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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a “Private Communication”. Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.
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Deadline Dates: No. 137: 2 February 1970
No. 138: 2 March 1970

All Newsletter correspondence, etc., should be addressed to:
Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843
Dear Professor Shapiro,

I would like to start this letter by thanking the authors of DNMR, Daniel A. Kleier and Gerhard Binsch, for very kindly supplying me with a copy of their program.

Unfortunately as we are not endowed with a 65K Univac, it became necessary to reduce the core requirements to suit our humble Control Data 3600 which has a 32K core with Drums And Display. The net available core under standard operation is about 24K.

The total number of cards to change is small (about 60). The changes may be done in two stages. The first will reduce the program by 4600 words and if a RANDOM ACCESS DRUM is used a further reduction of 4600 words is achieved. The extra time is only 2 secs in 1 minute. All this is only necessary of course if it is required to calculate the larger configurations.

A copy of the changes will be available from either of us.

Sincerely yours,

(W.P.A. Pascoe)
The following changes to DNMR will reduce the core requirements from 29814 to about 20600 words.

In main program,

- **COMPLEX** (delete **CR,CL,EIG**) (insert **LAMBDA(48)**)
- **COMMON/EIVEC/** (change to **A,QQNV,LAMBDA**)
- **DIMENSION TEXT(10)**
- **CALL STADAT(TEXT)**
- **CALL ALLMAT(N,T)**
- delete **CALL CONVEC(K,NT)**
- **EQUIVALENCE (CR(1,1),A(1,1))**
- **CALL SPECT(J,TEXT)**

**SUBROUTINE STADAT(TEXT)**

**SUBROUTINE ALLMAT(N,KS)**

- **COMPLEX** (delete **CR,CL,EIG**) (reduce H array to (2,2))
- **COMMON/EIVEC/** **A,HL,LAMBDA**
- **COMMON/TEM/** **H**

delete **DO 19 I=1,N** insert **CALL WDRUM(66,A,4608,0)**

**500 IF (UNIT,66) 500,501**

**501 CONTINUE**

The above change uses a RANDOM ACCESS DRUM to write out the A matrix.

delete cards between 38 and 40 and insert the following,

**38 DO 56 L=1,NCAL**

**IF (N.EQ.2) GO TO 602**

**CALL RDRUM(66,HL,4608,0)**

**600 IF (UNIT,66) 600,601**

**601 CONTINUE**

**IF (N.NE.2) GO TO 603**

**HL(1,1) = H(1,1)**

**HL(1,2) = H(1,2)**

**HL(2,1) = H(2,1)**

**HL(2,2) = H(2,2)**

**603 CONTINUE**

**DO 40 I=1,N**

**HL(I,1)=HL(I,1)-LAMBDA(L)**

change **53 VECT(J)=HL(J,N11)*VECT(N11+1)+VECT(J)**

**CALL NVRT(N,KS)**
SUBROUTINE NVRT(N,KS)

change dimension statements to the following,

COMPLEX QQNV(48,48), TEMP(48,48), F(48), Q(112), D(112), CRS(48)
COMMON/EVEC/ TEMP, QQNV, LAMBDA
COMPLEX TFR, CLS, LAMBDA (48)
COMMON/VECT/Q,D
COMMON/VEC/ V(112), POV(112)

CONVEC is divided and incorporated with NVRT.

NT = N
KM = KS
K1 = 1
KK = KS - 1

505 CRS(K1) = CMPLX(0., 0.)
DO 506 LA = 1, NT
LAK = LA + KK
506 CRS(K1) = CRS(K1) + V(LAK) * TEMP(LA, K1)
KS = KS + 1
K1 = K1 + 1
IF (K1.LE.NT) GO TO 505

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

October 24, 1969

Dear Barry:  

The Structure of a Streptothricin Type Antibiotic

I'm afraid that most of our work during the past few months has utilized NMR in fairly straightforward fashion. In conjunction with continuing work on antibiotics by Dr. D. Borders at our Lederle Laboratories, we have used NMR extensively to determine the structure of LLAC541 (I), a new antibiotic of the streptothricin class, as well as other related compounds. As far as we are aware, no NMR investigations of these types of antibiotics have been reported. The coupling constant data supported the stereochemistry of the hexosamine and streptolidine rings, indicated in Figure 1. A rather high vicinal coupling of 14.8 Hz was noted for the two axial-axial oriented protons a & b. This work will be published shortly.

Very truly yours,

John E. Lancaster, Group Leader  
Nuclear Magnetic Resonance Group  
Research Service Department
Professor Barry L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Dear Barry:

MO Calculations of Quadrupole Coupling Constants

Betsuyaku (1) has recently shown that the nitrogen net p-orbital populations calculated for nitrite ion by the LCAO-MO-CND0 method (2), when used in the quadrupole coupling constant expression derived by Cotton and Harris (3), yield values for the coupling constants in very good agreement with those determined experimentally.

We have performed similar CND0/2 calculations (4) on CH₃NC and HCN, and have found that there is poor agreement between the calculated and experimental coupling constants for these compounds. To make matters worse, the calculated e²qQ for MeNC is larger than that calculated for HCN:

<table>
<thead>
<tr>
<th></th>
<th>HCN</th>
<th>MeNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>calc.</td>
<td>0.725</td>
<td>3.345</td>
</tr>
<tr>
<td>exp.</td>
<td>4.58</td>
<td>0.48</td>
</tr>
</tbody>
</table>

We doubt that the well-known sensitivity of the calculations to geometry can be responsible for such large discrepancies, and are inclined to suspect that the parameters may require adjustment for nitrogen in the triply-bonded (sp) state.

Sincerely,

W. B. Moniz  
C. F. Poranski, Jr.  
NMR Spectroscopy Section  
Chemistry Division

4. J. L. Ragle, R. Gentzler and P. A. Clark, QCPE 144, obtained from QCPE, Indiana Univ., Bloomington, Indiana
December 3, 1969

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

Dear Barry,

Scope Display for the T-60

Sometimes it is convenient to tune the magnetic field of the T-60 while observing an nmr signal on a scope rather than using the existing NSBO or lock level indicator. While there does exist an optional accessory which provides this facility, anyone with an appropriate oscilloscope can build his own for the cost of a SPST switch and a 20 k potentiometer. Whatever scope is used, it must be capable of providing an external linear sawtooth (from the internal sweep circuit) without being overloaded internally. This sawtooth is used to synchronously sweep the magnetic field and the horizontal axis of the scope. The 20 k pot provides an independent control for the field swept, and the SPST switch returns the spectrometer to recorder control without having to turn off the scope.

The scope we used was an Hp Model 1208 (standard on the HA-100). The schematic below shows the modification as discussed for the horizontal axis. The vertical input to the scope is taken directly from the standard "Signal Out" jacks at the side of the T-60. With the scope switched to an internal sweep rate of approximately 100 milliseconds/cm, nmr signals may be conveniently monitored while electrically shimming the magnetic field.
Yours Sincerely,

Michael H. Gross
Applications Scientist

William Hatfield
Service Engineer
Dear Prof. Shapiro,

Rotational Isomerism in Ethylene Glycol and 2-Fluoro-ethanol

An NMR study of the solvent dependence of 1,2-disubstituted ethanes may yield information on vicinal coupling constants and on rotational isomerism. We have extended our investigations to ethylene glycol and 2-fluoro-ethanol, two compounds which are supposed to exist as gauche isomers only. Small but significant solvent effects on the vicinal couplings were observed and attributed to changes in the relative rotamer populations (see Table). The gauche populations (ng) in the Table were obtained using Abraham's equations, which relate the vicinal couplings in the individual rotamers to the electronegativity of the substituents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>J</th>
<th>J'</th>
<th>ng</th>
<th>Solvent</th>
<th>J</th>
<th>J'</th>
<th>ng</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et3N</td>
<td>6.06</td>
<td>4.42</td>
<td>.79</td>
<td>CHCl3</td>
<td>5.97</td>
<td>2.48</td>
<td>.95</td>
</tr>
<tr>
<td>CH3COCH3</td>
<td>6.16</td>
<td>4.13</td>
<td>.82</td>
<td>neat</td>
<td>5.98</td>
<td>2.44</td>
<td>.95</td>
</tr>
<tr>
<td>CH3OH</td>
<td>6.16</td>
<td>3.71</td>
<td>.86</td>
<td>D2O</td>
<td>6.00</td>
<td>2.25</td>
<td>.97</td>
</tr>
<tr>
<td>D2O</td>
<td>6.25</td>
<td>3.56</td>
<td>.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The relatively small proportion of trans isomer found in 2-fluoro-ethanol does not necessarily contradict previous IR results since it is apparently difficult to detect an isomer population of 5% by IR. However, the results on ethylene glycol are obviously in disagreement with conclusions drawn from other investigations, but one has to bear in mind that in this case IR measurements are hampered by the presence of various inter- and intramolecularly hydrogen bonded species, while dipole moments, governed by the larger OH bond dipole, reflect a rotation around the O-O bond rather than the C-O bond.

Please address all correspondence to the Director.
Thus NMR spectroscopy could be a very powerful tool in the study of rotational isomerism, being more sensitive and more selective than other techniques, provided one is able to obtain reliable values for the vicinal couplings in the individual rotamers.

Yours sincerely,

[Signature]

K. Pachler
Chief Research Officer
Chemical Physics Group
National Chemical Research Laboratory

References:

Dear Barry:

RE:  $^{19}$F Lock for $^{13}$C on an HA-100

Some of your readers who have HA-100's with 25.1 MHz rf units might be interested in recent modifications we have made on our system for $^{13}$C. After three years of struggling with $^{13}$CS$_2$ locks¹ we decided to try for a more convenient technique, and worked out the internal $^{19}$F lock system shown in the accompanying figure. Vic Bartuska and Tom Nakashima have done nearly all of the work on this project.

The internal $^{19}$F lock circuit is based upon a single-coil that is wound concentrically about the 25.1 MHz receiver coil of the Varian insert for 8mm tubes. Using a "magic T" bridge and FEI preamps, this provides adequate signals for the 94.1 MHz V4311 unit. The basic frequency (provided by a 15.678 MHz crystal in the original Varian configuration) is derived from appropriate mixing and division of signals available at the HP510A Synthesizer Driver. From the front of the attached HP510A Synthesizer a variable 6.28 MHz signal is taken as a basic frequency that replaces the crystal in the 25.1 MHz rf unit. This permits the $^{13}$C centerband to be placed in any region desired to resonate $^{13}$C nuclei in the field fixed by the $^{19}$F lock (usually a capillary of CF$_3$CO$_2$H).

The V-4354A unit was modified so that the $^{19}$F control signal and $^{13}$C analytical signal pass through entirely separate components. Proton decoupling uses a slightly modified Varian V3512-1 unit.

All of the individual modifications or circuits have previously been used individually in closely analogous systems.²³ The impressive frequency stability of the system makes it ideal for high-precision measurements and for CATing.

With best regards from Ronnie,

Gary E. Maciel

Reference:

Dec. 9, 1969

Dr. Bernard L. Shapiro
Texas A & M University
College of Science
College Station, Texas 77842
ATTN: TAMU NMR

Title: HR 220 sweep modification
Dear Dr. Shapiro:

Enclosed please find an HR 220 modification procedure which I trust will serve as my reinstatement to the TAMU NMR newsletter.

Our HR 220 has been bubbling along happily now for many months and we are quite pleased with its overall performance. We have had no difficulty routinely exceeding specifications as the instrument appears to be conservatively rated in the best Varian tradition.

A minor inconvenience, however, is encountered when controlling the oscilloscope readout from the SS 100 console. Since no attempt has been made to logically interface the SS 100 readout with the scope z-axis, considerable manual manipulation of scope controls is necessary each time one switches from computer driven to instrument driven scope display or vice versa. The enclosed circuit, which is quite simple and can be built for under $20, reduces this procedure to moving the z-axis switch from 1 v/cm to 2 m sec/cm corresponding to the time (20 m sec) necessary for one sweep through memory.

The simplification is brought about by making the HR 220 scope sweep signal equivalent to the SS 100 scope sweep signal and is accomplished by breaking the line at J 305 M of the V-4356 sweep unit and inserting the adaptation circuit between this point and scope output J 304. The range pot is adjusted to give a 10 cm. trace with the scope z control in the 1 v/cm position. The z-axis is then centered and zero is adjusted so that the trace does not shift when going from HR 220 to SS 100 display.

This circuit was constructed on ½ by 3 inch card and mounted in the V-4356 chassis to the right of J 302. Access holes were drilled so that zero and range could be adjusted after the instrument reaches nominal operating temperature.

Sincerely,

Dennis E. Wisnonsky
Electronics Research
December 12, 1969

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

Dear Barry:

We offer the following contribution under the class of "partly explained mysteries". If any readers can offer a more complete explanation, we would like to hear from them, either directly, or in a future issue of your esteemed newsletter, which we hope to continue receiving.

31P NMR OF METHYL ETHYLENE PHOSPHITE: AN APPARENT ANOMALY

The 60 MHz proton spectrum of methyl ethylene phosphite has been analyzed by Haake, McNeal, and Goldsmith(1), who concluded that envelope conformation II (see Fig. 1) is favored over I and made tentative peak assignments on that basis. Moreover, they used the vicinal hydrogen-hydrogen coupling constants as evidence for preferring two equivalent twist-envelope conformations, one of which is approximated as III. They were unable to rule out the possibility of rapidly interconverting conformations, however.

We have had occasion recently to measure the 40.5 MHz 31P NMR spectrum of freshly distilled, neat methyl ethylene phosphite. Under low resolution we observed a rather broad multiplet centered at -131.4 ppm from H_3PO_4. (Previously reported shifts are -132.4 and -131.6(2).) The intensity ratios approximated the 1, 3, 5, 5, 3, 1 expected from observation of the six most intense peaks of a pseudo-first order eight-fold multiplet arising from coupling of the P to seven nearly equivalent protons. Under higher resolution (see Fig. 2) we found this spectrum to be made up of more than 40 individual peaks of less than 0.5 Hz width, arranged in a clearly asymmetric multiplet. The asymmetry initially suggested to us that methyl ethylene phosphite at room temperature might be locked into two or more non-equivalent conformations which were not rapidly interconverting and in which the 31P chemical shifts of the phosphorus nuclei differ slightly. Since this was not apparent from the previously published proton work(1), we subjected the spectrum to more diligent scrutiny and were able by inspection to decompose it into three simpler multiplets. These were a major symmetrical multiplet of at least 36 peaks, and two superimposed lower intensity quartets, one displaced to lower field by 0.07 ppm and one displaced to higher field by 0.15 ppm (see Fig. 2).
Although we have not attempted a complete and detailed study, including rigorous repurification of the sample and all the obvious possible temperature, decoupling, $^{13}$C, and solvent experiments, the present observations are sufficient in themselves to define a mystery. The two independent quartets which contribute to the overall spectrum could logically arise from impurities, and this should be ruled out first. We are unable, however, to conceive of any hypothetical structures which would be expected to have a $^{31}$P chemical shift nearly identical to the cyclic five-membered ring phosphite and yet give rise to only simple quartets with the 10 Hz splitting expected from coupling of a single methoxy group with the phosphorus without evidence of other H-P coupling of any kind. The chemical shifts of known and expected impurities are nearly all several ppm removed from this region of the phosphorus spectrum, which is rather unique for trivalent phosphorus, particularly cyclic five-membered ring phosphites. If the two quartets do not arise from impurities, but from stable conformational isomers, the same absence of additional H-P coupling is equally puzzling. Could rapid torsional oscillation along the C-C bond effectively decouple proton-phosphorus spin coupling in one conformational isomer and not in another?

Sincerely,

M. M. Crutchfield

C. W. Heitsch

References:


December 16, 1969

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

Dear Barry:

Our studies of substituent effects on four-bond HH couplings in propanic fragments established that, in molecules of the type

$$^{13}\text{CH}_3 \text{-CXY-}^{12}\text{CH}_3$$

as the combined electronegativity of X and Y increases, $^{4}_\text{HH}$ also increases. We were therefore rather surprised when we began to look at the methylene-methyl coupling in some neopentane derivatives:

$$(\text{CH}_3)_3\text{C CH}_2\text{X}.$$ 

Since the couplings are quite small, we've been forced to estimate their magnitudes by lineshape analysis. Some preliminary results (shown below) indicate a substituent dependence opposite to that in the propane derivatives! Clearly (and significantly), what happens to the coupling constant depends not only on whether electrons are added to or removed from the carbon chain, but where along the chain the perturbation occurs. We are actively pursuing this intriguing observation.

<table>
<thead>
<tr>
<th>X</th>
<th>$^4_J_{HH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.9</td>
</tr>
<tr>
<td>Cl</td>
<td>3.2</td>
</tr>
<tr>
<td>OH</td>
<td>3.5</td>
</tr>
</tbody>
</table>


Best wishes to all.

Sincerely,

Dennis J. Sardella
Assistant Professor

Short Title: An Unusual Substituent Effect on $^4_J_{HH}$, or "Pornography is Question of Geography."
Professor B. L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas 77843

December 16, 1969

Dear Professor Shapiro:

As part of our interest in the high resolution proton magnetic resonance spectra of paramagnetic transition complexes, we have attempted to exploit the very large non-linear expansion of the chemical shift scale due to proton-electron coupling to monitor rapid intramolecular ligand rearrangements.

Our most recent experiments have yielded estimates of the rate of intramolecular optical racemization of some "labile" octahedral cobalt(II) compounds. To date nothing is known about the kinetics and mechanisms of such inversions in cobalt(II) complexes.

Thus in the chelate bis(acetylacetonate)-(4,7-dimethyl-1,10-phenanthroline)-Co(II) the two acetylacetonate methyl groups are magnetically non-equivalent. In the process of optical inversion, these two methyl groups are interchanged (although not necessarily in a one-to-one ratio). In analogous diamagnetic compounds, this non-equivalence of the methyl groups has yielded chemical shift differences of ~0.1 ppm. In our cobalt chelate, this paramagnetic shift difference is ~40 ppm! As the two spectra in the figure illustrate, at high temperature only an average acetylacetonate methyl signal is observed, which clearly splits at low temperatures. Addition of excess ligand precludes intermolecular ligand exchange as a source of the averaging.

Standard analysis of the linewidths in the limit of slow inversion yields a first order rate constant ~5 x 10^8 sec^-1, with Ea ~13 kcal mole. Preliminary analysis of the origin of this sizable magnetic non-equivalence between the methyl groups which allows the detection of this kinetic process indicates that a strong dipolar coupling between the protons and the highly anisotropic electronic moment is responsible. Furthermore, such sizable magnetic non-equivalence between the two sides of a symmetric bidentate ligand, A-A, appears to be a general property of complexes of structural formula Co(A-A)₂(B-B). Preprints are available to those interested.

Sincerely yours,

Gerd N. La Mar

Title: Rapid Intramolecular Ligand Rearrangements in Paramagnetic Complexes.
PROTON NMR TRACES OF Co(II)₂(4,7-PHEN) IN CDCl₃ IN THE LIMIT OF FAST (+40°) AND SLOW (-67°) ENVIRONMENTAL AVERAGING
Title: Long recovery time after saturation by high power magnetic resonance.

Dear Barry,

Isolated as we are in Australia, we hope you will understand that the perturbation induced by the International Symposium on Magnetic Resonance in August has taken some time to die away. The most direct result of such a long relaxation time is that we have nothing of our own to contribute.

However, the Monash Department is now large enough to provide a steady flow of interesting compounds, some of which involve novel, or at least unusual, features in their n.m.r. spectra. For example the spectrum of ethyl 2-(1-methyl-3-indolyl)-pyruvate shows an interesting long range coupling to the enol proton, maximized, no doubt, by favourable geometry. The observed parameters are (CDCl₃, 60 MHz):

![Chemical Structure Image]
\[ \delta H_a = 7.83 \quad J_{ab} = 0.6 \text{ Hz} \]
\[ \delta H_b = 6.97 \quad J_{bc} = 1.6 \text{ Hz} \]
\[ \delta H_c = 6.25 \text{ (lost on D}_2\text{O exchange)} \]

We are indebted to Dr. R. F. C. Brown and Mr. P. Newman of this department for the above example, but we will take the subscription credit just the same! We will write and tell you about our own things when we have stopped nutating wildly.

Best wishes for 1970

Ian D. Rae

Michael L. Heffernan
December 18, 1969

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

Dear Dr. Shapiro,

Charge Calculations, Dianions and Paramagnetic Ring Currents.

In the course of a study with Professor L. M. Jackman we became interested in trying to develop an empirical model for the calculation of charge induced shifts in aromatic systems. Our study was based on the Buckingham equation for charge effects and used a range of nitrogen heterocycles to establish the empirical relationship. The equation obtained was

\[ \Delta \sigma_i (\text{ppm}) = 11.75 \sum \frac{\Delta q_j \cos \theta_{ij}}{R_{ij}^2} - 3 \times 10^{-4} \left( \frac{\Delta q_i}{R_{ij}^2} \right)^2 \]

where \( \Delta q_i \) is the charge induced shift for proton \( i \) caused by the system of charges \( \Delta q_j \) around the proton (all shifts and charges relative to benzene) \( x_{ij}, R_{ij} \) and \( \theta_{ij} \) are defined in the figure below.

This equation calculated the shifts of 117 protons covering a range of 4 ppm with a mean deviation of 0.18 ppm. The calculations were then extended to determine the shifts in several aromatic carbanions and carbonium ions with moderate success and also to the estimation of the effect of the alkali metal cation on carbanion shifts in ion paired systems. Two manuscripts covering this work are currently in preparation.
We then pressed our luck too far and tried to calculate the shifts for the aromatic dianions recently reported by Lawler. The results were very poor (see Table) with differences of as much as 2.9 ppm between observed and calculated shifts, with the calculated shifts generally being too low. This observation combined with the knowledge that these dianions are 4nπ electron systems suggested the possibility that paramagnetic ring currents might be the cause of the discrepancy. An attempt was made to calculate the ring currents in these systems using the Hall, Hardisson, Jackman SCF method. These calculations yielded the values shown in the table which are obviously far too high, but at least they do show that a paramagnetic current is possible in these ions and that the ring current effects tend to parallel the differences between observed and calculated values. No allowance was made for bond alternation in the calculations and this should serve to diminish the paramagnetic current.

There are obviously many possible conclusions that can be drawn from the results discussed here, our aim has been to present one possible treatment and invite comments from your readers. We are planning to measure the magnetic susceptibilities of a couple of these ions to provide some experimental justification for these ideas (possibly even a scaling factor for the calculated values).

Please count this contribution towards Dr. Muller's subscription.

Yours sincerely,

John B. Grutzner

JBG:mf


<table>
<thead>
<tr>
<th>Proton</th>
<th>$\delta_{\text{obs}}$</th>
<th>$\delta_{\text{calc}}$</th>
<th>$\delta_{\text{obs}} - \delta_{\text{calc}}$</th>
<th>$\delta_{RC}$</th>
<th>$\Delta \chi_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.91</td>
<td>2.25</td>
<td>1.66</td>
<td>-7.15</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.02</td>
<td>2.24</td>
<td>0.78</td>
<td>-6.07</td>
<td>225.5</td>
</tr>
<tr>
<td>9</td>
<td>5.34</td>
<td>2.43</td>
<td>2.91</td>
<td>-9.20</td>
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<tr>
<td>1</td>
<td>2.81</td>
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<td>1.30</td>
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<td>2</td>
<td>2.62</td>
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<td>2.63</td>
<td>0.14</td>
<td>-0.56</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.23</td>
<td>2.21</td>
<td>0.02</td>
<td>-0.93</td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>3.94</td>
<td>2.57</td>
<td>1.37</td>
<td>-0.89</td>
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<td>7</td>
<td>2.81</td>
<td>3.00</td>
<td>-0.19</td>
<td>+1.84</td>
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<td>1</td>
<td>2.46</td>
<td>2.12</td>
<td>0.34</td>
<td>-0.43</td>
<td></td>
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<tr>
<td>2</td>
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<td>1.81</td>
<td>0.42</td>
<td>-0.96</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.00</td>
<td>1.90</td>
<td>2.10</td>
<td>-0.96</td>
<td>-18.7</td>
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<tr>
<td>7</td>
<td>0.38</td>
<td>1.07</td>
<td>-0.69</td>
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<td>8</td>
<td>1.21</td>
<td>1.91</td>
<td>-0.70</td>
<td>2.16</td>
<td></td>
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<tr>
<td>1</td>
<td>2.28</td>
<td>1.31</td>
<td>0.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.34</td>
<td>1.47</td>
<td>-0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.40</td>
<td>1.95</td>
<td>0.45</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Reference 1, relative to benzene in ppm.

(b) Using equation in text and VESCF charge densities.

(c) Calculated using procedure in reference 2, the benzene value is 2.35 from these calculations.
to: Dr. Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843

Dear Dr. Shapiro:

Mr. Hughey Rush, who wrote the technical report describing a plotting routine for LAOCOON II (NMRN 108-26), spent his two-week reserve duty tour with me last summer. During that time he streamlined his 75-card subroutine and incorporated it in LAOCN3.

When used with Castellano and Bothner-By's LAOCN3, the output consists of the usual printout followed by a printed stick plot of the calculated spectrum. Also, the line identification numbers are printed along the frequency axis. Therefore, not only can the calculated spectrum be seen at a glance but the calculated line numbers can also be directly transferred to matching experimental frequencies. In the iterative part of LAOCN3, the "best fit" spectrum is also plotted.

Modification of the main program is minimal. Data input format is unchanged. The plotting option is simply punched on the second data card - after the minimum intensity option.

A listing is available upon request.

Sincerely,

ROGER E. RONDEAU
Exploratory Studies Branch
Materials Physics Division
December 18, 1969

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

Factor Analysis of Solvent Effects in NMR

Dear Prof. Shapiro,

We have been applying Factor Analysis in an attempt to decipher the nature of solvent effects in NMR. Preliminary work on simple substituted methanes, dissolved in a variety of solvents, leads us to believe that only three factors are involved. Since only three factors are required we decided to rotate the resulting vectors from the analysis into three solvent vectors: acetonitrile, carbon tetrachloride and methylene bromide. Resulting equations are listed below:

\[
\begin{align*}
\delta^i_{\text{CH}_3\text{CN}} &= 1.0016f_1 - 0.0038f_2 + 0.0022f_3 \\
\delta^i_{\text{CH}_2\text{Cl}_2} &= 0.806f_1 + 0.7150f_2 + 0.2070f_3 \\
\delta^i_{\text{CHCl}_3} &= -0.0458f_1 + 0.8169f_2 + 0.2300f_3 \\
\delta^i_{\text{CCl}_4} &= -0.0018f_1 + 1.0041f_2 - 0.0022f_3 \\
\delta^i_{\text{CS}_2} &= 0.0064f_1 + 1.1281f_2 - 0.1394f_3 \\
\delta^i_{\text{CH}_2\text{Br}_2} &= 0.0010f_1 + 0.0090f_2 + 0.9922f_3 \\
\delta^i_{\text{CH}_3\text{I}} &= 0.5613f_1 - 0.2237f_2 + 0.6527f_3 \\
\delta^i_{\text{CH}_2\text{I}_2} &= -0.1092f_1 - 1.1972f_2 + 2.2946f_3 \\
\delta^i_{\text{CHBr}_3} &= -0.2562f_1 - 1.1972f_2 + 2.2946f_3 
\end{align*}
\]
In these equations $\delta_{\text{CH}_3\text{CN}}^i$ is the chemical shift of solute $i$ in acetonitrile.

$$f_1 = \delta_{\text{CH}_3\text{CN}}^i, \quad f_2 = \delta_{\text{CCl}_4}^i, \quad \text{and} \quad f_3 = \delta_{\text{CH}_2\text{Br}_2}^i$$

The success of this choice is illustrated in Table I attached, which is self-explanatory. Furthermore, with three factors the Factor Analysis scheme allows us to predict gas phase chemical shifts from solution measurements. These results are shown in Table II.

Sincerely yours,

Paul H. Weiner

Edmund R. Malinowski

Table II. Test of Gas Phase Chemical Shifts as a Solute Factor Using three Factors in the Rotation Matrix

<table>
<thead>
<tr>
<th>Solute</th>
<th>$\delta_g$ (predicted)</th>
<th>$\delta_g$ (experimental)</th>
<th>diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Cl</td>
<td>168.2</td>
<td>427.1</td>
<td>-0.2</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>427.1</td>
<td>427.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>CH$_3$Br</td>
<td>147.1</td>
<td>146.9</td>
<td>0.2</td>
</tr>
<tr>
<td>CH$_2$Br$_2$</td>
<td>285.5</td>
<td>285.0</td>
<td>0.5</td>
</tr>
<tr>
<td>CHBr$_3$</td>
<td>406.8</td>
<td>406.9</td>
<td>-0.1</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>118.5</td>
<td>119.0</td>
<td>-0.5</td>
</tr>
<tr>
<td>CH$_2$I$_2$</td>
<td>227.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CHI$_3$</td>
<td>301.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CH$_2$ClBr</td>
<td>297.7</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 1. Comparison of Calculated and Experimental Chemical Shifts of Substituted Methanes

<table>
<thead>
<tr>
<th>Solvents</th>
<th>CH₄</th>
<th>CH₃CN</th>
<th>CH₂CN</th>
<th>CH₂Cl₂</th>
<th>CHClBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CN</td>
<td>12.1</td>
<td>--</td>
<td>117.6</td>
<td>--</td>
<td>256.8</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>12.1</td>
<td>13.7</td>
<td>118.0</td>
<td>119.4</td>
<td>248.2</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>12.7</td>
<td>13.8</td>
<td>120.0</td>
<td>118.8</td>
<td>246.1</td>
</tr>
<tr>
<td>CCl₄</td>
<td>13.8</td>
<td>--</td>
<td>17.4</td>
<td>--</td>
<td>244.2</td>
</tr>
<tr>
<td>CS₂</td>
<td>13.3</td>
<td>13.6</td>
<td>114.8</td>
<td>116.1</td>
<td>242.8</td>
</tr>
<tr>
<td>CH₂Br₂</td>
<td>13.8</td>
<td>--</td>
<td>122.7</td>
<td>--</td>
<td>252.3</td>
</tr>
<tr>
<td>CHBr₃</td>
<td>15.2</td>
<td>14.3</td>
<td>127.3</td>
<td>124.6</td>
<td>253.0</td>
</tr>
<tr>
<td>CH₃I</td>
<td>12.9</td>
<td>12.7</td>
<td>122.9</td>
<td>119.8</td>
<td>255.3</td>
</tr>
<tr>
<td>CHI₂</td>
<td>15.1</td>
<td>13.8</td>
<td>128.8</td>
<td>128.1</td>
<td>257.3</td>
</tr>
<tr>
<td>Exp. Range of Data</td>
<td>3.0</td>
<td>14.0</td>
<td>15.0</td>
<td>13.0</td>
<td>21.8</td>
</tr>
<tr>
<td>Aver. Error</td>
<td>0.9</td>
<td>1.7</td>
<td>0.7</td>
<td>0.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>
1. Mitteilung

zum 7. Kolloquium über Kernresonanz-Spektroskopie in Aachen


Hauptthema des Kolloquiums:

"Kernresonanz-Spektroskopie an natürlichen und synthetischen Hochpolymeren".

Eine vorläufige Vortragsübersicht liegt bei.


Die Teilnehmergebühr beträgt DM 60,-.

Für Studenten, Diplomanden und Doktoranden, die keine planmäßigen Assistenten sind, beträgt die Teilnehmergebühr DM 10,-.

Das endgültige Programm wird allen Teilnehmern Mitte Februar 1970 zugesandt.

(R. Kosfeld)

2 Anlagen
Vortragsübersicht
Anmeldeformular
Vortragssübersicht

Dr. K. Bergmann
Ludwigshafen

Untersuchung von Beweglichkeiten in Polymeren durch NMR

Dr. F. A. Bovey
Murray Hill (USA)

High Resolution NMR of Polymers

Prof. Dr. Cantow
Freiburg

Kettenstruktur und Kinetik der Polymerisation, untersucht durch NMR

Prof. Dr. H. Fischer
Zürich, Schweiz

ESR-Untersuchungen an Hochpolymeren

Prof. Dr. E. Forslind
Stockholm

NMR-Untersuchungen an Zellulose

B. Groß
Aachen

Spin-Echo-Untersuchungen an Polymeren

Dr. J. Guillot und
Dr. Pham Quang Tho
Villeurbanne, Frankreich

Sequenzlängenverteilung in Copolymeren

Prof. Dr. H. J. Tarwood
Akron (USA)

Problems Concerning Copolymer Structure

Prof. Dr. W. Holzmüller
Leipzig

Neuere Ergebnisse auf dem Gebiet der Platzwechseltheorie

Dr. E. Klesper
Zürich, Schweiz

Sequenzlängenverteilungen, untersucht durch NMR

Dr. R. Kosfeld
Aachen

Relaxationserscheinungen und Linienbreitenphänomenen bei NMR-Spektren

Prof. Dr. P. Laslo
Princeton (USA)

Solvent Effects in High-Resolution NMR

Dr. W. D. Phillips
Wilmington

NMR-Studies in Biopolymers

Prof. T. Shimanouchi
Tokio, Japan

Conformations fo Polymers as revealed by Infrared Spectroscopy

Prof. W. P. Slichter
Murray Hill (USA)

NMR-Studies of Solid Polymers

Ich werde voraussichtlich am 7. Kolloquium über Kernresonanz-spektroskopie teilnehmen:

Name, Vorname: ________________________________

Titel: ________________________________

Institut/Firma: ________________________________

Adresse: ______________________________________

Ich werde ein/kein Quartier benötigen.

Ich bitte weitere Anmeldeformulare zu senden an: ________________________________

Datum: ________________________________

(Unterschrift)
Dear Professor Shapiro,

Trifluoroacetic acid as low-field lock for routine H-100 proton spectra and 2,5-dichlorothiophene for wide-temperature range locks

For routine H-100 proton spectra that need to be recorded under standard operating conditions, we prefer to lock on the low-field carboxyl proton signal of trifluoroacetic acid (TFA) instead of the high-field signal of TMS. The TFA is dried by addition of 10% of TFA anhydride and sealed in a capillary tube; the drier the sample, the further down-field is the lock. The lock is, depending on solvent, between 1050 (CDCl$_3$) and 1250 Hz (C$_6$D$_6$) below TMS in the solution in which the capillary is inserted; a full 1000 Hz sweep is thus practicable. A saturated solution of trichloroacetic acid in TFA anhydride gives a slightly lower down-field lock, permitting a 1100 Hz sweep, which is useful for observing low-field NH groups; the lock is, however, weaker and more oscillator power is needed.

In setting up the H-100 spectrometer for a day's work, we use a sealed sample tube containing TFA, a little TMS and sufficient acetone to give three peaks of roughly equal height on the oscilloscope using HA mode. When locked on TFA, the acetone peak is useful for checking inter alia line-shape and sensitivity. Lock-transference either to a working sample or between samples fitted with sealed TFA capillaries is immediate, allowing only for probe-leakage nulling.

The great advantage of the TFA method is that for measurements on solutions in normal deuterated or proton-free solvents, the same routine procedure can be used to "lock" the instrument. Each solution, as in A-60 operation, contains only a trace of the relevant reference compound. Solutions in...
proteopyridine (not deuterio) are locked on the lowest-field band of pyridine, the TFA capillary signal being too close to that of pyridine to be satisfactory; rather surprisingly, good resolution is obtained. For measurements on TFA solutions, sealed TFA capillaries are unnecessary and are in fact undesirable; the instrument can "jump lock" between the signals due to the sealed and to the inevitably damped unsealed TFA solutions.

A few Hz drift, relative to the recorder chart, occurs until the sample and TFA capillary have attained probe temperature. Nevertheless, by the time normal instrumental adjustments have been made, stability is usually adequate.

In order to zero on TFA or its equivalent, the manual oscillator frequency must be adjusted to between about 3550 Hz (CDCl₃) and 3750 Hz (CD₂N). This range is not attained by the built-in manual oscillator, but we have extended the range of our spectrometer by modifying it to permit the substitution of an external oscillator (cf. B.J. Goodfellow, ITT M.R. Newsletter, 1967, 101, 52). The oscillator of our machine may be switched either through an attenuator to the V4594 or coupled to the probe, via a transformer, for precise impedance matching when spin-decoupling. When the V4594 is modified in this way, the manual oscillator level switch, S1203, and the signal monitor switch are in circuit with the external oscillator; the output of which is adjusted to give 1 v. peak-to-peak on the oscilloscope; S1203 is then operated normally. To avoid loss or lock, it is expedient to work in the field-sweep mode; this allows for large changes in the external oscillator frequency. In spin-decoupling, using frequency sweep, the range of the built-in manual oscillator is sufficient to set on the chart almost any band upfield of the lock; zeroing on TFA is unnecessary and the external oscillator is free for double-irradiation.

The precision coaxial capillary tubes supplied by the Wilmad Glass Co. (Cat. No. 526) are suitable for holding the TFA mixture. They fit inside Varian sample tubes, but unfortunately each capillary is only 7" long, and so does not project beyond the open end of the sample tube. 8" Capillaries, which were specially supplied by the Wilmad Glass Co., proved to be more satisfactory. Spinning side-bands are sometimes (particularly for D₂O spectra) troublesome. However, fast spinning is possible, since the capillaries damp vortex formation.

With reference to Drs. H. Halts and D.J. Sardella's suggestion (TTM M.R. Newsletter, 1969, 127, 2) to use 2-substituted thiophene for wide temperature range locks (-58° to +165°), we wish to mention that we have used 2,5-dichlorothiophene (-40° to +160°); it gives a signal at about 75-3, which does not obscure the high-field region.

Yours sincerely,

J.B. Page R.A. Fletton G.F.H. Green
Dear Barry,

Is it possible to improve Fourier transform spectroscopy or is it the optimum method with respect to sensitivity? There is one possibility which has some advantage compared with conventional Fourier spectroscopy. Particularly, it is able to produce a better sensitivity for the same resolution, in principle. We like to call it "Noise Resonance" or "Stochastic Resonance".

In noise resonance, the sample is excited with random noise. The response of the spin system will again be noise (wanted noise + unwanted noise) and the crosscorrelation function between the input noise and the output noise just gives the Fourier transform of the conventional absorption mode spectrum. In contrast to noise decoupling, it is no double resonance experiment, no decoupling occurs under appropriate conditions. With its broadband excitation of resonance it is completely analogous to Fourier spectroscopy. The instrumental requirements are obvious, a means to generate and modulate noise onto an rf carrier and a means to crosscorrelate and Fourier-transform the data. Both problems are easily solved with a computer (Varian 620i) which generates a binary random sequence for excitation of the sample.

What is the real advantage of this method? In Fourier spectroscopy, the resolution requirements demand a long interval between pulses, but best sensitivity is achieved with closely spaced pulses. This
discrepancy does not exist in noise resonance. It produces a sensitivity equal to the optimum achievable one with conventional Fourier spectroscopy but without deterioration of resolution. There are some further advantages with respect to power consumption.

An actual spectrometer output of noise and its Fourier transform are shown in the attached figure. Here, not the crosscorrelation function was computed but simply the power spectrum of the spectrometer output, which is equivalent to $(v^2 + u^2)^{1/2}$, is plotted. Some of the basic ideas of this experiment are due to Wes Anderson.

Sincerely yours,

Richard R. Ernst
Internal rotations in an enamine: large positive entropies of activation

Dear Professor Shapiro:

In the course of our investigations of hindered internal rotation in enamines, we have studied the following compound (I), which at room temperature was found to undergo a rapid equilibration between the isomers a and b.

From a complete lineshape analysis of the dimethylamino proton spectrum (Fig. 1) it was possible to evaluate the activation parameters for the hindered rotations around the N-C bonds in the two isomers, as well as the corresponding data for the isomerization around the C=C bond. A virtually temperature-independent isomer ratio (a/b or b/a) of 1.30 was observed.

One can see from the Table below that the activation parameters for the rotations around the N-C and C=C bonds are of the same order of magnitude, which indicates a significant delocalization of the π-electrons.

/cont./
<table>
<thead>
<tr>
<th>Rotation</th>
<th>$\Delta H^\ddagger$ kcal/mole</th>
<th>$\Delta F^\ddagger$ $298^\circ K$ kcal/mole</th>
<th>$\Delta S^\ddagger$ e.u.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N - C</td>
<td>14.88±0.21</td>
<td>10.75±0.35</td>
<td>13.9±2.0</td>
</tr>
<tr>
<td>N - C</td>
<td>15.36±0.28</td>
<td>12.99±0.43</td>
<td>8.2±2.4</td>
</tr>
<tr>
<td>C = C</td>
<td>13.78±0.14</td>
<td>14.82±0.21</td>
<td>-3.5±1.2</td>
</tr>
<tr>
<td>C = C</td>
<td>14.10±0.17</td>
<td>14.73±0.25</td>
<td>-2.1±1.4</td>
</tr>
</tbody>
</table>

The error limits given in the Table were calculated assuming only random errors.

a) Evaluated from the spectrum of the dimethylamino protons.
b) Evaluated from the spectrum of the C=C-CH$_3$ protons.

The observation of large positive entropies of activation for the N-C rotations (also found for other enamines $^1$,$^2$) was at first sight quite a surprise, especially in view of the slightly negative value found for the C=C rotation and the fact that $\Delta S^\ddagger$ values close to zero are obtained for simple amides $^3$,$^4$.

However, since the rate data for the three internal rotations have all been evaluated from the exchange broadening of the N-CH$_3$ signals, we believe that the observed differences in $\Delta S^\ddagger$ are significant. Furthermore, since it is sometimes assumed that $\Delta S^\ddagger$ for internal rotation should be zero $^5$, comments on possible sources of our large positive entropies of activation are welcome.

Sincerely yours,

Kjell-Ivar Dahlqvist

References
Dear Dr. Shapiro,

The use of a synchro resolver to shift the phase of audio frequencies is certainly not new to NMR (Noggle, Rev. Sci. Instr. 25, 1166 (1964), Gutowsky et al., Rev. Sci. Instr. 39, 805 (1968)) but neither of the resolvers used seems generally available. We have used a Kearfott R931-43E (available from American Relays Electronics Division, 59 Lispenard Street, New York, N.Y. 10013 for $21.50) for phase-shifting over a wide frequency range. We found that tuning the output portion of the resolver was sufficient to keep the output voltage reasonably constant with change in frequency. The frequencies at which no change in amplitude occurs with phase shift are shown along with the nominal values of the tuning capacitance. For other frequencies in the range indicated, there is of course some change in amplitude as the phase is shifted, but it is tolerable for our purpose which is providing a drive for the X-axis of a scope.

We have funds for a postdoctoral appointment to work on the NMR of solids starting as soon as possible and I would be interested in hearing from anyone who is interested.

Sincerely yours,

[Signature]

Gerald Ray Miller

[Diagram]

Scope X-Axis

- yellow
- black
- red

Synchro Resolver
Kearfott R931-43E

center frequency in Hz
capacitance in mfd.

16
50
100
150
450
800
1700

[Table]

- 0.12
- 0.05
- 0.02
- 0.01
- 0.005

December 1969

Wide-band Audio Frequency
Phase-Shifter; Postdoc Position
Steric Effect on Isomerisation of C-N and C-S Double Bonds

Dear Dr. Shapiro,

Large groups in ortho position of N-aryl-imines (for instance in N-aryl-guanidines I) cause an increasing rate of isomerisation (1). This is a proof of the inversion mechanism ("lateral shift" mechanism) on the imino nitrogen, in which a linear transition state is involved (the hybridisation of the nitrogen atom changes from $sp^2$ to $sp$). A rotation about double bonds should be hindered by large groups in ortho position. Therefore we synthesized the pentamethyl-aryl-guanidinium salts II in which no inversion is possible because there is no lone electron pair. The variable temperature NMR spectra of these compounds show hindered rotations about the three CN bonds a, b and c. The free enthalpies of activation $\Delta G^\ddagger_{c}$ of the rotation about the partial CN-double bond c were calculated at the coalescence temperature in the usual manner. The bond c is in $\beta$ position to the aromatic ring as it is the corresponding CN double bond in the guanidines I. The $\Delta G^\ddagger_{c}$-values of II increase with increasing size of R as it is expected for the rotation case (table).

The low temperature spectra of the thiuronium salts III show four signals for the N-methyl-groups: the rotation about both CN bonds and the isomerisation on the CS partial double bond has to be "slow".

\[ \text{I} \]
\[ \text{II} \]
\[ \text{III} \]
\[ \text{IV} \]
At room temperature a singlet for these signals is observed. The calculated free enthalpies of the CS bond isomerisation are shown in the table.

Table: Steric effect on isomerisation of CN and CS double bonds

<table>
<thead>
<tr>
<th>bond</th>
<th>mechanism</th>
<th>compound</th>
<th>R</th>
<th>Tc</th>
<th>ΔG°c</th>
<th>Tc</th>
<th>ΔG°c</th>
<th>Tc</th>
<th>ΔG°c</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=N</td>
<td>inversion</td>
<td>H</td>
<td>-35</td>
<td>12.1</td>
<td>29</td>
<td>15.0</td>
<td>-83</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rotation</td>
<td>CH3</td>
<td>-24</td>
<td>12.6</td>
<td>147</td>
<td>21.1</td>
<td>-64</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>rotation</td>
<td>C2H5</td>
<td>-37</td>
<td>11.9</td>
<td>180</td>
<td>22.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>rotation</td>
<td>i-C3H7</td>
<td>-47</td>
<td>11.4</td>
<td>&gt;200</td>
<td>&gt;24</td>
<td>-29</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

a) Tc = temperature of coalescence [in °C]; ΔG°c = free enthalpy of activation at the coalescence point [in kcal/mole].

The increasing values of ΔG°c with increasing size of R is an argument against the atom inversion of the sulfur and gives evidence for the rotation mechanism in the sulfur compounds III. The observed effect is smaller than in II as it can expected by going from the larger sulfur atom to the smaller nitrogen atom.

Our results on the corresponding oxygen compounds (uronium salts) are in progress. More complete data will be obtained by studying the cyclic compounds IV (X = N,S,O).

Sincerely yours,

Horst Kessler

Dieter Leibfritz

References

    H. Kessler and D. Leibfritz, Tetrahedron in press
Dear Professor Shapiro

Restricted Rotation in Certain Silanes

We have recently been examining some monosubstituted methyl silanes on the Perkin-Elmer R1 instrument. Working with the normal scale-factor of 6 cycles/division we found a splitting of the methyl peak with allyltrimethylsilane (Fig. 1) which, on expansion of the scale twelvefold (scale factor 3 cycles/division), we were able to show, by integration, that the three CH$_3$ groups are not equivalent, one being in a different environment to the other two.

This prompted us to make up a Stewart model of the molecule and it was immediately obvious that the 'bent' nature of the allyl group prevents free rotation about the CH$_2$-Si bond. Two of the CH$_3$ groups flank the CH=CH$_2$ group, the third being spatially distant from the allyl group.

This suggested that other silanes should show a similar effect and acetoxyltrimethylsilane (Fig. 2) does indeed show a much wider splitting of the methyl absorption, again in the ratio of 2:1.

There does seem to be an anomaly here though; we would have expected that proximity to the allyl or acetoxy group would have brought the signal due to the adjacent two CH$_3$ groups further downfield that the single CH$_3$ absorption whereas the reverse is the case. We are still working on this problem and hope to publish some of our results shortly.

Yours sincerely,
December 30, 1969

Professor Bernard L. Shapiro  
Texas A&M University  
Department of Chemistry  
College Station, Texas 77840

Dear Barry:

Computer Time-Averaged $^{13}$C-Indor

We have been using $^{13}$C Indor for some time in our studies of stable carbonium ions at low temperatures (in cases as low as -150°). Time-averaging has proved to be a helpful and time-saving technique. Many of the systems we studied were obtained in concentrations too low to observe either the $^{13}$C-$^1$H satellites or the one percent $^{13}$C-$^1$H main peak enhancement upon satellite decoupling. Our general setup is a Varian HA-100 spectrometer and a Monsanto Model 310QA Frequency Synthesizer. The C-1024 time-averaging computer is hooked up to the HA-100 in the usual way, except the voltage ramp is used to drive the frequency synthesizer giving, in our case, sweep ranges in the 25.1 MHz region. The C-1024 is internally triggered for the desired number of passes.

We have succeeded in obtaining $^{13}$C-Indor spectra from "invisible" satellites as also described recently in TAMU-NMR NEWSLETTER #135 by Dr. Dreeskamp. The method is also advantageous in observing $^{12}$C-$^1$H peak enhancement. Rapid sweeping of the 25.1 MHz region (150 Hz/sec) gives satisfactory results. This is especially important where unstable species are being observed, but also results in substantial time-saving as a general method. Maintaining homogeneity for long periods of time at low temperatures is difficult, but necessary in observing main peak enhancement. Time-averaging rapid sweeps enables one to stop at frequent intervals, observe what has been compiled in the CAT, maximize the homogeneity, and continue with no loss of information.

Best regards,

Yours sincerely,

Richard D. Porter

George A. Olah

Professor G. A. Olah  
Department of Chemistry  
Area Code 216 • 368-3623
Re: Relaxing with an HA-100

Dear Barry:

In our laboratory we have been measuring proton NMR relaxation times by a $T_{1p}$ method. The technique was described by Solomon\(^1\) and Meiboom\(^2\), and recently Sykes\(^3-5\) has successfully employed this method for the study of the rates of exchange of inhibitors from enzymes. Sykes' experiments were performed with Varian HR-100 and HR-60 spectrometers.

The technique involves adiabatic rapid passage into the center of a (dispersion mode) resonance. This aligns the magnetization along the rf field, $H_1$, and the magnetization relaxes along $H_1$ with a time constant, $T_{1p}$. $T_{1p}$ equals $T_2$ under appropriate conditions. In addition, Sykes has shown that $T_1$ may be obtained from the variation of the amplitude of the response as a function of the time spent off resonance. The method is quite sensitive, relatively simple, and particularly useful for obtaining relaxation times of individual resonances in reasonably complex spectra.

However, the method requires that the sweep be exactly into the center of resonance and with the HR instruments the adjustments for drift can become tedious. The logical alternative is to use a field-frequency locked instrument. The problem here is that the dispersion mode must be used for the measurements. With
our Varian HA-100 this requires a phase shift in the analytical signal section since in its usual configuration the spectrometer puts out only an absorption mode signal. We modified our instrument by simply replacing card 910872 with card 911636 in the "lock box".

To do the adiabatic sweep we use a voltage controlled oscillator (MF Electronics, 118 E. 25th St., N.Y., model no. 301-2501-10-1001) in place of the sweep oscillator of the HA-100. Fig. 1 shows a schematic of the input to the voltage controlled oscillator. The output of the voltage controlled oscillator is plugged into J1307 (sweep osc. out) of the lock box. In addition, card 910868 in the lock box must be pulled.

The pots are adjusted so that the spectrometer sits close to resonance. The 10K pot is then adjusted so that when switch 1 is closed the spectrometer goes off resonance 50-100 Hz. The switch is opened and the 40K pot is again adjusted to bring the spectrometer close to the center of resonance and the trimmer pot (2K) is used to place the spectrometer exactly on resonance. Switch 2 allows one to choose the direction of the jump off resonance to avoid the problem of sweeping through a nearby resonance. Closing switch 1 puts the spectrometer off resonance and opening it makes the oscillator sweep adiabatically back into resonance with a time constant determined by the RC circuit. This time constant is usually about 0.05 - 0.1 sec. The output of the spectrometer is recorded on a fast response recorder. No filtering is used. We have found that best results are obtained when the lock signal lies far away from the signal of interest.

$T_1$ is obtained by progressively varying the time off resonance $t \gg T_1$, then a plot of $\ln(A_\infty - A_t)$ vs. $t$ has slope $T_1$. *
A prime advantage of $T_{1\rho}$ with a field-frequency locked system is the possibility of time averaging the signal. To this end, we have constructed a rather pedestrian, but effective switching set-up. A synchronous motor, appropriately geared down, drives a wheel to whose face is bolted a lucite disc. The disc is programmed with notches along the edge. Micro-switches for starting the C-1024 sweep and for switching on and off resonance are poised so that they are activated by the notches as the wheel rotates. The CAT is run in the ext. trig. mode and its sweep is started by a momentary short to the ext. trig. jack through one of the micro-switches. The other micro-switch replaces switch 1 of Fig. 1. Programs for either $T_2$ or $T_1$ or both are easily constructed from the lucite. The period of rotation is variable in our set-up so that a wide range of relaxation times can be accommodated. Fig. 2 shows a single absorption mode scan of 0.005 M sodium succinate in $D_2O$ and also the $T_{1\rho}$ decay obtained from 9 accumulations in the CAT.

We hope this communication may prove useful to TAMUNMR newsletter readers and that it will get us off the hook until the next pink letter day.

Yours sincerely,

Paul G. Schmidt  Thomas R. Krugh

PGS:TRK:mc
* We have learned that Dr. Brian Sykes has designed a set-up similar to the one we describe here for obtaining $T_{10}$ and $T_1$. In a paper describing the set-up, he discusses in detail the requirements for adiabatic sweep with regard to rf power levels, sweep rates and relaxation times. The paper should appear shortly in Rev. Sci. Instruments.

1. I. Solomon, Compt. Rend., 248, 92 (1959)
4. B. D. Sykes, Biochem., 8, 1110 (1969)
FIG. 1.
FIG. 2.

SINGLE SCAN

9 ACCUMULATIONS OF $T_1$ DEcAY

$5 \times 10^{-3}$ M Succinate
Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A and M University,  
College Station, Texas.

More Cautionary Tails  

Dear Barry,  

In Fourier transform NMR, there are several factors that may introduce frequency-dependent phase shifts of the signal and thus cause the ratio of absorption mode to dispersion mode to vary across the spectrum. For example, an insufficiently strong rf pulse will cause a spread of the phases of individual magnetization vectors as they begin their free precession, or an incorrectly-timed start of the data acquisition process after the pulse will introduce a phase shift that is strongly frequency-dependent.

Although such phase errors can be satisfactorily corrected, there is a strong temptation to sidestep the problem entirely by calculating and displaying the absolute value of the transverse magnetization, $(u^2 + v^2)^{1/2}$ instead of the traditional v mode (absorption) signal. There are dangers in such a procedure.

The most evident artifact of the absolute value display is perhaps the least serious -- much longer tails on each side of the line caused by the slower decrease of the resonance denominator as a function of the offset $\Delta \omega$:  

$$v = \gamma H M T_1^2 / (1 + \Delta \omega T_2^2)$$  

$$v = (u^2 + v^2)^{1/2} / (1 + \Delta \omega T_2^2)$$

More insidious problems arise when two lines overlap, since the resultant line profile is no longer the sum of the two overlapping components (as in the conventional v mode) due to interference of the dispersion-mode components which tend to cancel in the region of overlap. For only moderate degrees of overlap, where the absorption-mode display would show negligible effects, the absolute value plot exhibits line displacements and intensity variations. However the main indictment of the absolute-value display must be made when a weak line falls in the tail of a strong line, for then the weak line appears to have the dispersion-mode shape -- the very problem the trick was designed to circumvent.

This behavior can be likened to the detection of the absolute-value signal in a simple diode detector. A tail from a strong nearby resonance will introduce a second signal component that will bias the diode detector, and since this component is predominantly in the dispersion phase and is relatively constant in amplitude across the profile of the weak line, it has the effect of converting the simple diode detector into a phase-sensitive detector adjusted for a dispersion-mode display. Another way to visualize this is as the interference between the dispersion-mode component on one side of the weak line and the strong (almost uniform) dispersion background from the nearby resonance.

Figure 1 illustrates this effect. It shows the calculated profile of two overlapping Lorentzian lines with intensity ratio 10:1 for both the absolute-value mode (upper traces) and the conventional v mode (lower traces). Note the tendency for a dispersion-like shape of the weaker line in the absolute-value plot. The effect persists for surprisingly large separations. A practical illustration is provided by part of the carbon-13 spectrum of Vitamin A acetate obtained by the Fourier transform technique (Figure 2). The line at 133 ppm (assigned to the CH$_2$O carbon) is seen to exhibit considerable dispersion-like character in the absolute-value plot owing to interference from the strong resonance from nearby dioxane solvent, whereas in the absorption-mode display such interference is negligible.

Happy New Decade,

Rau
Figure 1. Computed line profiles of two overlapping Lorentzian lines with intensity ratio 10:1. The horizontal scale represents 100 units of frequency, the full width of each line is 5 units and the separation of line centers increases in equal steps from 10 to 50 units. The absolute-value plot (upper traces) is compared with the traditional v mode plot (lower traces) with the same baseline zero. Note the much longer tails and the apparent frequency shifts and intensity changes in the absolute value display. Note in particular the dispersion-mode character of the weak line at intermediate separations.
Figure 2. Comparison of the absolute-value mode with the conventional absorption-mode display for a portion of the carbon-13 spectrum of Vitamin A acetate in solution in dioxane. The spectra were obtained in about 17 minutes on an HA 100-15 spectrometer by the Fourier transform technique with the usual proton noise decoupling. The CH$_3$O carbon resonance near 133 ppm exhibits the most marked effects of interference from the nearby dioxane solvent resonance in the absolute-value mode, having a lineshape resembling that of a dispersion signal. Other more distant lines still show detectable distortion of the line shape.
December 30, 1969

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

Dear Barry:

Subjects: Advanced Workshop; News Items

Some of your readers may be interested in knowing of the Second Advanced Workshop and Seminar in NMR which we will be conducting in Gainesville during the week of April 6, 1970. The five days of the Workshop will include lectures on the more mathematical aspects of NMR and on recent developments in techniques and in instrumentation. The workshop is designed for persons with some experience in NMR who wish to build up their background of principles and theory. For those who wish experience in high-resolution spectral analysis, there will be opportunity for practice with the IBM 360/65 computer. We hope also to have our XL-100 instrument in operation in the laboratory by the time of the Workshop. The group of participants will be limited so that each person will have adequate opportunity for individual instruction.

Among the lecturers and staff for the program will be Rex Richards, J. M. Anderson, Frank Anet, Roy King, R. W. Kreilick, and Charles Moreland. Some of the topics to be emphasized include the use of computers in spectral analysis, relaxation effects in high resolution spectroscopy, NMR spectra of free radicals, use of spectrometers with superconducting magnets, spectroscopy of \(^1^3\)C, \(^1^1\)B, \(^3^1\)P, and \(^1^9\)F, molecular conformation, and dynamic nuclear polarization.

Those who wish more information or application blanks should write to me at the address on the letterhead.

On the subject of short courses, meeting, and symposia concerning magnetic resonance, I should like to invite others who are planning such events to publicize them by listing them in the column "Announcements and News Items" which the Journal of Magnetic Resonance is now carrying. Our current production schedule requires a lead time of eight to ten weeks before the first of the month in which the item is to appear in the Journal, although we hope to be able to reduce this somewhat a bit later on. It would seem particularly valuable to announce symposia or sessions which, because they are parts of larger meetings, might be missed by some of those active in magnetic resonance. Either a phone call (904-392-0520) or a letter to me will suffice to have the information included in the Journal.

Cordially yours,

Wallace S. Brey, Jr.
Professor of Chemistry
Frequency Sweep on HA-100

Dear Barry:

Frequency sweep on Varian HA systems is limited in the available sweep widths, the range of frequency in which one may sweep, and the fact that all sweeps start at 2500 Hz minus whatever is available from the sweep offset. Furthermore, the stability and linearity of the Varian sweep are less than desirable.

To alleviate the above problems what we have done is to replace the Varian sweep system with a voltage controlled oscillator, Wavetek #114 whose frequency is linear with the voltage. This oscillator has a reasonably flat output over a wide frequency range. The voltage which drives it is swept by means of the recorder sweep pots in conjunction with the dividing network shown in Figure 1. In this way we can set the recorder sweep for any frequency difference from 10 Hz to a maximum of 8 KHz (4 KHz above and below the lock). This arrangement is very useful for 31P resonance where the spectra can be swept in increments of 8 KHz using, if necessary, different lock signals. At frequencies beyond 4 KHz from the lock it is hard to maintain lock.

Two switches which disable the manual and sweep oscillators, respectively, have been installed behind the 4354 lock box. They are ahead of the amplitude control on the front panel. A BNC was added to feed an external sweep signal into the lock box. Note also, as is common practice, an external frequency can be fed into the manual oscillator jack allowing any lock frequency to be selected. A third switch, three poles, two positions, and a three terminal jack was installed on the recorder frame. In this way we can switch between the Varian and the Wavetek sweep options.

Our Varian HA 100 spectrometer is now routinely run with the Wavetek sweep.

Sincerely yours,

Gideon Fraenkel,
Professor of Chemistry.
CHANGES ARE WITHIN DASHED LINES

See Varian Schematic
V 4354A
87-109-705
Rev. 61066
Dr. Bernard L. Shapiro,  
TAMUNMR Newsletter,  
Dept. of Chemistry  
Texas A and M University,  
College Station,  
Texas 77843,  
U.S.A.

Dear Barry:

IBM 1620-II For Sale

We would like to advertise the fact that our IBM 1620-II is for sale and immediately available. This is the computer on which we have been running all our NMR analyses. We have a very extensive library of programs. Of particular interest is our 7-spin version of LAOCOON II. The computer has been under maintenance contract which we understand can be extended at the option of the purchaser. The system includes a Calcomp plotter and 1311 disk drive.

Anyone interested in obtaining further details should contact me, preferably by phone.

J. H. Goldstein  
Professor of Chemistry  
Office Phone  
404-377-2411 Ext. 7527  
Home Phone  
404-636-4814
Description of 1620-II System
(Prices given are current IBM list Prices)

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