Texas A and M University  
N-M-R Newsletter  
July, 1975  
No. 202

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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.

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B. L. Shapiro
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.

D LN:an

University of Nebraska Medical Center, 42nd and Dewey Avenue, Omaha, Nebraska  68105
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 moiety quite accurately. It is given below with other molecules for comparison.

Yours sincerely,

P. Diehl  A.S. Tracey
<table>
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<th>COMPOUND</th>
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<td>ethylene</td>
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<td>1.653</td>
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<td>zeise's salt</td>
<td>1.940</td>
<td>1.672</td>
<td>-</td>
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<tr>
<td>ethylene sulphide</td>
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<td>ethylene oxide</td>
<td>1.353</td>
<td>1.682</td>
<td>2</td>
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</table>

*errors in distance ratios are less than 0.002

References:
3. $\delta$PtH in isotropic micellar soap solution is $66.22 \pm 0.06$ Hz
Dear Professor Shapiro,

As a result of your reminder Dr. Bovee, who does the HR-NMR work in our group, has written the following note about relaxation measurements on AB systems.

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.; 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 \( \pi \) radians about the C8-C9 and C9-R bond, only two occur, namely those in which the CH3 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 former in which the C7-C8 and C9-O double bonds are trans to the C8-C9 bond has an energy which is at least 0.7 kcal/mol lower than the corresponding cis conformer. The correlation time for molecular re-orientation 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 \(^{1}H\)N-H coupling constants in this molecule is found:

Fig. 1
\[ J_{\text{NA}} = \pm 0.95 \pm 0.07 \text{ Hz} \]

\[ J_{\text{MA}} = \pm 0.47 \pm 0.09 \text{ Hz} \]

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

Yours sincerely,

Dr. W.M.M.J. Bovee

\(^*)\) 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. Bovee.

Prof. Dr. Ir. J. Smith

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

The t.-Butyl-Group as Sensor Group

Forced by your blue reminder we would like to present some preliminary results of C¹³ measurements of a series of substituted t.-butyl-benzenes¹).

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 benzenes²). Least squares analysis shows a very good Hammett type correlation of these data, which is not too common for aliphatic carbon atoms³). 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 week⁴) 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
1) VARIAN CFT-20, 1-molar CDCl₃ solutions.

2) Some of the compounds have been already reported, cf. J.B.Stothers, C¹³ NMR Spectroscopy, Academic Press 1972 and C.D.Schaeffer, J.J.Zuckermann and C.H.Yoder, J.Organo- 


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

\[
\begin{align*}
N\equiv N^\bigoplus & \quad 6.88 \\
K\equiv O & \quad 4.35 \quad 4.89 \\
C\equiv N & \quad 4.30 \\
COOH & \quad 4.06 \\
COCH₃ & \quad 3.98 \\
COOEt & \quad 3.89 \\
J & \quad 3.38 \quad 6.73 \\
COO⁻ & \quad 3.38 \\
H & \quad 3.21 \quad 3.21 \\
Br & \quad 3.26 \\
Cl & \quad 3.17 \\
Phenyl & \quad 3.13 \\
OCOOH & \quad 3.02 \quad 4.21 \\
F & \quad 2.84 \\
CH₃ & \quad 2.83 \\
t.-Butyl & \quad 2.71 \\
OH & \quad 2.52 \quad 4.85 \\
OCH₃ & \quad 2.46 \quad 3.02 \\
NH₂ & \quad 2.28 \quad 4.59 \\
N(CH₃)₂ & \quad 2.18 \quad 4.64 \\
O⁻ & \quad 1.04 \quad 4.64
\end{align*}
\]

a) in CD₃OD as R-N≡N^\bigoplus BF₄^\bigoplus 
b) in D₂O 
c) in DMSO-d₆
T₁ Errors on a Bruker HX-90 with a 1083 Computer.

Dear Prof Shapiro,

We have started an extensive programme of ¹H, ¹⁵N and ¹³C T₁ studies on a variety of compounds and at an early stage in these investigations it became apparent that the measured values of the T₁ 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 ¹³C) 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 time 1.76 μsec). This meant the T 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 by locating O1520 and is reset from O144 to O120. The T values typed in now correspond to those actually used.

We would recommend other Bruker users to check this point out before doing any T₁ studies.

Yours sincerely,

D. Doddrell

R. Bendall
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 $(\text{CF}_3\text{P})_4$ and $(\text{tBuP})_4$ dissolved in liquid crystals.

The experimental and theoretical spectra of $(\text{tBuP})_4$ 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 $(\text{tBuP})_4$ and 24° for $(\text{CF}_3\text{P})_4$). For this latter molecule, the result is in good agreement with X-ray data (PALENIK and DONOHUE, Acta Cryst., 12, 564, 1962).

- The chemical shift anisotropy $\Delta \sigma = \sigma_{2z}^0 - \frac{\sigma_{xx}^0 + \sigma_{yy}^0}{2}$ which are equal to +167 ppm and +141 ppm respectively for $(\text{tBuP})_4$ and $(\text{CF}_3\text{P})_4$.

- And finally the $J(PP)$ n.m.r. coupling which was not accessible from n.m.r. spectra in isotropic liquid. One obtains 148.4 Hz for $(\text{tBuP})_4$ and 100.6 Hz for $(\text{CF}_3\text{P})_4$. These small values as compared with the one measured in other cyclopolyphosphines of diposphines 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 $|J(PP)|$.

Sincerely yours,

J.P. ALBRAND
A. COGNE
J.B. ROBERT
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Specifications subject to change without notice

Printed in USA
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, $C_6D_8$). $^{15}$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$_3$ 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 $\alpha$-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
NOISE DECOUPLED
RANGE 6024 Hz (HIGH FIELD PART PLOTTED)
PULSE WIDTH 3 μs (25°)
REPTITION 15
PULSES 16 K

^D 15.3583540 MHz
^C 25.1500974 MHz

SELECTIVELY DECOUPLED
^H 99.981979 MHz
PULSES 16 K
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(415) 948-9053

941 Sherwood Lane, Los Altos, Ca. 94022 (415) 948-9053
Dear Professor Shapiro,

June 2, 1975

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.A. KNIGHT
Analytical Branch
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 H₃ 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 Miller¹ dealt with p-substituted toluenes (II), while Fraser and co-workers² 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 H₄ and H₅ 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

The plot of the chemical shifts of H₄ 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 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

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.

Young Sincerely,

George C. Levy
Associate Professor

GCL/dlh
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Fisher Scientific Company
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 1H n.m.r. spectra (HA-100) of 6-deoxy-6-fluoro-1,2,3,4-di-O-isopropylidene-α-D-galactopyranose.

![Diagram]

The spectrum in B shows the normal spectrum and that in A the spectrum obtained with simultaneous irradiation at the 19F 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.
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,

L. D. Hall

L. Evelyn
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:

$$
\begin{align*}
\text{CH}_3 & \quad 14.1 \\
\text{CH}_2 & \quad 62.1 \\
\text{O} & \quad 54.3 \\
\text{S} & \quad 170.0 (J = 4.8) \\
\text{C} = \text{O} & \quad 43.3 (J = 3.1) \\
\text{CH} & \quad 37.9 (J = 3.7) \\
(\text{CH}_3\text{O})_2\text{P}-\text{S}-\text{CH} & \quad 171.6 (J = 3.7)
\end{align*}
$$

$$
\begin{align*}
\text{CH}_2 & \quad 169.9 \\
\text{O} & \quad 38.1 (J = 3.6) \\
\text{C} = \text{O} & \quad 171.6 \\
\text{CH}_3 & \quad 14.05 \\
\end{align*}
$$

(An equal opportunity/affirmative action employer)
Coupling constants are ± 1.2 Hz. This assignment is consistent with the previous assignment based on proton spectra. (1)

Sincerely yours,

Richard H. Cox
Associate Professor

Dear Dr. Shapiro:

α-Tripiperideine 1 shows a fluxional behaviour in its $^{13}\text{C}-\text{NMR}$ spectra caused by nitrogen inversion/ring inversion. The apparent $C_3$-symmetry (5 lines) at room temperature changes to $C_1$-symmetry below about $-40^\circ\text{C}$ (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,

[Signature]

[Signature]
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.

random exchange

one way exchange

Figure 1: $^{13}$C-DNMR-Spectra of α-Tripiperideine (α-Carbons).
You can update a T-60 for $^{13}$C measurements at a fraction of the cost of a new, dedicated system with the Nicolet TT-7 pulsed FT nmr accessory. The sensitivity provided by this combined system is comparable to that of instruments specifically designed for $^{13}$C spectroscopy. Features offered with the TT-7/T-60 combination include:

- $^{13}$C spectra on 50 mg samples in 15 minutes;
- 6.5 mm sample size;
- no lock material required (expensive deuterated solvents are not required);
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Signal input, accumulated free induction decays, or transformed spectra can be displayed on the TT-7's cathode ray tube for visual monitoring. The spectra can be plotted using the T-60 recorder and digital integration of spectra can be viewed or plotted as well.

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NICOLET TECHNOLOGY CORPORATION
145 East Dana Street
Mountain View, California 94041
Phone: 415/969-2076
(formerly Transform Technology Inc.)
June 11, 1975

Dear Barry:

The axial/equatorial ratio for molecules of the type:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{M} \\
\end{array}
\begin{array}{c}
\text{M} \\
\text{CH}_3
\end{array}
\]

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 (\( \Delta G^0 \approx 1.4 \text{ kcal/mol} \), 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 \( \Delta G^0 = 0.12 \) (2/1 equatorial preference) at \(-110^\circ\) and \(-0.35 \text{ kcal/mol} \) (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 (\( \Delta G^0 = 0, K = 1.9 \)) at \(-140^\circ\). Ring reversal is slow on the nmr time scale (\( T_{1} = 140^\circ \)), \( \Delta G^0 = 6.8 \text{ kcal/mol} \), and separate resonances can be observed for both isomers below \(-140^\circ\) at 270 MHz, using a \( \beta \)-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 reference for the axial conformation. The series N, P, As has a \( \Delta G^0 \) 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 \( M-\text{CH}_3 \) above) would be of interest.

Sincerely,

Joseph B. Lambert

Hsiang-ning Sun

JBL/kp

Title: 1-Methylarsenane
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 (11)-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,

Thomas L. James
Assistant Professor of Chemistry and Pharmaceutical Chemistry

(2) T.L. James and G.G. McDonald, J. Mag. Reson., 11, 58 (1973)
Dr. Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station, TX 77843
U.S.A.

University of Salford
Salford M6 4WT
Department of Chemistry
and Applied Chemistry
Telephone 061-736 5843
Telex 668680 (Univ Salford)

10th June 1975

Dear Dr. Shapiro,

Exchange between trimethyltin halides in solution

The nmr 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 decaesence 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 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. 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 3-coordinate bridged intermediate.

Meanwhile, Brian Glasberg was looking at these exchange systems in CDC13 and CH2Cl2 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 $\Delta S^\circ$ explain why no transition state species is observable but this $\Delta S^\circ$ is consistent with the associative mechanism

\[
\text{Me}_3\text{SnX} + \text{Me}_3\text{SnY} \rightleftharpoons \text{Me}_3\text{Sn} \quad \text{SnMe}_3 \rightleftharpoons \text{Me}_3\text{SnY} + \text{Me}_3\text{SnX}
\]
and with the dissociative mechanism

\[
\text{Me}_3\text{SnX} \rightleftharpoons \text{Me}_3\text{Sn}^+ + X^- \\
\text{Me}_3\text{SnY} + X^- \rightleftharpoons \text{Y} \quad \quad \quad \text{Me} \quad \quad \quad \quad \quad \text{X} \rightleftharpoons \text{Me}_3\text{SnX} + Y^-
\]

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

2. Peregudov et al., Zh. Obshchei Khimii, 42 (1972) 2194.
Table 1. Arrhenius and Eyring Activation Parameters for the Exchanges\(^a\)

<table>
<thead>
<tr>
<th>System</th>
<th>Solvent</th>
<th>Total halide concentration mol (^{-1})</th>
<th>Temperature range K</th>
<th>Ea kJ mol(^{-1}) l</th>
<th>A [^{\Delta H}^#] kJ mol(^{-1}) l</th>
<th>[^{\Delta S}^#] J mol(^{-1}) l</th>
<th>[^{\Delta G}^#] kJ mol(^{-1}) l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl/I</td>
<td>toluene(^b)</td>
<td>0.3</td>
<td>203.2-303.2</td>
<td>9.5 ± 0.4</td>
<td>8.54 \times 10^{3}</td>
<td>7.5 ± 0.4</td>
<td>-171 ± 2</td>
</tr>
<tr>
<td>Cl/I</td>
<td>methylene dichloride</td>
<td>0.2146</td>
<td>215.0-305.5</td>
<td>17.1 ± 0.3</td>
<td>4.05 \times 10^{6}</td>
<td>14.9 ± 0.3</td>
<td>-120 ± 1</td>
</tr>
<tr>
<td>Cl/I</td>
<td>chloroform-d</td>
<td>0.2502</td>
<td>199.0-300.9</td>
<td>12.0±0.4</td>
<td>2.87 \times 10^{5}</td>
<td>10.11±0.08</td>
<td>-141 ± 1</td>
</tr>
<tr>
<td>Br/I</td>
<td>methylene dichloride</td>
<td>0.2500</td>
<td>207.0-303.0</td>
<td>16.0 ± 0.3</td>
<td>1.11 \times 10^{6}</td>
<td>15.97±0.04</td>
<td>-121 ± 1</td>
</tr>
<tr>
<td>Br/I</td>
<td>chloroform-d</td>
<td>0.3100</td>
<td>214.5-300.0</td>
<td>10.5 ± 0.8</td>
<td>4.77 \times 10^{4}</td>
<td>11.04±0.04</td>
<td>-143 ± 1</td>
</tr>
</tbody>
</table>

(a) Errors quoted are least squares errors.

(b) Values computed from data of ref. 3.
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 31P 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 31P spectrum (Fig. 1b) they appear as an AB quartet (J 31P-31P = 20.8 Hz). In the single resonance 31P spectrum (Fig. 1c) it is obvious that the pyrophosphate phosphorus nuclei are coupling to different extents to their 5'CH2 protons. From spectrum simulation studies we can estimate the ranges of J31P-0-31P 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 31P facilities.

Yours sincerely,

J. Feeney, Barry Birdsell,
G.C.K. Roberts and A.S.V. Burgen.
NADPH

1H DECOUPLED

31P Spectra

a

NADPH : ENZYME

1H DECOUPLED

b

c

0 -10 ppm -20
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 H and 13C NMR SPECTROMETRY.**

Representative 13C 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:

<table>
<thead>
<tr>
<th>Coal</th>
<th>Aromatic H</th>
<th>Aromatic C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total H</td>
<td>Total C</td>
</tr>
<tr>
<td>Adaville</td>
<td>.15</td>
<td>.44</td>
</tr>
<tr>
<td>Pittsburgh</td>
<td>.27</td>
<td>.62</td>
</tr>
<tr>
<td>Powellton</td>
<td>.29</td>
<td>.61</td>
</tr>
<tr>
<td>Lower Banner</td>
<td>.29</td>
<td>.64</td>
</tr>
<tr>
<td>Pocahontas No. 3</td>
<td>.53</td>
<td>.81</td>
</tr>
<tr>
<td>Pocahontas No. 4</td>
<td>.50</td>
<td>.78</td>
</tr>
</tbody>
</table>

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,

H. L. Retcofsky (F. K. Schweighardt, Tom Link, and R. A. Friedel)
June 18, 1975

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,

Rolf G. Tschudin
Dr. A. Steigel
Institut für Organische Chemie
der Universität Düsseldorf
Direktor: Professor Dr. L. Birkofler

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$_3$CO$_2$H (1.45), the smallest one for CF$_3$CO$_2$H as solvent (1.03). For all other studied solvents (CCl$_4$, Cl$_2$C=CCl$_2$, CH$_3$OH) as well as for the trifluoroacetate dissolved in CH$_3$OH 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$_3$CO$_2$H 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 CC1$_4$) 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 CC1$_4$ 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

(A Steigel)
The ultimate in low-cost FT NMR Spectroscopy...

- Full multinuclear capability
- High resolution magnet for proton FT
- 10 mm variable temp for C$^{13}$
- Superior sensitivity

For details, please contact your nearest Bruker representative.
Thank you for your blue reminder.

RADATION 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 $\text{Si}^{29}$ 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 H1 to avoid saturation of the resonance. Traces C, D, E in the lower part show what happens when H1 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,

[Signature]
R. Kaiser
Professor

RK/vmm
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 $^{1}$J$_{CH}$ should be smaller for C-2 than for C-6, assuming $^{1}$J$_{C_{2}H}$ is greater than or not much less than $^{1}$J$_{C_{4}H}$. The assignments were made on this basis. The shifts of the $\alpha$ and $\beta$ 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
Robert L. Lichter
Associate Professor
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 $R_1^A$ be the initial relaxation rate of proton $A$ when it alone is inverted by a selective $180^\circ$ pulse, and $R_1^A(\text{NS})$ be its initial relaxation rate when all protons are inverted by a non-selective $180^\circ$ pulse. If the only mechanism determining the relaxation of $A$ is dipolar interaction with other protons, $R_1^A(\text{NS})/R_1^A = 1.5$. If two protons, $A$ and $B$, are inverted by a selective pulse on each, the initial relaxation rate of $A$, $R_1^A(B, B)$, will be greater than $R_1^A(\text{A})$ depending on the fraction, $f_B$, of the relaxation of $A$ arising from the dipolar interaction between $A$ and $B$:

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

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:

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

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 $R_1^A(\text{A})$ with an accuracy of $\sim 2\%$. If requirement (c) is also approximately satisfied, other relaxation rates may be determined to $\sim 2\%$ and the fractional dipolar interaction between a pair of protons to an absolute limit of about $\pm 0.05$. The accuracy of internuclear distance ratios will vary with their magnitude and the best that we have observed is $\sim 5\%$. 


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 $\sim 10\%$.

We have recently tried to use a selective $90^\circ$ pulse to perturb proton A and selective $180^\circ$ pulses to perturb other protons. This doubles the dispersion 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,

H.D.W. Hill
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(17) 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 $\theta \leq 180^\circ$. When $\theta \leq 120^\circ$ (i.e. $^4\text{C-C-C-P}$), $J = 1.8$ Hz and for $\theta \leq 90^\circ$
(i.e. $^7\text{C-C-C-P}$), $J$ is not resolvable (less than 0.6 Hz).

For 2, however, the coupling from C-4,6 to $^{31}P$ is only 11.8 Hz for $\theta \leq 180^\circ$
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)
This is perhaps the reason for the small $^7$C-$^{31}$P coupling (0.7 Hz) for $\theta \approx 60^\circ$ in 2. For the tricyclic case 3, $\theta \approx 170^\circ$ for the path P-C-C-1-5C, yet $J$ is only 6.1 Hz. Apparently the cyclopropyl ring is a rather inefficient transmitter of vicinal C-P coupling information.

![Diagram](image)

Some examples of this phenomenon for vicinal $^1$H-$^{31}$P vicinal coupling are known.$(?)$

For compound 4, which is epimeric at C-3 to 3, $J$ for the path $^1$5C-C-P = 1.1 Hz, for $\theta \approx 10^\circ$, indicating a highly asymmetric $|J|$ vs $\theta$ 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

References

1. Lapper, et. al., JACS 94, 6243 (1972).
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,

[Signature]

J. Wilson Quail

JWQ/crm
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 $^{13}$C 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 Shoulders

Please credit this contribution to the account of Dr. Charles Wade.
Relative Signs of $^{13}\text{C}-^{13}\text{C}$ Coupling Constants

Dear Prof. Shapiro,

Knowledge of signs of $^{13}\text{C}-^{13}\text{C}$ 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 $^{13}\text{C}-^{13}\text{C}$ 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 $\alpha$ and $\beta$, a ring carbon, say C-1, may be the X-part of an $\text{AA'X}$ system and thus showing a triplet with the separation $|J_{\text{AX}} + J_{\text{A'X}}|$ providing $|J_{\text{AA'}}|$ 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 $^{13}\text{C}$ NMR signals of $\text{AX}$ systems or non-coupled carbons, respectively. From the superimposed spectra of C-1 the quantities $|J_{\text{AX}} + J_{\text{A'X}}|$, $|J_{\text{AX}}|$ and $|J_{\text{A'X}}|$ can be measured. A comparison between these quantities will give the relative signs of $J_{\text{AX}}$ and $J_{\text{A'X}}$.

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 symmetric compounds...
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 $\rightarrow$ benzil $\rightarrow$ benzildihydrazone $\rightarrow$ diphenyl acetylene $\rightarrow$ cis-stilbene $\rightarrow$ phenanthrene.

Table 1 shows the data for phenanthrene and 9,10 di-phenylphenanthrene. 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.

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

Dear Professor Shapiro

TITLE:SUPER-COOLED 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 data yielded a straight line for each liquid crystal we examined (PAA, EBA, 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 data can 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

RESEARCH TRIANGLE INSTITUTE
CHEMISTRY AND LIFE SCIENCES DIVISION

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. L. Carroll
Charles G. Moreland

Enclosure
**Varian's Special Offer: Over 30 Additional Nuclei**

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