B. L. Shapiro  
Newsletter Finances and Practical Economics 1

R. C. Westcott, D. P. Kelly, R. A. Craig and D. Flego  
MA-60IL - Digilab - PDP-15 Spectrometer 2

D. E. Dorman  
13C NMR Spectroscopy of a-Lactam Antibiotics 5

E. Nee and M. Raban  
The Effect of Crown Ether Upon The Conformational Equilibrium of Sodium Acetylacetonate 7

T. Prange  
DECHAMIT Analysis of 4-hydroxy-N-acetylproline 10

R. Freeman  
Dipolar Relaxation 14

R. E. Lankinski and J. Reuben  
A Comment on Line Broadenings Guessed by LSR’s 17

C. G. Wade  
Deuteron Relaxation in Liquid Crystals 19

C. D. Hall and T. Pooner  
13C NMR Spectra of A Crown Ether and Its Potassium Ion Complex 22

D. Canet  
Elimination of Solvent Background in Nematic Phase NMR By Fourier Transform 24

Some Developments in Nitrogen NMR Spectroscopy 28

R. Knorr and H. Polzer  
Conformational Analysis by Spin Transmission Into The Rotating Prin- Alkyl Group 31

S. Caccamese and G. Montaudo  
An Authentic A2B2 System 34

M. Barfield  
Postdoctoral Position Available; Bruker WH-90; Tick Marks 35

A. Kumar and R. R. Ernst  
NMR - Fourier - Zeugmatography 36

I. D. Kuntz  
Water in Red Cells; Position Available 40

B. M. P. Hendriks and H. Fischer  
CIDNP in Photochemical Charge Transfer Processes 41

R. J. Abraham  
1H(13C) Study; 13C Shift of TMS in TFA; Position Available 43

W. B. Smith  
2-(3-Thienyl)Furan; Proton NMR; Position Available 45

J. L. Faivre and R. Gassend  
1H, 13C and Low Temperature Measurement on T1r Derivatives of Nitrogen Heterocycles 46

J. A. Laad  
Inter- and Intra-Molecular Exchange in the System 1,3,5-Trioxan/1,3,5,7-Tetroxan 49

C. S. Yannoni  
Quest for a 13C Knight Shift in TTF/TCNQ 51

M. Llinas, D. M. Wilson and M. P. Klein  
13C=O Spectral Assignments in Peptides by Double Resonance Techniques 53

J. L. Burdett  
Postdoctoral Position Wanted 54

H. D. W. Hill  
Selective Relaxation in Proton NMR 55

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The Newsletter financial situation continues to be in a most precarious state. Like everything else, our costs are rising markedly and our income is not keeping up with this rise. It is therefore essential that we do everything possible to keep costs down, while at the same time generate the maximum amount of income, if the Newsletter is to survive.

It will be most helpful if all Newsletter subscribers can expedite payment of their annual subscription invoices without delay. Anyone who has not received an invoice by the time they read this notice has the responsibility to let us know immediately. The subscription rates have not increased in the past three years, and only by scrupulous attention to payment matters on the part of all subscribers is it possible for us to try and survive another year at the same rates.

This is certainly the appropriate time and place to say once again what an important and major help with the Newsletter finances has been provided by our Advertisers, Sponsors and Contributors. Please take note of who they are and try to find appropriate ways to let them know directly that their support of the Newsletter is appreciated.

For the coming Newsletter fiscal year, several of our most faithful Advertisers, Sponsors and Contributors have already indicated that they will be renewing their support, some at a substantially higher level than in the past. I am personally not only very grateful for their willingness to do so, but also for the alacrity of their responses to our requests for additional help. Our Newsletter is made possible by a number of individuals who are not only generous but extremely pleasant. The only problem with these very important patrons of the Newsletter is that there are so few of them: all Newsletter subscribers are once again urged to suggest specific contacts in industry or elsewhere where additional advertising and/or sponsorship revenue can be generated. You should also feel free to make appropriate representations to suppliers of hardware, chemicals, etc., with whom you do business to the effect that support of the TAMU NMR Newsletter is worthy of their attention. Only three or four more advertisers per issue would make a major, stabilizing change in the Newsletter finances—conceivably to the point where individual subscription rates could be lowered.

Along the lines of effecting all possible economies, allow me to again make a most strenuous plea for greater care in the preparation of your contributions to the Newsletter contents. Please avoid using half a page for letterhead and inside address, etc., but confine this information to the minimum amount of space. Please avoid the use of wide margins; we MUST have 3/4" (2 cm) on both sides and on the top and bottom of each page, but no more please. Single spacing is essential, except where formulas or abundant subscripts, etc., would be a problem. Condense signature space and the spacing of these and references at the end of your letters. Plan your figures carefully, and do not force us to condense your contribution by carving up your figures.

Please adhere to the three-page per contribution maximum. Please do not type or place figures on both sides of a page—one side only!

B. L. Shapiro

5 August 1974
Dr. B.L. Shapiro,
Department of Chemistry,
Texas A&M University,
College Station, TX, 77843,
U.S.A.

Dear Dr. Shapiro,

HA-60IL - DIGILAB - PDP-15 Spectrometer

In the past, Drs. Ian Rae and Michael Heffernan at Monash University have kindly allowed us access to the newsletters, which we have found most valuable. Although we have made one contribution previously, on their behalf (TAMU 17436) we would like to start our own contribution.

In this Department we have a Perkin Elmer R12 for undergraduate and post-graduate use, an HA-100, interfaced to a PDP-15 for C.W. time averaging (1H and 31P) and an HA-60IL modified for FT operation by DIGILAB and also interfaced to the PDP-15 (1H and 13C).

Since the third instrument is probably of an unusual configuration other readers may be interested in some of the details. In order to provide for 1H and 13C pulsed FT operation with deuterium stabilization, DIGILAB supplied a frequency synthesizer (9.2, 15.1 and 60 MHz), 9.2 and 60 MHz transceivers, 400-2 pulser with 15.1 and 60 MHz plug-ins and modifications to our 15.1 MHz V4311 and two probes, V4333 (1H) and V4336 (13C).

Proton decoupling for 13C operation is achieved by mixing the 60 MHz ("Variable") signal with the digital output of an S.A.I.P. noise generator and amplifying in an E.N.I. 320-L power amplifier. Optimum noise decoupling is achieved with a band width (-3db point) of 450 Hz and 4 watts output to the probe. The S.W.R. is 1.5.
Our home-built interface unit comprises (i) a variable gain (2 to 100) amplifier, (ii) an active filter (4-pole Butterworth) 100-5000 Hz, (iii) a DC offset control (FID baseline must be set at +5 volts above ground for input to the unipolar Raytheon ADC (0 to 10 volts), (iv) an adjustable, 'Lock Gate', and other controls for external frequency sweeping (CW) and for plot-back gain.

Our 'Mark 1' home-built pulse programmer provides gating pulses for the DIGILAB pulser as well as clock pulses for the ADC. At present we are limited to recycle times of 0.1 to 9.9 seconds and dwell times of 100 to 900 μsec. Pulse width control is achieved via a DATAPULSE pulse generator. The 90°-pulse time for 13C (ethylene glycol) is 35 μsec.

The PDP-15 has 16K core and DECTape. The time domain signal is stored in 4K, the transform in 4K and programs in 4K. These programs, written by R.C.W. with some assistance from R.A.C. provide for all the usual data manipulations. 'Spikes' in the first few locations, resulting from initial transients, are removed prior to transformation of the data. Transformation of 4K data points takes ca. 5 seconds.

Reproduced herewith is a single scan 13C spectrum of 95% ethyl benzene (5% acetone-d6) in a 12 mm tube showing a S:N of 70:1. Since we have a hybrid system, its performance cannot be predicted. We would therefore welcome comments from interested readers. D.P.K. will be c/- Department of Chemistry, Purdue University, W. Lafayette, Indiana from August 1974 to January 1975.

Yours sincerely,

R.C. Westcott.

R.A. Craig.

D. P. Kelly.

U. Flego.
### Chemical Shift Determination

**Spectrum Type:** Carbon

**Chemical Shift Determination**

<table>
<thead>
<tr>
<th>Frequency (ppm)</th>
<th>Type</th>
<th>Internal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1289.13</td>
<td>87.21</td>
<td>396</td>
</tr>
<tr>
<td>1289.15</td>
<td>100.99</td>
<td>450</td>
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<tr>
<td>1289.29</td>
<td>100.99</td>
<td>393</td>
</tr>
<tr>
<td>1289.32</td>
<td>100.99</td>
<td>393</td>
</tr>
<tr>
<td>1289.99</td>
<td>100.99</td>
<td>393</td>
</tr>
</tbody>
</table>

---

**Spectrum Type:** Carbon

**Coast 140 A**

---

**Chemical Shift**

**Sample:** Unknown

**Operator:** Unknown

**Frequency:** 29.91 MHz

**Power:** 100 W

**Resolution:** 12 bps

**Number of Reduction Points:** 8

---

**Input Parameters:**

- **Chemical Shift (ppm):**
  - 87.21
  - 100.99
  - 1289.13
  - 1521.12
  - 2978.48
  - 2999.63
  - 3245.64
  - 3814.24
  - 4988

---

**Recording Conditions:**

- **Date:** 3/14/78
- **Temperature:** Unknown
- **Field Strength:** 810 Gauss

---

**Spectrum:**

[Graph of spectrum with peaks marked]
During studies directed toward the interconversion of penicillin and cephalosporin antibiotics, Stephan Kukolja and co-workers here at Lilly have found that penam derivatives such as 1 can be readily converted to cephams (2) [cf. S. Kukolja and S. R. Lammert, J. Amer. Chem. Soc., 94, 7169 (1972)]. In some cases—for example, when X is Br or ONO₂—rearrangement of 1 to 2 takes place in the solid state! Such conversions presumably occur through the intermediacy of the episulfonium ion 3.
Because ion 3 can be opened by $X^-$ to either 1 or 2, its generation during chemical reactions leads to mixtures of these two products. Using $^1$H nmr spectroscopy, it is frequently difficult to distinguish between 1 and 2. Inspection of these two structures shows that the general features of the $^1$H nmr spectra will be identical: a methyl singlet, an AB pattern due to the methylene, a one-proton singlet, and a second AB (or AX) pattern due to the azetidinone methines. Arguments based on $^1$H chemical shifts or long-range proton-proton couplings seldom suffice to distinguish between penam and cepham structures.

Fortunately, structures 1 and 2 can be easily distinguished by $^{13}$C nmr spectroscopy. The easiest method relies on the chemical shift of the methylene carbon, which is easily identified by off-resonance decoupling. In 2, this carbon is substituted by sulfur and carbon, two atoms which are known to exert only moderate $\alpha$ effects. In 1, the methylene is substituted by X, which, by chemical necessity, is electronegative and therefore leads to substantially larger $\alpha$ effects. As a result, the methylene resonance of basic structure 2 occurs at $35 \pm 4$ p.p.m., while those of 1 have never, in our experience, occurred above 41 p.p.m.

Of course, the methine carbon resonances can also be easily identified by off-resonance decoupling. This permits a second way of distinguishing between penam and cepham systems. We have found that the sums of the methine carbon chemical shifts of 1 are uniformly about 20 p.p.m. toward lower field than the analogous sum of 2. This parallels the dependence of shielding on ring size noted for furanose and pyranose sugars [cf. A. S. Perlin et al., Ann. N. Y. Acad. Sci., 222, 935 (1973)] and suggests that such a dependence is a widespread and therefore useful phenomenon.

A more complete report of these results is in preparation.

Best regards,

LILLY RESEARCH LABORATORIES

Douglas E. Dozman, Ph.D.
Physical Chemistry Research
Department MC525
Dear Professor Shapiro:

The Effect of Crown Ether upon the Conformational Equilibrium of Sodium Acetylacetonate.

We have examined the low-temperature pmr spectra of sodium acetylacetonate in pyridine-$d_5$, and have added different amounts of 18-crown-6 to complex with Na$^+$ and promote dissociation of the sodium enolate. The $Z,Z$ conformation of the free anion might be expected to suffer considerable destabilization from coulombic repulsion between the two oxygen atoms, but chelation to Na$^+$ should stabilize this configuration. In the absence of the cation, the $E,Z$ or $E,E$ conformation could predominate because of a more favorable separation of the carbonyl oxygens in these conformations.

Spectra were taken under the following conditions: (a) $-50^\circ$, crown/enolate ratio 1.6; (b) $-44^\circ$, crown/enolate ratio 1.6; (c) $-50^\circ$, crown/enolate ratio 3.7.

The observation of two methyl singlets of unequal intensities at 0.2.09 and 2.38, as well as two methine signals at 5.48 and 6.05, indicates the presence of $Z,Z$-1 and $E,E$-1 in equilibrium. If $E,Z$-1 were present, it
should give rise to two equally intense singlets, and its presence in significant amounts can therefore be excluded. A straightforward assignment of configuration can be based upon the changes in peak ratios as a function of the crown ether concentration. Thus, an increase in the crown/enolate ratio from 1.6 to 3.7 (spectra a and c) decreases the intensity of the upfield methyl and methine singlets. These resonances must arise from $Z,Z$-$\text{E, E-1}$, whose concentration is lowered as a result of the decreased concentration of sodium ion available for complexation, and the low field singlet of each set must then be due to uncomplexed $E,E$-$\text{E-1}$.

The ratio of $E,E$ to $Z,Z$ conformations decreases at higher temperatures, as shown in spectra a and b. An increase of only $6^\circ$ lowers the percentage of $E,E$-$\text{E-1}$ from 30% to 23%. In another experiment with the same crown/enolate ratio, the percentage decreased from 41% at $-65^\circ$ to 25% at $-46^\circ$.

Complete line shape analysis at the coalescence temperature, $-21^\circ$ C, afforded a first order rate constant of $30 \text{ sec}^{-1}$ for conversion of $E,E$-$\text{E-1}$ to $Z,Z$-$\text{E-1}$, which corresponds to a free energy of activation of 12.9 kcal/mol. The barriers for related R-COXCOR systems are in the order expected for increased C-X double bond character as the electronegativity of X is decreased: diacetamide, $^1 X = \text{NH}$, 10.8 kcal/mol, and formic anhydride, $^2 X = \text{O}$, 4.4 kcal/mol.

Sincerely,

Eric Noe

Morton Raban

A new computer programme called DECHAMIT has been developed in these laboratories for the resolution of 1/2 spin systems. The general procedure is well-known but in order to facilitate data handling for our students it was found advantageous to incorporate certain modifications to the so-called standard programmes.

The $2^N$ observed energy levels ($E_{\text{obs}}$) and the associated errors ($\epsilon_i$) are calculated from $m$ observed lines and their connection numbers determined by the method of least squares. Next an agreement factor

$$\epsilon_i \sqrt{\sum (E_{\text{obs}} - E_{\text{calc}})^2}$$

is iteratively minimized by step by step modification of the trial input parameters $\delta$ and $j$, which are monodimensioned in the same array.

Finally the complete spectrum is calculated and the classical Lorentzian profile realised on a listing and Benson plotter.

The $E_{\text{obs}}$ error ($\epsilon_i$) obtained in the first step is a limit for the final convergence and the line error parameter

$$\epsilon_{\text{lin}} \sqrt{\sum (v_{\text{obs}} - v_{\text{calc}})^2}$$

cannot be less than $\epsilon_i x (m/2^n)^{1/2}$ where $m > 2^n$.

The initial error $\epsilon_i$ is generally due either to imprecise readings of $v_{\text{obs}}$ or random fluctuations in the spectrometer recorder - even FT computer data should not be always accepted implicitly!

However a permitted range of 0.2 Hz for each $v_{\text{obs}}$ can give a good final convergence provided that the best values be chosen in order to minimize $\epsilon_i$.

As iterative methods are not normally applied to seven spin systems this particular programme is at the moment dimensioned to six spins and it has been useful to use the compressed notation for symmetrical matrices in all the sub-routines. It has also been expedient to make use of the "EQUIVALENCE" FORTRAN IV statement.
It has proved possible by means of this programme to examine the 2X6 spins pattern of 4-hydroxy-N-Acetyl proline in D$_2$O and to produce the cis- and trans- conformations superimposed.

You will see that the vicinal J couplings are different in the two conformations on the accompanying Benson curve of the H$_3$/H$_3b$ spectrum run at 300 MHz and thus it is clear that a modification of the averaged cycle geometry occurs by reason of the rotation of the N-acetyl group. More information will be given in a paper which is at present prepared.

Please credit this letter to Bernard ROQUES' account.

Sincerely,

Thierry PRANGE

---

1-Technical data:

a) Average UNIVAC-1108 times:

<table>
<thead>
<tr>
<th>n</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>8 spins</th>
</tr>
</thead>
<tbody>
<tr>
<td>non iterative:</td>
<td>10s</td>
<td>20s</td>
<td>45s</td>
<td>1.5 mn</td>
</tr>
<tr>
<td>iterative:</td>
<td>30s</td>
<td>1-2mn</td>
<td>15mn</td>
<td>30mn</td>
</tr>
</tbody>
</table>

b) Size: 8 K octets (6.7 without Benson sub-routines)

18 K in a (REAL*) off-resonance version (decoupling power and frequency must be added).

Listings and BCD cards are available upon request.

   S. Castellano and A.A. Bothner-By, ibid. 41, 3863 (1964).
3- For comparisons see Y. Kato and A. Saika, ibid. 44, 2824 (1966).
4- T. Prange, C. Garbay-Jaureguiberry, M. Anteunis, B. Roques
Deuterated Solvents
Reference Compounds
Chart Papers Etc:
Shift Reagents

NUCLEAR MAGNETIC RESONANCE LTD.
MAGNETIC HOUSE/SCRUBBS LANE/ BLEDLOW RIDGE/
HIGH WYCOMBE/ BUCKS/ HP14 4AF
Dipolar Relaxation

My relaxation mechanism is being sorely tried by your barrage of subpoenas. I hope the attached transcript will prove acceptable.

As $T_1$ gains acceptance as a respectable parameter for high resolution NMR spectra, it is becoming more and more important to discover something about relaxation mechanisms. The key experiment for determining the dipolar contribution to relaxation is of course the well-known internuclear Overhauser effect. Its importance is such that one feels it would have been much more widely employed were it not for the experimental difficulties involved. But the application to homonuclear spin systems, requiring the measurement of small changes in the integral of a signal in coupled and decoupled spectra, is beset by problems of systematic error.

While the Overhauser experiment explores steady-state disturbances of spin populations, the relaxation paths may also be probed in transient experiments. This note describes an alternative method of assessing the dipolar contribution to spin lattice relaxation by preparing the spin populations in various ways and following the rates at which they relax.

The simplest system to think about is a molecule with two spins $I$ and $S$. We may define the usual relaxation parameters:

$$\rho = 2 \omega_1 + \omega_2 + \omega_0 \quad \text{(purely dipolar)}$$
$$\rho^* = 2 \omega^*_1 \quad \text{(all other mechanisms)}$$
$$\sigma = \omega_2 - \omega_0 \quad \text{(cross-relaxation)}$$

In the limit of high correlation frequencies, $\rho = 2 \sigma$ since

$$\omega_2 : \omega_1 : \omega_0 :: 12:3:2$$
We may write the deviations of the spin populations from Boltzmann equilibrium for two different modes of preparation: (a) a non-selective 180° pulse which affects all four lines uniformly, (b) a selective 180° pulse which affects both lines of the I multiplet but leaves the S spin unperturbed.

In case (a) the relaxation is purely exponential and the rate is given by
\[-\frac{dx}{dt} = \rho + \rho^* + \sigma\]  
(1)

In case (b) the relaxation is only approximately exponential but an initial rate may be defined:
\[-(dx/dt)_0 = \rho + \rho^*\]  
(2)

We take the ratio of the rate after a non-selective pulse to the rate after a selective pulse on the I spins:
\[R = 1 + \frac{\sigma}{\rho + \rho^*}\]  
(3)

Now if we consider the relaxation time of the I spins measured under double irradiation conditions where the S spin populations are held saturated, it is readily shown that:
\[\frac{1}{T_{1I}} = \rho + \rho^*\]  
(4)

Whereas for exclusively dipolar relaxation,
\[\frac{1}{T_{1D}} = \rho\]  
(5)

Thus
\[\frac{T_{1I}}{T_{1D}} = \frac{\rho + \rho^*}{\rho} = \frac{2\sigma}{\rho + \rho^*} = 2(R - 1)\]  
(6)

The determination of R thus gives us the degree to which dipole-dipole interactions control spin-lattice relaxation of the I spins.
The experimental measurement of the two rates is straightforward. Case (a) is the conventional experiment. For case (b) the usual inversion-recovery sequence is modified so as to extend the pulse width of the 180° pulse considerably. For example a width of 50 milliseconds would correspond to a setting of radiofrequency level where $\gamma H / 2\pi = 10 \text{ Hz}$, which is about the selectivity normally required to perturb one spin multiplet but leave others unaffected. This radiofrequency field would be derived from an auxiliary oscillator that could be tuned into the desired group of lines (the source might be the proton decoupler for example).

The $T_1D$ obtained in this way represents the contributions from dipolar interactions of spin I with all other resonant spins S. For proton spectroscopy this would mean interaction with all other protons in the sample. However, it would be possible to examine individual proton-proton interactions if the spin populations were prepared in a slightly different manner — by applying selective 180° pulses to two chemically shifted groups I and S, leaving all other groups $S'$, $S''$ etc. unperturbed. This experiment would replace the non-selective preparation to give a rate expressed by Eq (1).

This idea has been used to show that proton relaxation in a pyranose sugar derivative is essentially dipolar; the experiments were carried out in collaboration with Howard Hill at Varian and Laurie Hall at U.B.C. Vancouver.

Happy Thanksgiving,

Ray Freeman
The addition of a lanthanide shift reagent (LSR) to a solution containing an organic molecule (substrate) results in both shifts and line broadenings in the NMR spectrum of the substrate. The magnitude of these line broadenings, for a given resonance, varies with the lanthanide used. Under the condition of fast exchange, assuming the exchange is a first order process, the line broadening is given by:

\[
\frac{1}{T_2} = \frac{\sigma}{T_{2M}} + \frac{(1 - \sigma)}{T_{2F}} + \sigma(1 - \sigma)\frac{T_M}{2(\Delta\delta_m)^2}
\]

where \(\sigma\) is the fractional substrate population in the complexed state; \(1/T_{2M}\) and \(1/T_{2F}\) are the transverse relaxation rates in the complexed and free states, respectively, \(\Delta\delta_m\) is the chemical shift difference between the two states and \(T_M\) is the mean lifetime in the complex. The last term in equation (1) is referred to as chemical exchange broadening (CEB). For two nuclei within the same molecule, the CEB is generally different (different \(\Delta\delta_m\)'s). Moreover, the CEB term will vary with temperature (via \(T_M\), \(\Delta\delta_m\)), concentration (via \(\sigma\)) and frequency of measurement (via \(2(\Delta\delta_m)^2\)). The ratio of the line broadening of two nuclei within the same molecule can be written as

\[
\frac{\Delta N_i}{\Delta N_j} = \frac{\sigma(\frac{1}{T_{2M_i}} - \frac{1}{T_{2F_i}}) + CEB_i}{\sigma(\frac{1}{T_{2M_j}} - \frac{1}{T_{2F_j}}) + CEB_j}
\]

July 5, 1974

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

Dear Barry:

The addition of a lanthanide shift reagent (LSR) to a solution containing an organic molecule (substrate) results in both shifts and line broadenings in the NMR spectrum of the substrate. The magnitude of these line broadenings, for a given resonance, varies with the lanthanide used. Under the condition of fast exchange, assuming the exchange is a first order process, the line broadening is given by:

\[
\frac{1}{T_2} = \frac{\sigma}{T_{2M}} + \frac{(1 - \sigma)}{T_{2F}} + \sigma(1 - \sigma)\frac{T_M}{2(\Delta\delta_m)^2}
\]

where \(\sigma\) is the fractional substrate population in the complexed state; \(1/T_{2M}\) and \(1/T_{2F}\) are the transverse relaxation rates in the complexed and free states, respectively, \(\Delta\delta_m\) is the chemical shift difference between the two states and \(T_M\) is the mean lifetime in the complex. The last term in equation (1) is referred to as chemical exchange broadening (CEB). For two nuclei within the same molecule, the CEB is generally different (different \(\Delta\delta_m\)'s). Moreover, the CEB term will vary with temperature (via \(T_M\), \(\Delta\delta_m\)), concentration (via \(\sigma\)) and frequency of measurement (via \(2(\Delta\delta_m)^2\)). The ratio of the line broadening of two nuclei within the same molecule can be written as

\[
\frac{\Delta N_i}{\Delta N_j} = \frac{\sigma(\frac{1}{T_{2M_i}} - \frac{1}{T_{2F_i}}) + CEB_i}{\sigma(\frac{1}{T_{2M_j}} - \frac{1}{T_{2F_j}}) + CEB_j}
\]
If the CEB term is important, the ratio of the line broadening should be dependent on temperature, frequency and concentration of LSR. In addition, different lanthanides may have different relative proportions of the two terms, (1/T₂₂₄, CEB). Therefore, the ratio of line broadenings of two nuclei within the same molecule may vary with the lanthanide used. Observations consistent with our interpretation can be found in the literature. Additional and conclusive results recently obtained in our laboratory are now being prepared for publication.

Sincerely yours,

R.E. Lenkinski
J. Reuben

References

1. For review see: J. Reuben, Prog. in NMR Spectrosc., 9, 1 (1973).

Title: A Comment on Line Broadenings Caused by LSR's
Title: Deuteron Relaxation in Liquid Crystals

In collaboration with Prof. Bing Fung, University of Oklahoma, and Dr. Richard Orwoll, a former postdoctoral now at Fiber Industries, we have been applying deuteron relaxation to liquid crystals.

The theory of deGennes (1) indicates that in the nematic phase, relaxation is influenced by the orientational fluctuation modes (collective modes). This predicts spin lattice relaxation, $T_1 = f(\omega^{1/2})$ where $\omega$ is the Larmor frequency. $T_1$ can also be influenced by intermolecular diffusion effects which predict $T_1 = f(\omega^{-1/2})$ in the limit of slow diffusion. Both types of frequency dependence have been observed for protons in nematic phases. Various other frequency dependence is predicted (and observed) just above nematic-isotropic phase transition ($T_c$) depending upon which branch of the collective modes most strongly influences $T_1$. Protons have an inherent limitation for use to test relaxation theories: they are subject to intermolecular (diffusion) contributions which are not easily separated from the (intramolecular) collective mode mechanisms except by expensive isotopic dilution studies (2). To avoid this problem we have utilized deuteron relaxation which is almost completely intramolecular. We have studied $T_1$ of the deuterons in ring deuterated para-azoxyanisole (PAA) and 4,4' diheptyloxyazoxy benzene (HOAB). $T_1$ increases with temperature across the mesophases. Relaxation is discontinuous at the clearing point with the isotropic phase having the shorter $T_1$. In contrast to measurements of deuteron $T_1$ in other compounds (3), $T_1$ of the deuterons in PAA is independent of frequency in the range 4.5 to 10.5 MHz (Fig. 1). Deuteron relaxation in oriented samples of HOAB is independent of the angle between the nematic director and the applied field. The apparent lack of sensitivity to collective mode fluctuations is explained on the basis of the molecular geometry of the C-D bond which presumably reduces the relative influence of collective modes and makes other mechanisms, such as molecular tumbling, more effective. 1) P.G. deGennes, Molec. Cryst. & Liquid Cryst. 12, 193 (1971). 2) E.T. Samulski, C.R. Dybowski and C.G. Wade, Phys. Lett. 29, 340 and 1050 (1972). 3) B. deloche and B. Cabane, Molec. Cryst. & Liquid Cryst. 19, 25 (1972).

Yours truly,

Chuck

Assoc. Professor

CGW:dj
Figure 1. For n = 1, • - 10.5 MHz, cooled; ■ - 4.5 MHz heated. For n = 7, all measurements are at 10.5 MHz: • - cooled, ■ - heated. The line labelled "Calc" is calculated from the theory of Doane and Johnson.
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WH 90

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DEPARTMENT OF CHEMISTRY


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

Dear Professor Shapiro,

There appears to be little published information concerning the $^{13}$C spectra of the rapidly developing field of Crown ethers and their cation complexes. Hence, in response to your latest blue note we should like to report our initial findings in this area.

The Table shows the chemical shifts and assignments for (i) dibenzo-18-crown-6 (1), (ii) the 1:1 complex of (1) and potassium iodide and (iii) a 1:1 molar mixture of the complex and (1).

The spectra were run at ambient temperature (~298°K) in 50% MeOH-CDCl$_3$ as solvent, on a Bruker HFX 90 spectrometer with broad band decoupling and using a Nicolet Fourier Transform system with tetramethylsilane as internal standard. The concentrations of Crown ether (and complex) were maximised at 0.9% (2.5 X 10$^{-2}$M) and the quoted chemical shift values are accurate to ± 0.06 ppm. The chemical shift assignments A, B and C are based on a comparison with those for catechol.$^1$ (2)
The $^{13}$C chemical shift differences between the Crown ether and its complex with KI vary between 0.14 ppm (for $^{13}$B) to a maximum of 2.54 ppm (for $^{13}$C). These differences are small but two important conclusions may be drawn from the data. First, within experimental error the chemical shifts of the 1:1 mol mixture of Crown ether and its complex lie exactly half way between the extremes of Crown ether and complex which confirms the known fact \( \text{log}_{10} K \approx 5.0 \) with methanol as solvent. Second, it would appear that since only averaged chemical shifts are observed with the mixtures, the dissociation of the complex is rapid on the $^{13}$C nmr time scale. The observation of averaged signals persists down to -60°C (with a little line broadening) and rough calculations reveal that the rate coefficient for the dissociation of the complex at room temperature, \( k_D \), is at least 1000 s$^{-1}$.

\[
(1) \quad \text{DB-18-C-6} \quad \begin{array}{c}
149.31 \\
148.38
\end{array}
\]

\[
(2) \quad \text{DB-18-C-6} \quad \begin{array}{c}
147.41 \\
145.0
\end{array}
\]

Thus both association and dissociation in Crown ether complex formation seem to be extremely rapid.

Yours sincerely,

Varian catalogue, $^{13}$C nmr spectra, spectrum number 161 (in water).


1. Tunnan Poorn.
Title: "Elimination of solvent background in nematic phase NMR by Fourier transform"

Dear Professor SHAPIRO,

This is my first contribution to TAMU NMR Newsletters. We are mainly interested by nematic phase NMR and $^{13}$C longitudinal relaxation times measurements. We are working with a Bruker HX 90 equipped with a Fourier transform accessory (Nicolet 1080 computer-20k memory). The spectrometer is operating for the following nuclei: $^{1}H$, $^{19}F$, $^{13}C$, $^{17}O$, $^{15}N$, $^{14}N$ and $^{2}H$. Furthermore, by lowering the magnetic field we were able to observe easily other nuclei, such as $^{27}Al$ or $^{7}Li$.

About NMR in the nematic phase, I wish to report FT procedures which allow the elimination of the solvent hump which is often troublesome mainly in case of dilute solutions. These procedures are based on the fact that the nematics FID vanishes much more rapidly than the FID of the solute molecules. It is then interesting to try and suppress or attenuate the beginning of the interferogram. This is illustrated on the figure. (A) represents the normal FT spectrum of terephthalaldehyde dissolved in Merck IV Licristal (5mm sample centered in a 10mm tube containing $D_2O$ allowing field-frequency stabilization). The interferogram was stored in 4K-words. Fourier computations were performed with 16K by artificially filling with zeroes the remaining 12K. (B) was obtained in the same manner but multiplying the interferogram by a trapezoidal window affecting the 150 first addresses. In (C) the first 10 addresses were deleted. Finally (D) is the theoretical spectrum. It is clear that experiments (B) and (C) are of quite better quality than experiment (A). The solvent background has almost been suppressed.
in (B). However small lobes appear around each peak in (B) as well as in (C); they are due to the alteration of the interferogram(I). We think that trapezoidal window is a better procedure for two reasons: (i) lobes are less important than in the case of pure truncation (with respect to the number of addresses concerned) (ii) pure truncation implies tedious phase corrections which do not occur with trapezoidal window.

Anyway, care must be taken in altering FID when measuring weak signals such as $^{13}$C satellites (2). Because of the dynamic range of the analog to digital converter, they may be inobservable, since information to them is mainly stored at the beginning of the interferogram.

Yours sincerely.

CANET

(I) T.C. FARRAR and E.D. BECKER "Pulse and Fourier transform NMR"
Academic Press (1971)

Residual H₂O in D₂O serving as lock signal
MICROSAMPLE ANALYSIS with a TT-7/T-60A System

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Phone or write for more details.
July 25, 1974

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

Dear Barry:

Title: Some Developments in Nitrogen NMR Spectroscopy

Apart from a few annoying birth pains, our JEOL PS/PFT-100 spectrometer is operating reasonably consistently, and we have made some initial forays in our ¹⁵N program.

1. In a series of stepwise approximations we are attempting to improve the signal-to-noise ratio of the detected ¹⁵N signals. On the assumption that, up to a point, bigger is better, we built a bigger insert by slightly space-winding a coil around a standard JEOL 10-mm bobbin such that the number of turns remained the same while the length was increased by about 50%. Figure 1 shows the result, where we obtain about a 30% improvement in the S/N ratio over the standard insert. We are now building a 12-mm insert.

2. As a prelude to studies of heterocyclic natural products we have been studying substituent effects on the nitrogen shifts of pyridines. Because the relaxation times are long we use Cr(acac)₃ to shorten the T₂'s, and can see signals of neat liquids within an hour. However, as shown in Table I, the resonance positions vary slightly with the concentration of Cr(acac)₃, not enough to cause difficulties for structure elucidation, but enough to suggest caution when subtle changes (e.g., solvent effects) are investigated in the presence of such additives.

3. Additionally, the inverted signal which arises on proton irradiation when N-H dipole-dipole interactions dominate the ¹⁵N relaxation can become less negative in the presence of a paramagnetic additive, so that in fact the absolute intensity can diminish. Figure 2 illustrates this for formamide with added Cr(acac)₃.

4. For large molecules T₁ values should be short and spectra within reasonable periods of time can be expected, providing enough material can be crammed into the tube. Figure 3 shows a spectrum obtained after 2 hours (6000 pulses) of penicillin-G methyl ester at a hardly biologically interesting concentration of ca. 2M. We have also determined the spectra of several cephalosporin antibiotics, although with somewhat more difficulty because of limited solubility.
Overall, although we have been on the air with $^{15}$N for only a short time, we are very much encouraged by these preliminary results. Let me again point out that to pursue these and related investigations I now have several postdoctoral openings which can begin at anytime.

Sincerely,

Alice J. DiGioia
E.R. Cole
Robert L. Lichter
Assistant Professor

Table I. Dependence of Pyridine $^{15}$N Chemical Shift on Cr(acac)$_3$ Concentration

<table>
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<tr>
<th>[Cr(acac)$_3$]</th>
<th>$\delta_N, ppm$</th>
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<tr>
<td>0.0250</td>
<td>293.3</td>
</tr>
<tr>
<td>0.0500</td>
<td>292.8</td>
</tr>
<tr>
<td>0.1000</td>
<td>292.5</td>
</tr>
<tr>
<td>0.1500</td>
<td>292.2</td>
</tr>
<tr>
<td>0.2000</td>
<td>291.6</td>
</tr>
</tbody>
</table>

*Neat liquid with respect to external $^{15}$NH$_4$Cl, estimated error ±0.15 ppm.

Fig. 1. Aniline-15N resonance, neat liquid, 2000 pulses, 30° pulse width.
Fig. 2. Effect of added Cr(acac)$_3$ on $^{15}$N signal intensity, formamide.

$$H_2NCH=O$$
$$2\text{ml} + 0.15\text{ml} (\text{CO}_2)\text{C}=O$$
$$200 \text{ pulses, } 30^\circ$$
$$2.1 \text{ sec rep. rate}$$

Fig. 3. Natural abundance $^{15}$N spectrum of penicillin-G methyl ester.
Conformational Analysis by Spin Transmission into the Rotating prim.-Alky Group

Dear Professor Shapiro:

NMR-shifts $\Delta H_i/H$ of paramagnetic nickel complexes may or may not follow a Curie-type $(1/T)$ temperature dependence. A convenient way of checking the Curie law is to define by eq. (I) a new isotropic shift which is reduced from the actual temperature $T$ to $298^\circ$K. ($\delta$ indicates the difference of resonance positions in the complex and the free ligand). Assuming only contact contributions to the shifts of complex $1^\prime$, we calculate eq. (II)

\[ \delta = \frac{\Delta H_i}{H} \cdot \frac{T}{298^\circ K} \quad (I) \]
\[ \delta = -60400 \text{ ppm} \cdot S_z^h \quad (II) \]

from the fundamental constants and an effective Landé-factor $g = 2.20(1)$. Notice from eq. (II) that $\delta$ depends only on the spin density $S_z^h$ at a hydrogen atom. Therefore, Curie-type behavior will cause temperature-independent values of $\delta$. 

![Diagram of molecular structures](image-url)
Plotting $\delta$ against the temperature we find from Figure 1 that
the $m$, $p$, and $A$-shifts of 1 are indeed reasonably constant. Therefore, the Curie law is valid and the magnetic properties of the complex as a whole do not change over the broad range of working temperatures (spectra were taken in 1,1-dideuterio-1,1,2,2-tetrachloroethane). In marked contrast, the reduced shifts of the two equivalent $\beta$-hydrogens drift strongly downfield with increasing temperature. We postulate that this "abnormal" temperature dependence is due to a modulation of the spin density, eq. (II), by torsion and/or rotation about the C-C bond in 1. The geometrical situation is shown in the Newman projection in Table 1, looking from C$_3$ toward C$_1$ and the nickel atom.

$$\delta_\beta = \delta_0 + \delta_2 \cdot \langle \cos^2 \theta \rangle$$  \hspace{1cm} (III)

$$\langle \cos^2 \theta \rangle = \int \cos^2 \theta \cdot e^{-V(\theta)/RT} d\theta / \int e^{-V(\theta)/RT} d\theta$$  \hspace{1cm} (IV)

$$V(\theta) = V_2 \cdot \sin^2 (\theta - 60^\circ)$$  \hspace{1cm} (V)

Spin transmission from a 2p-orbital into a C$_9$H$_7$ bond depends on the dihedral angle $\theta$ of the respective axes; eq. (III) is well established by theory as well as esr spectroscopy. The expectation value $\langle \cos^2 \theta \rangle$ may be computed classically according to eq. (IV) if the potential energy function $V(\theta)$ for the rotation is known. Assuming a $\sin^2$ potential, eq. (V), with a rotational barrier $V_2$ and an equilibrium angle of $60^\circ$, a theoretical temperature dependence may be calculated. The heavy trace through the $\beta$-shifts of Figure 1 results with $V_2 = 2.5$ kcal/mole; the parameters of eq. (III) are $\delta_0 = +17$ ppm and $\delta_2 = -200$ (±20) ppm. Data on a whole series of related complexes are collected in Table 1, taking always the same equilibrium conformation and the same $\delta_2$. The picture is quite consistent, including free rotation of the $\beta$-methyl group. The $\delta_2/\delta_0$ ratio of -0.08 is in line with theoretical estimates which have been positive or negative. Spin polarisation and hyperconjugation of positive spin density from C$_3$ account for the low-field $\beta$-shifts.

Ethylbenzene 2 should be a good model for the electronic and steric requirements of the ethyl rotation in 1. A previous ab-initio calculation by Pople et al. (2) provided a barrier-to rotation of 2.2 kcal/mole which compares very well with our estimate. Furthermore, the theoretical equilibrium angle $\theta_0$ is identical with ours. The theoretical curves can be fitted to the experimental shifts only with $\theta_0 = 60:20^\circ$. Apparently our method is in the right ball park and constitutes a very sensitive tool of conformational analysis.

Please credit this contribution to the account of Prof. Gerhard Binsch over whose shoulder we are reading these Newsletters. Sincerely yours,

R. Knorr
Rudolf Knorr

H. Polzer
Heinz Polzer
We find this same \( \delta \) value for more than 50 nickel complexes of 1,3-dianils, independent of the temperature, in accord with some earlier observations of:


Dear Prof. Shapiro,

please excuse us for being slow in submitting this to you. We are now reporting\textsuperscript{1} LACOCOON III simulation of $^1\text{H}$ nmr spectra of some photodimers of cinnamic acid and related compounds, containing the cyclobutane ring.

Among the compounds we studied, an interesting example is the methine pattern of the cyclobutyl ring in the $N,N$-dimethyl-$\delta$-truxilloylamide (trans,trans,trans). This provides a theoretical $A_2B_2$ spin system with a very good half-spectrum of seven lines. $J_{AB} = J_{AB}' = 9.21$; $J_{AA} = J_{BB} = 0$.

In a recent review\textsuperscript{2} and in the book of Bovey(3), it was remarked the lack of examples of such symmetrical systems. However, in a literature survey, some $A_2B_2$ systems for cis,cis,cis substituent relationship between the ring protons are reported.\textsuperscript{4}

sincerely yours

Salvatore Caccamese
Giorgio Montaudo

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

Dear Barry:

POSTDOCTORAL POSITION AVAILABLE; BRUKER WH-90; TICK MARKS

A postdoctoral position is available starting September 1, 1974. The general area of interest is experimental and theoretical studies of magnetic resonance parameters. Recent work has been concerned with conformational and substituent effects on various types of nuclear spin-spin coupling constants, especially those involving C-13. I would appreciate receiving a resume and two letters of recommendation. The University of Arizona is an equal opportunity employer.

Experimental NMR data is obtained on a Bruker Scientific WH-90 FT Spectrometer, equipped for C-13 and proton NMR. We have now had about eighteen months experience with this spectrometer system, which was the first one installed in the U.S. We are quite pleased with the instrument. Except for some early minor difficulties with the deuterium lock system, there have been no problems with the electronics. Most of the down-time has been due to a bad batch of recorder pots and problems with the cooling water.

In my extreme haste to meet your final deadline on my previous contribution, I forgot to put the tick marks on the figure. So here they are: -- --- --.--. | | | | .

Sincerely yours,

Michael Barfield  
Professor of Chemistry
Dear Barry,

P.C. Lauterbur (TAMU NMR Newsletter 175, 34; Nature 242, 190 (1973)) has recently described an ingenious technique to determine two- or three-dimensional images of the nuclear spin density in a macroscopic sample. In a set of experiments, linear magnetic field gradients are applied in different directions and the resulting spectra are recorded. From a sufficient number of such traces, it is possible to partially reconstruct the two- or three-dimensional spin density function by means of well-known image reconstruction techniques.

We propose here another technique which is remarkable by its simplicity and by its inherent high sensitivity. It is based on the application of a sequence of pulsed linear field gradients to the sample during a free induction decay. The spin density function can then be reconstructed by means of a straightforward two- or three-dimensional Fourier transformation. No interpolation procedure is required to obtain equally spaced data in the Fourier space.

The principle of the technique for the two-dimensional case is shown in Fig. 1. After the application of a 90° pulse to the sample, a linear gradient, e.g. along the z-axis, is applied. At time $t_z$, the gradient is removed and a linear gradient is applied along an orthogonal direction, e.g. along the x-axis. N equally spaced samples of the FID are recorded during the second time interval as a function of $t_x$. These values are functions of $t_x$ and $t_z$ and are denoted by $s(t_x,t_z)$. A set of N experiments is performed for
equally spaced values of $t_z$. The $N \times N$ samples of $s(t_x,t_z)$ are submitted to a two-dimensional Fourier transformation to obtain the two-dimensional spectrum $S(w_x,w_z)$. It can be shown that this function represents a filtered image of the spin density function $c(x,z)$:

$$S(w_x,w_z) = \overline{c}(x,z) = \int \int c(x',z') \cdot G(\eta_x(x'-x)) \cdot G(\eta_z(z'-z)) \, dx' \, dz'$$

where $G(w) = M_0 / (l/T_2 - iw)$ is the complex line shape function and $\eta_x$ and $\eta_z$ are the linear field gradients expressed in frequency units. $\overline{c}(x,z)$ is thus related to a two-dimensional convolution of the undistorted spin density $c(x,z)$. For a sufficiently narrow line shape or for sufficiently strong gradients, it is a good measure for $c(x,z)$. In a Fourier zeugmatogram, the absolute value $|\overline{c}(x,z)|$ is plotted as a function of $x$ and $z$.

An example of a Fourier zeugmatogram is shown in Fig. 2. The sample consisted of two parallel sample tubes with an inner diameter of 1.0 mm and a separation of the centers of 2.2 mm filled with H$_2$O and surrounded by D$_2$O. 64 x 64 samples have been Fourier transformed to obtain a 64 x 64 zeugmatogram printed directly on the teletype. The method is completely automatic, requires a small on-line computer only and produces without any intervention by the operator in about 15 minutes a two-dimensional zeugmatogram. A full paper with an analysis of this technique is in the process of being submitted for publication.

Sincerely yours,

Anil Kumar

Richard R. Ernst
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(415) 849-2415
Dr. Barry Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas

Title: Water in Red Cells; Position Open

Dear Barry:

Your recent reminder catches us between experiments.

We have completed the first stage of a study on the properties of water in sickle and normal red cells. The general findings are quite similar to most water/cell experiments: T2's are considerably shorter than T1's; line widths are somewhat broader than would be calculated from T2's. These effects are much more marked for sickled (deoxygenated) red cells than for normal or unsickled cells.

There is no single correlation time that is consistent with our data or that of others (G.L. Cottam, S.H. Koenig), and we are led (naturally enough) to the three state model for water in biological preparations that I spoke of last time. Our preliminary experiments suggest that there is no dramatic change in hemoglobin hydration on sickling. Presumably the water motion is being influenced by a slow tumbling of the (aggregated) sickled hemoglobin. This work has been in collaboration with Drs. Adam Zipp and Tom James of our department and Drs. Jerry Rehfeld and Steve Shohet of Hematology.

We expect to have a position open for this fall for an operator/maintainer/spectroscopist for the departmental NMR equipment. Salary will depend on qualifications. Anyone interested should contact me for more details.

Regards,

[I.D. Kuntz]  
Associate Professor of Chemistry  
and Pharmaceutical Chemistry

IDK:ftf
CIDNP in Photochemical Charge Transfer Processes

Dear Dr. Shapiro:

UV-irradiation of a solution containing an aromatic hydrocarbon (A) and a cyano compound (C) leads to electron transfer via [1]

\[ A(S_0) \xrightarrow{\text{hv}} A(S_1) \]
\[ A(S_1) + C(S_0) \rightarrow A^+ \cdot C^- \]

and possibly to the following secondary reactions

\[ A^+ \cdot C^- \rightarrow A^+ \parallel C^- \parallel T \rightarrow A^+ \parallel C^- \parallel T \]

In such reversible processes CIDNP caused by nuclear spin dependent intersystem crossing of the radical ion pairs can be expected for the products \( A(S_0) \) and \( C(S_0) \) only if nuclear relaxation in the free ions or in the T-state molecules effectively competes with product formation. Since this is seldom the case only small effects should appear. In accord with expectation NMR-spectra taken during irradiation of solutions of several hydrocarbons (A) with 1,2-dicyanocyclobutene, tetracyanoethylene and p-dicyanobenzene in acetonitrile exhibit only minor CIDNP for A and C. However, for benzene,
naphthalene and chrysene with t-dicyanoethylene (t-DCNE) large effects for t-DCNE (enhanced absorption) and c-DCNE (emission) are found. Also, large effects are observed for t-stilbene (emission) and c-stilbene (enhanced absorption) during the photoreaction of t-stilbene with p-dicyanobenzene and t-dicyanoethylene in acetonitrile. Following Roth [2] this is explained in terms of the above reactions and the additional trans-cis-isomerization of t-dicyanoethylene or t-stilbene in the triplet states (C(T1), A(T1)). For t-dicyanoethylene with anthracene and pyrene no isomerization and CIDNP is found, in agreement with their low triplet energies (E^T(A) < E^T(C)). Since radical ions are formed also with these compounds isomerization in the anions can be ruled out.

Sincerely yours

B.M.P. Hendriks

H. Fischer

Dear Barry,

\(^1\)H\(^2\)D Study; \(^{13}\)C shift of TMS in TFA; position available.

We were interested in the TAMUNMR letters of Professor De Puy (186-38) and Drs. Tseng and Mihailovski (188-28) as we have some related results.

For the former Jose Monasterios has been utilizing the reverse technique of Professor De Puy i.e. \(^1\)H\(^2\)D spectroscopy to determine the stereochemical course of the addition of DBr to cis and trans-2-t-butylstyrene and also thus to assign the diastereotopic methylene hydrogens of Ph.CHBr.CH\(_2\).tBu. (see figure). It would appear that the method offers a general route to the assignment of such protons, which formerly could only be made by assumptions about the most stable rotamer.

We can extend the cautionary tale of TFA as solvent to the question of \(^{13}\)C chemical shifts in this solvent. Geoff Hawkes has just finished an investigation on the effect of protonation on the \(^{13}\)C shifts of porphyrins both in CDCl\(_3\) with TFA added and neat TFA. The shifts were always further downfield in neat TFA, and we decided to run some reference compounds in CDCl\(_3\) and TFA from an external reference. It turns out that it is the TMS signal which moves upfield in TFA by 1.5 ppm compared to CDCl\(_3\). The origin of this shift may be related to the silicon polarisability, in the same manner as the large upfield shifts found for fluorine attached to Cl and Br groups, but whatever the reason this must be taken into account when determining protonation shifts from measurements in CDCl\(_3\) and neat TFA.

19th July, 1974.
Finally, if all the available P.D.F. talent has not already been tapped, we have a possible opening for someone interested in a C study of metal-porphyrin interactions. Anyone interested contact me.

With best wishes, 

Yours sincerely,

Dr. R.J. Abraham.

Figure 1.

Methylene (lower-trace) protons (AB part of an ABX spin system) of PhCHBr.CH₂tBu. The same region (upper-trace) for the mixture of products obtained (erythro and threeo PhCHBr.CH₂tBu) when DBr was added to the trans-olefin. The middle-trace is the corresponding deuterium decoupled spectrum.
July 22, 1974

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

Dear Barry:

One of Manny Reinecke's students made the rather unusual heterocyclic below, and we thought it appropriate to record the proton NMR parameters here. The molecule was treated as two three spin systems though there is clearly a small long range internuclear coupling as noted.

2-(3-thienyl)furan

\[
\begin{align*}
H_A & = 7.32; H_B = 7.18; H_C = 7.12; \\
H_X & = 7.24; H_Y = 6.30; H_Z = 6.26 \\
J_{AB} & = 3.02; J_{AC} = 1.21; J_{BC} = 5.22; \\
J_{XY} & = 0.73; J_{XZ} = 1.82; J_{YZ} = 3.40; \\
J_{AX} & \approx J_{AY} \approx 0.25
\end{align*}
\]

Also I have a postdoctoral position available in September for someone to do synthesis and NMR on steroids related to the moulting hormones. Interested parties may consult me for details.

Sincerely,

W. B. Smith
Dear Barry,

$^1$H, $^13$C and low temperature measurement on tin derivatives of nitrogen heterocycles

The structure of tin derivatives of aromatic heterocycles such as imidazole including a tin nitrogen bond is well known. It is a polymer, with five coordinated tin atoms, compatible with the 1,3 position of the two nitrogens.

These compounds are not soluble in usual organic solvents but methanol, where tin-nitrogen bonds are broken, and the $^1$H NMR spectra in CD$_3$OD gives the same chemical shift for protons 4 and 5.

The structure is quite different when the two nitrogens are in 1,2 position such as pyrazole derivatives.

Polymeric association is sterically impossible. The N-tributylstannylpyrazole is a liquid. The $^1$H NMR spectra in different solvents, even in pure liquid, still give the same chemical shift for protons 3 and 5. Same results have been obtained with N-triethylstannylpyrazole. We also recorded the $^{13}$C spectra in the same conditions but we found the same chemical shift for carbons 3 and 5. The reason can be a fast exchange of the tin atom between the two nitrogens. So, we did some low temperature measurement on N-tributylstannylpyrazole. Using pentane like solvent, even at -80°C, we still have the same spectrum. If we replace pentane by acetone one can see a change. The exchange of Bu$_3$Sn- is slowed enough to allow a complexation of the second nitrogen to give the equilibrium:
As we decrease the temperature the quantity of complexed form increased. At -70°C we just have the complexed form.

Room temperature spectra of N-tributylstannyl 1,2,4 triazole have also been recorded.

N-tributylstannyl 1,2,4 triazole is a solid soluble in different organic solvents. There is a change in solubility and in chemical shift with the solvent, but protons 3 and 5 still give one peak.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CS₂</th>
<th>CCl₄</th>
<th>pentane</th>
<th>CDCl₃</th>
<th>dioxan</th>
<th>THF</th>
<th>CD₃OD</th>
<th>CD₃COCD₃</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical shift</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of protons 3 and 5 in ppm</td>
<td>775</td>
<td>7.84</td>
<td>7.87</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8.14</td>
<td>8.15</td>
<td>8.16</td>
</tr>
</tbody>
</table>

Low temperature measurements and protons spectra have been recorded on a Jeol C 60 H and ¹³C spectra on a Varian NV 14 with FT.

Yours Sincerely,

J.C. MAIRE

R. GASSEND
Temperature study on N-tributylstannylpyrazole

-46°C

+20°C
29th July, 1974

Dear Professor Shapiro,

Inter- and Intra-molecular Exchange in the System 1,3,5-Trioxan/1,3,5,7-Tetroxan

Few studies of ring inversion in 8-membered rings have been reported in the literature and the simplicity of the proton spectrum of 1,3,5,7-tetroxan provides an ideal system for examination. Bearing in mind that the barrier to ring inversion in cyclo-octane is relatively high, one expects decoalescence into an AB-spectrum to occur readily on lowering the temperature.

We were surprised to find that the proton spectrum of a 5% solution of this material in a 1:1 mixture of chloroform-d and m-fluorotoluene, which was a singlet at ambient temperatures, decoalesced below -17°C into the expected AB-spectrum but with an additional peak (approx. 33% contaminant) near the centre.

After four sublimations of the solid tetroxan this singlet still persisted in the low-temperature proton spectrum and it was identified as trioxan by addition of some of this material to the sample. Evidently a dynamic equilibrium between tetroxan and trioxan existed in solution and this was further confirmed by the observation of a symmetric, sharp singlet resonance (at 100 MHz) for the sample at ambient temperature.

We therefore investigated the exchange in this system as being AB ⇄ BA, using Blasch's program UNMRE3. In this way we were able to identify the inter- and intra-molecular exchange processes in the following scheme:

Here rate $r_1$ gives directly the rate of ring inversion $k$, while rate $r_2$ is related to the inter-molecular exchange rate by $k_2 = 2r_2$ since the populations of all the sites are equal.

Temperature dependence studies therefore yielded a value of $\Delta G^\circ = 57.7$ kJ mole$^{-1}$ for the inversion barrier in tetroxan (assuming crown) compared with 38.8 kJ mole$^{-1}$ for cyclo-octane. The activation energy for the inter-molecular exchange was comparable at 58.9 kJ mole$^{-1}$.

Yours sincerely,

J. A. Ladd.

July 30, 1974

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

Quest for a $^{13}$C Knight Shift in TTF/TCNQ

Dear Barry:

Some time ago, Wiebren Veeman (now at Nijmegen) and I looked for a Knight shift for $^{13}$C in TTF/TCNQ and failed to detect one, at least in the signals we observed. We were able to see $^{13}$C signals from -110°C to -180°C using the Bleich-Redfield double resonance technique. The material acts like a metal down to 60K. We recorded a strong, rather broad (600 Hz) but symmetrical resonance centered in the same frequency region where one observes $^{13}$C in solid benzene (5.783 - 5.784 MHz at 5400 gauss). We looked over a very large frequency range, but found no additional signals. We therefore conclude that the Knight shift (if there is one) for the detected carbons is no larger than 100 ppm. From the simplest double resonance ideas, one would guess that these are the carbons to which protons are bonded, and may not be the ones for which a Knight shift would be predicted. Still, we do not understand the symmetry of the signal (no chemical shift anisotropy ?) and we welcome suggestions from interested readers. We have been able to observe both a narrow methyl carbon resonance and not-so-narrow signals from other carbons in the pure tetramethyl derivative of TTF.

Sincerely yours,

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

Dear Professor Shapiro:

1 August 1974

Spectral Assignments in Peptides
by Double Resonance Techniques

Allerhand and coworkers have shown that nonprotonated aromatic carbons of proteins give resolved $^{13}$C resonances which are sensitive to conformational and redox state effects. Since backbone carbonyl resonances are similarly narrow, they too should be of use as probes of solution structure, providing they may be assigned to individual amino acid sites, and $^{13}$C shift models are found which reproduce the observed spectral effects.

The ferrichromes offer an excellent prototype system for such an approach. This class of ferric cyclohexapeptides has been well characterized by x-ray crystal analysis and $^1$H NMR. The parent compound, ferrichrome, has the primary structure

cyclo (Gly-Gly$_2$-Gly-Orn$_3$-Orn$_2$-Orn$_1$)

where the Orn residue denotes $\gamma$-N-acyl-$\gamma$-N-hydroxy-L-ornithine, and the iron atom is octahedrally coordinated to the three Orn hydroxamate groups.

Selective enrichment techniques have been reported for carbonyl assignments of other peptides. We have made these assignments for ferrichrome (where, for NMR spectra, aluminum replaces iron to eliminate paramagnetic line broadening) by isolating approximately 95% $^{15}$N-enriched ferrichrome and taking advantage of the known peptide $^1$H assignments. By selectively decoupling $^{15}$N and observing the $^1$H spectra, then selectively decoupling the $^{15}$N and observing the $^{13}$C spectra, individual $^{13}$C=O resonances can be connected to these $^1$H assignments in a manner similar to that reported by Birdsall et al. This technique avoids the complications of selective enrichment (metabolic branching, availability of aa mutants, etc.).

Figure 1A shows the $^1$H-noise decoupled spectrum of approximately 100 mg $^{15}$N-enriched ferrichrome, at 50°C in DMSO. Figure 1B shows $^1$H-noise decoupled, $^{15}$N-coherently decoupled $^{13}$C spectra of the same sample at various $^{15}$N-decoupling
Figure 1.

A

B

10.14001 MHz
10.14002 MHz
10.14003 MHz
10.14009 MHz
10.14028 MHz
10.14025 MHz
frequencies. The abscissa is in ppm from the $C_\alpha$ resonance of free glycine at neutral pH, which is taken to be 25.4 ppm upfield from an internal dioxane reference. These results were obtained on a Varian XL-100 instrument set up for double-decoupling and dual phase detection, each spectrum representing 5-hour accumulation time. The four upfield resonances arise from the hydroxamate carbonyls of the Orn sidechains, and are not affected by $^{15}N$ decoupling since their $^{15}N$ resonances are distant from the amide decoupling frequencies.

Figure 2 shows the assignments of the ferrichrome carbonyls in DMSO and trifluoroethanol which were made using our technique. The resonance least shifted between these two solvents is seen to be the Gly$^3$ carbonyl, which is not exposed to solvent, taking part in a transannular hydrogen bond to the peptide N-H of Orn$^3$. We are presently trying to rationalize the nonequivalence of the three Orn and three Gly residues in terms of specific chemical shift models. At this time we can eliminate electric field effects caused by the ligand field, and peptide group magnetic susceptibility anisotropy, as dominant determinants of the backbone carbonyl shifts.

Please credit the account of D. M. Wilson for this contribution.

Figure 2.

DMSO solvent

Orn

Gly$^2$

Orn$^3$

TFE solvent

Gly$^2$

Gly$^3$

Gly

-135

-130

M. Llinás*

D. M. Wilson*

M. P. Klein*

Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory* and Space Sciences Laboratory*, University of California, Berkeley, California 94720


10 July 1974
1517 Birch
Richland, Wa. 99352

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

Dear Barry,

I would very much appreciate your inserting my letter in
the NMR newsletter.

I am interested in a postdoctoral position for research in
NMR. The Ph.D. was a study of keto-enol tautomerism in \( \beta \)-dicarbonyls.
Other research was performed in NMR for two years.

Sincerely,

Jane L. Burdett
August 1, 1974

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

Dear Barry:

Selective Relaxation in Proton NMR

We have recently been using a modification of the Fourier synthesized excitation technique (1), in which a spin system is excited by a sequence of modulated pulses, to perform selective relaxation measurements in proton NMR.

Consider a sequence of rf pulses (carrier frequency $\nu_0$, amplitude $H_1$) with a repetition frequency $\nu_r$ and pulse widths given by $\tau = \tau_0 \cos 2\pi m$, i.e. the widths are modulated by a frequency $\nu_m$. If the pulse widths are small compared with the pulse spacing, then to a good approximation the frequency spectrum of the sequence consists of components with amplitudes $H_1 \nu_r \nu_0$ at frequencies $\nu_0 \pm n \nu_r \pm \nu_m$ for $n = 0,1,2...$. When these sidebands are well separated compared with their intensities, their effects may be considered independently and only nuclear resonances close to a sideband will be significantly affected.

By applying the pulse sequence for a time $T_s$, short compared with the relaxation times, a resonance close to a sideband will experience a "selective $\alpha^0$ pulse", where

$$\alpha = \gamma H_1 \nu_r \tau_0 T_s$$

As in other selective pulse methods (2), the selectivity depends on the effective rf field intensity ($H_1 \nu_r \tau_0$). A number of selective pulses may be applied simultaneously by superimposing modulation frequencies onto the pulse sequence. Following the method of reference (1), the modulation function is synthesized in a computer from the selected components and the length of the pulse sequence is chosen according to Eq. (1) to give the required flip angle.
The figure shows a set of inversion-recovery spectra for the ring protons of 3,4,6-tri-O-acetyl-1-O-benzoyl-2-chloro-2-deoxy-D-glucopyranose (3) in which the "180° pulse" was a sequence of pulses (at 250 µs intervals and total duration about 15 ms) which was selective for two of the resonance groups while the 90° pulse was non-selective. The initial rate of relaxation of a signal from a particular proton depends upon the perturbation of other protons to which it is coupled via a dipolar interaction. Measurement of this rate as other protons in turn are simultaneously inverted allows the evaluation of the relative dipolar interaction between the selected proton and each of the others. Results using this technique are in good agreement with results from nuclear Overhauser measurements on the same molecule.

Yours sincerely,

H.D.W. Hill

(3) from L.D. Hall, U.B.C. Vancouver
Now the XL-100A NMR Spectrometer lets you think small.

Thanks to another Varian first, a 1-mm Insert Accessory for the XL-100A Pulsed-Fourier Transform NMR Spectrometer, scientists such as biochemists and pharmaceutical chemists who have to work with limited sample quantities can obtain rapid proton NMR analysis of microgram samples.

Using the insert, it's possible to run spectra of 50 µg or less of sample. Spectra run thusly are obtained in less than 17 minutes, yet are superior to 8-hour runs in a 5-mm tube. Sensitivity for a fixed amount of sample can improve from 4- to 6-fold when the 1-mm Insert Accessory is used.

The two spectra of Δ⁸-tetrahydrocannabinol (THC) shown here demonstrate the dramatic results possible using the 1-mm Insert. Spectrum A, of a concentrated sample in a 5-mm tube, serves as a comparison for the other spectra. Spectrum B (20 µg of sample in a 1-mm tube) and Spectrum C (20 µg of sample in a 5-mm tube) were run under identical conditions. Note the well-defined peaks in the spectrum run using the 1-mm Insert.

This innovative approach is successful since reducing the sizes of both the sample tube and the receiver coil ensures maximum coupling of the available nuclear magnetic moments with the coil. It permits the use of commercially available capillary tubes costing less than one cent each.

To interchange the 1-mm Insert with standard XL-100A inserts, merely take one out, put in the other, retune and balance. The sample is dissolved in 5 µl of an NMR solvent containing TMS for a reference. It is then transferred into a 1-mm sample tube by using a drawn out glass pipette or a hypodermic syringe. This eliminates the bubble problems which sometimes arise with the use of microcells in larger tubes. The resulting column length is about 10 mm, assuring freedom from line shape distortion. Since spinning produces no vortex, spinning speed is not a critical factor.

The sample volume in the 1-mm Insert is so much less than the 400 µl required for 5-mm tubes that use of deuterated species becomes more economical. The 1-mm capillary has its own spinner turbine attached. Unlike other existing techniques designed to accommodate small quantities of samples, there are no plugs to adjust and no sample positioning is necessary. Proper positioning is automatic thereby assuring reproducible homogeneity.

Write for a copy of Varian's Application Report NMR-2, which describes the XL-100A Insert Accessory in more detail.

The spectrum of 20 µg of Δ⁸-THC (tetrahydrocannabinol) in a 1-mm capillary with 5 µl CDC1₃. Total time was 16¼ minutes (1000 pulses at 1-second intervals). The spectrum of a concentrated sample is partially reproduced above for comparison. Assignments are written over peaks.
The FX60 was recently previewed at the ENC Conference, Raleigh, North Carolina, April 28, 1974.