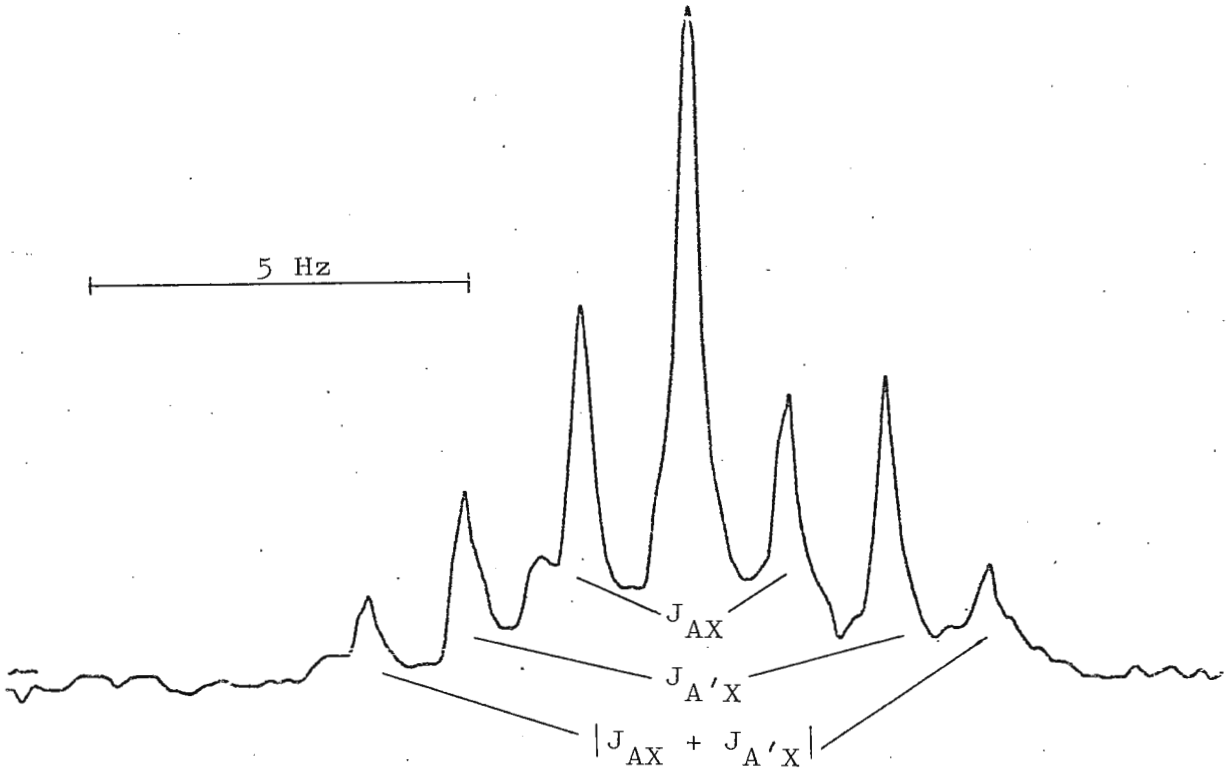


Fig.1. The ^{13}C proton noise-decoupled spectrum of C-1 in phenanthrene-9,10-$^{13}C_2$ (50% enriched)

(iv) The method is economical since a whole series of compounds can be made from one singly labelled starting compound, *e.g.* benzaldehyde →benzil → benzildihydrazone → diphenyl acetylene → cis-stilbene → phenanthrene.

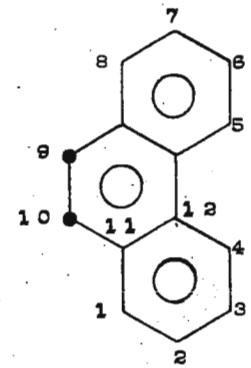
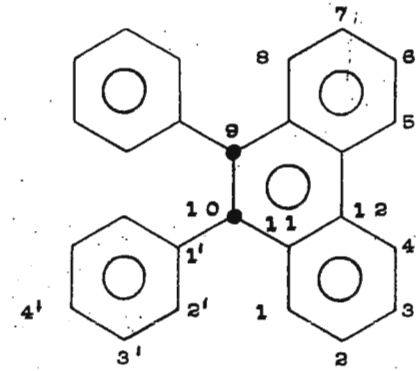
Table 1 shows the data for phenanthrene and 9,10 diphenylphenanthrene. Note that the two-bond coupling constants are positive if not zero. An alternation of the signs of ^{13}C-^{13}C coupling constants in aromatic compounds is obviously not a reality, although it would have been nice.

Please credit this contribution to the subscription of this institute.

Sincerely yours,

Poul E.Hansen Arne Berg

Table 1. $^{13}C-^{13}C$ coupling constants in phenanthrenes. Comparison of signs.

				
$^{1}J(C(11)-C(10))$	+54.8	+54.3	$^{1}J(C(1')-C(10))$	+56.2
$^{2}J(C(11)-C(9))$	+1.8	0.1	$^{2}J(C(1')-C(9))$	+1.3
$^{2}J(C(1)-C(10))$	(+)2.70	(+)1.84	$^{2}J(C(2')-C(10))$	(+)2.1
$^{3}J(C(1)-C(9))$	(+)5.50	(+)4.20	$^{3}J(C(2')-C(9))$	(+)1.1
$^{2}J(C(12)-C(10))$	0	0		
$^{3}J(C(12)-C(9))$	5.70	5.24		
$^{3}J(C(2)-C(10))$	5.15	4.33	$^{3}J(C(3')-C(10))$	3.42
$^{4}J(C(2)-C(9))$	0	0	$^{4}J(C(3')-C(9))$	0
$^{3}J(C(4)-C(10))$	(+)1.8 (±3.0)[a](±3.0)	+1.4 (±3.1)[a](±3.1)		
↕		↕		
$^{4}J(C(4)-C(9))$	(+)1.2 (∓1.2) (∓1.8)	+1.7 (∓1.4) (∓1.7)		
$^{4}J(C(3)-C(10))$	0	0	$^{4}J(C(4')-C(10))$	0
$^{5}J(C(3)-C(9))$	0	0	$^{5}J(C(4')-C(9))$	0
$^{1}J(C(9)-C(10)$		67.2		

[a] Most likely combination.

ת.ד. 2053
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הפקולטה למדעי הטבע
המחלקה לכימיה
FACULTY OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

אוניברסיטת בן־גוריון בנגב
BEN GURION UNIVERSITY OF THE NEGEV

תאריך: /DATE מספרנו: /OUR REF. June 27, 1975

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

Dear Professor Shapiro

TITLE: SUPERCOOLED LIQUID CRYSTALS, T_1 MEASUREMENTS

In the process of measuring the effects on spin lattice relaxation of lengthening the side chains of some nematogens we discovered that underappropriate conditions the nematic range can be considerably extended by supercooling. In the course of our measurements we were struck by the fact that Arrhenius plots of the datayielded a straight line for each liquid crystal we examined (PAA,EBBA,MBBA and APAPA) and furthermore, the activation energies were quite close for all of the species (5-6 kcal/mole). Recently, Doane, Tarr and Nickerson(1) have proposed that the relaxation for such nematogens as PAA and MBBA is due to a common mechanism and that the apparent differences in T_1 vs frequency measurements are due to a cutoff frequency dependent upon the length of the molecule. Our datacan support this idea since now the temperature behavior for all of the nematogens are seen to be the same. Tentatively we attribute the temperature behavior to viscosity related effects having gotten good agreement with the activation energies reported by Meiboom and Hewitt(2) for viscosity measurements on nematic liquid crystals. Credit for this work also goes to my colleagues Drs. Shaul Goren and Charles Korn of the physics department.

Please credit this contribution to the account of Dr. D. Kost.

Sincerely,

Stephen Marks

1) Doane, Tarr and Nickerson, Phys., Rev. Lett., 33, 620, (1974).
2) Meiboom and H ewitt, Phys. Rev. Lett., 30, 261, (1973).

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

CHEMISTRY AND LIFE SCIENCES DIVISION

June 16, 1975

WORKSHOP ON THE APPLICATION OF ^{1}H and ^{13}C FT-NMR
TO SUBMILLIGRAM SAMPLES

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

Dear Barry:

The Chemistry and Life Sciences Division of the Research Triangle Institute and the Department of Chemistry at North Carolina State University are making plans to sponsor a workshop on the application of ^{1}H and ^{13}C FT-nmr to submilligram samples. At present we plan to hold the workshop on November 24 and 25, 1975 in Raleigh at the Hilton Inn. The costs of the rooms are $17.00 for singles and $22.00 for doubles. The registration fee will be $15-$20 and will depend on the number of participants.

We would like to know if you or any of your co-workers would be interested in this type of workshop. Please let us know of your interest as soon as possible. If sufficient interest is forthcoming, we will be sending out detailed information.

Sincerely yours,

F. I. Carroll

Charles G. Moreland

/ssm

Enclosure

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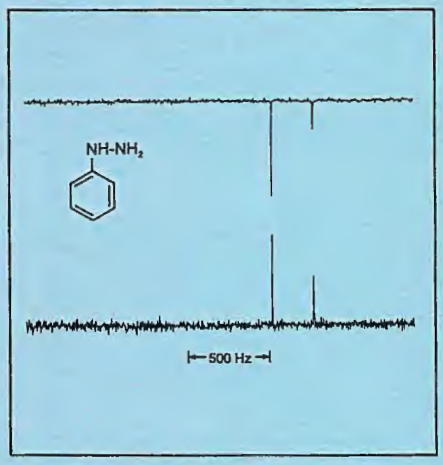
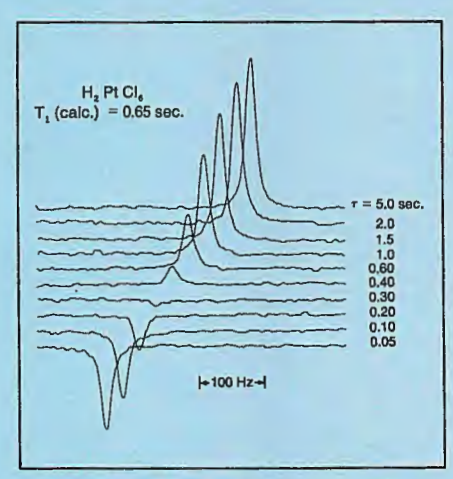
Let us send you our brochure on the GyroCode Observe Accessory. If, on the other hand, you do not own an XL-100 — this may be the time to reconsider. Write Varian Instrument Division, Box D-070, 611 Hansen Way, Palo Alto, California 94303.



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°-τ-90°) pulse sequence was used in the automatic measurement of the spin-lattice relaxation time (T_1) for the ^{195}Pt nucleide.

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

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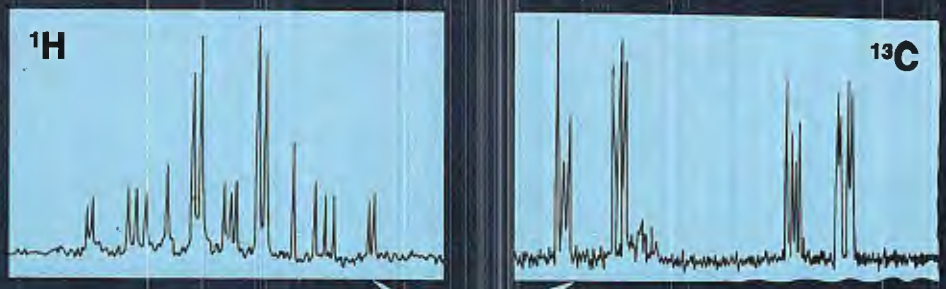

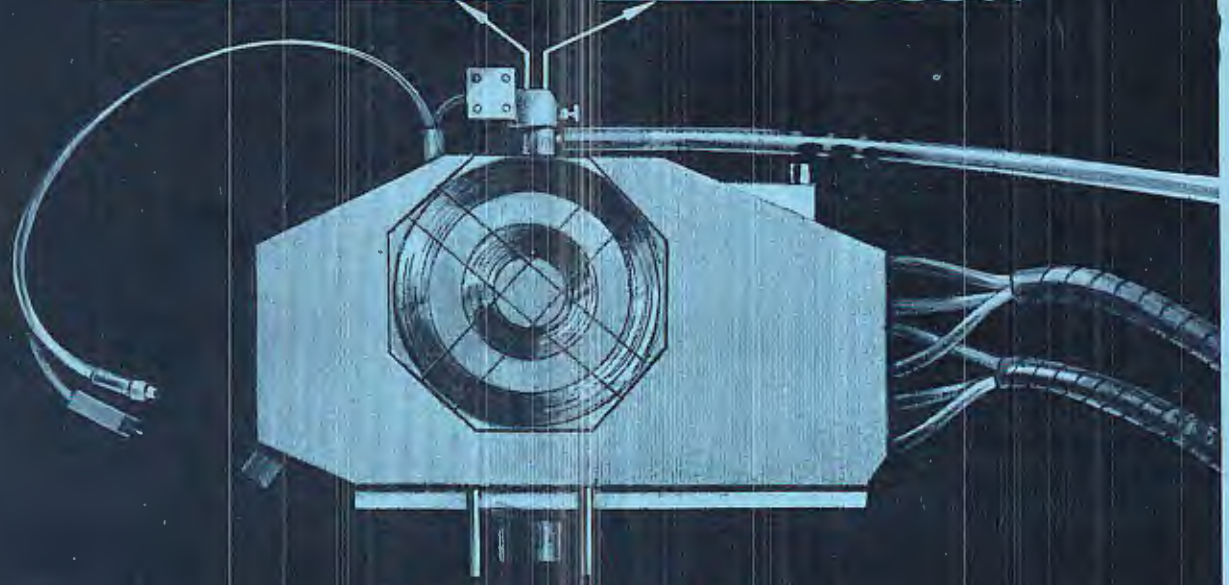

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Spectra: ^{1}H of ODCB; ^{13}C of ODCB with proton spin-coupling.