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12th ENC - University of Florida, Gainesville - February 18 to 20, 1971

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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All Newsletter correspondence, etc., should be addressed to:

Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843
November 6, 1970

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

Interaction of Aromatic Protons with Methoxyls in Ortho Position: Expected and Unexpected Effects.

Dear Professor Shapiro:

During the study of the mold pigment elsinochrome A (I), we have made some observations which may be of general interest.

The compound has been proven \(^{1a,b}\) to be the rapidly equilibrating tautomeric system Ia + Ib. In its nmr, the signal from one of the two pairs of methoxyls, unequivocally identified as (c), is reproducibly \(\sim 20\%\) shorter than those from (d) and (g), the latter two signals being of equal heights. The effect is accentuated at lower temperature (\(\Delta = \sim 66\%\) at \(-60^\circ\)), and disappears when the nuclear protons (a) are replaced by Br (see Fig. 1). All three signals: (c), (d), and (g), integrate precisely for 3 protons.

Compound I forms two dimethyl ethers \(^{1a}\): V, derived from Ia, and VI, derived from Ib. In both, the signals from methoxyls adjacent to the nuclear protons (a), i.e. (c) in V, (c) and (f) in VI, are shorter than the other methoxyl and -CO-CH\(_3\) signals, which are of equal heights (see Table I).

Similar shortening of signals from methoxyl ortho to aromatic protons, compared with reference signals from methoxyls without free ortho positions, has been observed in a number of simple aromatic model compounds: 2,3,4-trimethoxybenzaldehyde (II), 2,3-dimethoxyphenol (III), and apiol (IV).

---

\(^{1a}\) Compound I forms two dimethyl ethers:

\[ Ia: R = H \]
\[ \bar{I}a: R = CH_3 (\bar{c}) \]

\[ \overline{VI}: R = CH_3 (\bar{c}) \]

---

\[ II \]

\[ III \]

\[ IV \]
In these cases, the shortening seems to be due entirely to long-range coupling between aromatic and methoxyl protons; it disappears on decoupling, which leads to equalization of the heights of the methoxyl signals (in the case of compound III, an unexplained small difference, ~ 3\%, persists). Long-range coupling of this kind has been demonstrated recently. 2

In I, V, and VI, this long-range coupling is likewise present, and accounts for ~ 50\% of the difference in peak-heights (see Table I). However, the remaining half is uninfluenced by decoupling, and must be due to some other cause, which appears to be specific for I, V, and VI; presumably, it is this residual effect which is responsible for the increase of the peak-height difference at low temperature. Integration of the decoupled spectra shows no nuclear Overhauser effect. NOE in the reverse direction has been demonstrated: increase of the integrated area of (α) on irradiation with the frequency of (c) in I and with those of (c) and (f) in VI. In the NOE of I, the half-band width of (α) decreases, in spite of the increase in integrated area—good evidence for the participation of long-range coupling.

Table I

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>NORMAL</th>
<th>DECOUPLED</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>73%</td>
<td>89%</td>
</tr>
<tr>
<td>II</td>
<td>78%</td>
<td>~100%</td>
</tr>
<tr>
<td>III</td>
<td>73%</td>
<td>97%</td>
</tr>
<tr>
<td>IV</td>
<td>86%</td>
<td>~100%</td>
</tr>
<tr>
<td>V</td>
<td>78%</td>
<td>90%</td>
</tr>
<tr>
<td>VI</td>
<td>71%</td>
<td>82%</td>
</tr>
</tbody>
</table>

This specific effect seems difficult to rationalize. One tentative interpretation, suggested to us by Dr. J. A. Ferretti, is based on the presence of magnetic non-equivalences in I, if there should be spin-spin coupling between the (α) protons. (Such a 7-bond coupling seems plausible in view of 7-bond couplings of ~ 0.5 Hz in some dienes. 3) In this A3A3'XX' system decoupling might leave "residual splittings" (cf. Anderson and Freeman 4), hence provide a major line with a peak intensity less than expected.

We would welcome comments and suggestions.

Yours sincerely,

E. A. Sokoloski
Laboratory of Chemistry
National Heart and Lung Institute
National Institutes of Health, Bethesda, Maryland 20014

Karl H. Weisgraber and U. Weiss
Laboratory of Physical Biology
National Institute of Arthritis and Metabolic Diseases

REFERENCES


Figure 1:
Spectra of I (upper curve) and dibromo-I (lower curve); cf. Fig. 3 of Ref. 1A. CDCl₃, TMS as internal standard. Peaks shown (from left): CHCl₃; (a); (b); (d); (c); (g). The upfield shift of (c) on bromination is one of the arguments for assignment of peaks.
October 21, 1970

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

Dear Dr. Shapiro,

Deuterium NMR on the XL-100-15 with the CAT.

Recently (TAMUNMR 142-26) Brey and Block reported a method for obtaining deuterium nmr spectra with the XL-100-15. We have also used this method, but have found that sensitivity is a major problem. In order to alleviate this difficulty, we have constructed a circuit that interfaces the CAT with the XL-100 and allows accumulation of the signal displayed on the scope - the deuterium lock signal in this particular instance. After careful adjustment of the drift, we have been able to accumulate up to 100 25 second scans using HR mode. The scanning ramp of the CAT is used to drive the linear sweep coils; sweep widths are set by the sweep width control of the linear sweep module, sweep times are provided by the CAT, or more conveniently from the recorder as in the conventional time, averaging operation. Additional amplification of the signal may be selected. The circuit is shown on the following pages and may be constructed for about $100. A full description of the circuit and its operation is available on request.

As an example of the use of this circuit we recently ran a sample of bicyclo[4.2.1]nona-2,4,7-triene (D₂) for Dr. J. Berson at Yale. The spectrum shown below was the sum of 10 50 second scans on a 180 mg sample with CDCl₃ and (CD₃)₂CO as references.

Please credit this contribution to Dr. Muller's subscription.

Yours sincerely,

Robert E. Santini
John B. Grutzner

JBG:ch
FROM NMR TO SCOPE

OUTPUT FROM NMR TO SCOPE

TRIGGER OUTPUT

TO C-1024 INPUT
MODIFICATIONS TO LINEAR SWEEP UNIT

RAMP INPUT

S-1304

X

R-1308

DIVIDED

1.9K Ω

X = BREAK
Hindered rotation about C-N bonds in ureas and thioureas

Cher Professeur Shapiro,

Par une étude conformationnelle à très basse température (\(<-100^\circ\text{C}\)) nous avons mis en évidence la rotation empêchée autour des liaisons C-N dans les urées \(\text{CH}_3\text{NH} - \text{CO} - \text{NH} - \text{R} (\text{R} = \text{H, CH}_3)\). Parallèlement, les thiouées correspondantes ont été examinées en vue de compléter l'étude comparative des systèmes carbonele-thiocarbonyle.

Le calcul, par étude des formes de raies, des durées de vie \(\tau\) en fonction de la température, donne accès aux paramètres d'activation.

Dans la N-méthyluree, les valeurs de \(T_c\) et de \(\Delta G^\circ (T_c)\) sont de 153° K et environ 7,5 Kcal/mole. En raison des difficultés techniques propres à ce domaine de températures, la détermination des valeurs de \(E_a\), \(\Delta H^*\) et \(\Delta S^*\), est imprécise.
Dans le cas de la N-méthylthiourée, nous observons à $T_c = 285^\circ K$ ($\pm 3$) la coalescence relative à l'isomérie de rotation autour de $\text{CH}_3\text{NH} = \text{CS} :$

\[
\begin{array}{c}
\text{CH}_3 \quad \text{N} \quad \text{C} \quad \text{S} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad }\end{array}
\]

$\Delta G^*(T_c) = 15,1$ Kcal/mole ($\pm 0,2$) - $\Delta H^* = 15,07$ Kcal/mole ($\pm 2$)

$\Delta S^* = - 0,14$ u.e. - $E_a = 15,7$ Kcal/mole ($\pm 2$).

A plus basse température se manifeste l'isomérie de rotation autour de $\text{CS} = \text{NH}_2 :$

$T_c = 203^\circ K$ ($\pm 3$) - $\Delta G^*(T_c) = 10,2$ Kcal/mole ($\pm 0,2$)

Comme pour les amides et vinylogues d'amides, le remplacement de $\text{C}=\text{O}$ par $\text{C}=\text{S}$ s'accompagne d'un accroissement important de $\Delta H^*$.

Veuillez croire, Cher Professeur Shapiro, à nos sentiments cordiaux.

M.L. Filleux-Blanchard

G.J. Martin.
Professor B. L. Shapiro,  
Texas A. & M. University,  
College of Science,  
College Station,  
Texas 77843,  
U.S.A.  
28th October, 1970.

Dear Professor Shapiro,

Easier Decoupling on the C6OH with almost no Modification

Ron Dean has very kindly passed on to me your blue note, so please accept this letter as our contribution from Jeolco (U.K.) Limited.

In the past, two methods of homonuclear spin decoupling have been used on the C6OH and its predecessors: frequency sweep and field sweep using a fixed decoupling frequency. The former method takes rather longer as it requires a change from the normal field sweep mode of operation to the frequency sweep mode, while the latter is only satisfactory if the location of both signals is known before decoupling. The method now proposed has neither of these disadvantages, as it uses the synchro-track technique (i.e. a field sweep measurement is performed, but the decoupling frequency is swept together with the field, so that the decoupling condition is always maintained). The only modification required is to disconnect (and insulate) lead 8 from terminal block TM 3201 at the back of the VF amp unit. This permits the variable frequency oscillator to be switched on during external lock field sweep operation. The frequency should then be adjusted to 4 KHz, with the pen at 0 ppm on the chart, and the sweep control set to field/frequency. (This adjustment may be performed using the zero beat if a counter is not available).

After a normal field sweep spectrum has been recorded, decoupling is achieved by the following procedure:-

1. Adjust the fixed frequency modulation to approx. 2-2.
2. Reduce the RF gain (1 or 2).
3. Increase the RF level (~10 dB).
4. Turn sweep control to field/frequency if not already selected.
5. Put pen over signal to be decoupled.
6. Turn on sweep generator and set modulation to ~5-6.
7. Adjust frequency offset to give 4 KHz.*
8. Record decoupled signal (some phase correction may be required).

*If a counter is not available, subtract the frequency read on the chart, and perform fine adjustment by observing zero beat on the pen.

The enclosed spectra are of the old favourite trans-crotonaldehyde and also 1% ethyl benzene, decoupled by the synchro-track method. Originally, I was going to send some 13C results, but I think this decoupling method will be of more use to your readers.

Yours sincerely,

E. A. P. J. Beynon

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

Dear Barry:

First we would like to call your attention to our new address. The spectroscopy group is now part of Standard Oil (Indiana) Research Department whereas previously it was part of American Oil, the petroleum division. Our new laboratory is about 30 miles west of Chicago.

While moving into the new building we have recently (April 1970) received a new spectrometer, the Bruker HFX-90/7-12/14. The 12/14 designation indicates the intermediate size magnet. So far we have encountered the usual difficulties in setting-up the spectrometer. Particularly we have found utility requirements quite important and this may be of interest to Newsletter subscribers.

First, the raw water temperature, as well as pressure, are critical. Although a temperature of less than 65°F and a pressure between 60-100 psi is specified, we have been operating our system with the water at 59°F and 47 psi. by having the returning magnet water pass thru a small heat exchanger. In addition, although Bruker supplies a 200 to 220 VAC transformer, we found it to be not completely adequate, requiring small booster transformers, one on each phase. The voltage level input is quite critical, but small voltage drifts are not (i.e., we have not needed a large voltage regulator).

We experienced a 60 cycle beat signal (from TMS) in our HA60-IL. It interfered with the 1.0 ppm (δ) region when recording ¹H-NMR Spectra. The problem was corrected by isolating the probe from the probe holder with nylon spacers and using a nylon duplicate of the knurled hand screw that secures the probe to the holder.

In addition, we would like to pass on a useful aid. We find that the NMR sample tube caps (cat. no. 15-106) purchased from NMR Specialties, Inc.
are generally very loose. To correct this situation, we heat the plastic caps to between 95° and 100°C and cool at various rates, depending upon degree of tightness required.

We would also like to mention that Dr. G. Joseph Ray joined us this past June.

Suggested title: New Laboratory; New Bruker HFX-90/7-12/14; 60 Cycle Beat in HA60-IL; Sample Tube Caps

Best regards,

E. M. Banas

E. Wenzel
G. J. Ray
R. W. Dunlap

A. J. Bugajski
D. J. Slupski
Professor B.L. Shapiro,
Department of Chemistry,
Texas A. & M. University,
College Station,
TEXAS 77843,
U.S.A.

Dear Dr. Shapiro,

3 years non-stop with a supercon - Liquid crystal studies of some \( \tau \) cyclopentadienyl complexes of Tungsten

We have just completed 3 years of continuous operation of an HR-220 with relatively little trouble. The continuity was broken when, after suffering severe icing-up of the magnet cap and high liquid nitrogen boil off, we discovered a large block of ice inside the dewar and had to warm up the magnet system to room temperature. Over 2 Kg of water were removed from the dewar! I am pleased to say that we are once more back to normal and looking forward to another 3 years continuous operation.

The range of suitable molecules which can be studied by n.m.r. in liquid crystalline solvents is becoming exhausted with little attention having been drawn to organometallic species. This has been due mainly to the lack of symmetry in these molecules as well as poor stability and solubility in liquid crystalline solvents. A series of which we have been studying are transition metal complexes containing the cyclopentadienyl moiety. It was hoped that by making the right choice of complexes we might determine the angle, out-of-plane, of the cyclopentadienyl protons as well as some symmetry parameters. For the first problem it was necessary to use a transition metal with an isotope of nuclear spin of \( \frac{1}{2} \), as well as a large magnetic moment, and so far we have not succeeded. The second part of the problem is continuing and spectra of some Tungsten complexes are shown below. Figure 1 shows the spectrum of cyclopentadienyl Tungsten tricarbonyl iodide oriented in a liquid crystal mixture at 50\( ^{\circ} \)C. Analysis of this spectrum shows no \( ^{1}H - ^{195}W \) coupling but within the limits of accuracy of the experiment agree with the regular pentagonal geometry of the C.P.D. moiety. Figure 2 is the spectrum of oriented cyclopentadienyl Tungsten tricarbonyl hydride. Again no \( ^{1}H - ^{195}W \) couplings were observed in the C.P.D. portion of the spectrum but they were...
observed in the hydride region. A first analysis of this spectrum shows there to be no symmetry axis along the CPD-W-H axis but that this is an angle of about 127°. Figure 3 is the spectrum of oriented cyclopentadienyl tungsten tricarboxyl methyl. The computed spectrum (figure 4) again shows no $^1H - ^{135}W$ couplings but contains a great deal of structural information which we hope to extract in the near future. Spectral simulations were carried out using a LAOCN-II programme modified for 8 spins and to give a plot output.

Yours sincerely,

[Signature]

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

Dear Dr. Shapiro:

We have developed a simple procedure for the synthesis of isophosphindolonium salts from readily available materials. The first recorded PMR values for this family are shown:

\[ \text{J}_{\text{PCH}} = 10.6, \ X = \text{Br} \]

\[ \text{J}_{\text{PCH}} = 10.6, \ X = \text{pикрате} \]

(In DCCl₃)

Reduction in the \( J_{\text{PCH}} \) value of these compounds from that of many benzyltrialarylphosphonium salts is a subject under study.

Short Title: PMR Data for Certain Isophospholindolonium Salts.

Sincerely,

K. D. Berlin  
Professor

KDB:wp
October 12, 1970

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

Pseudorotation in Phosphoranes;
Stereochemistry of Vinyl Phosphates

Dear Barry,

In response to your vicious pink letter I enclose a report of some interesting NMR work by my colleague I.J. Borowitz. He would be interested in any response of the readers of TAMU NMR.

For myself, there is unfortunately little to report, except our recent postulate that "pseudorotation" in phosphoranes takes place via a non-symmetric dimer, e.g. for PF₅:

There is a variety of experimental evidence which is consistent with this dimer-mediated mechanism, or the analogous six-coordinated solvated complex and we find it inherently more satisfying than the accepted hypothesis of large vibrational amplitudes, as in the Berry-mechanism. Alan Cowley and I plan to publish something on this soon.

With best regards,

Yours sincerely,

Jeremy I. Musher

sg
ON THE STEREOCHEMISTRY OF VINYL PHOSPHATES 1

In many cases the predominant stereochemistry of the vinyl phosphates resultant from α-haloketones and triethyl phosphite (TEP) has (EtO)₃P=O \_H geometry (Z = H, Y = Cl, Br, H, R). The assignments are based on a combination of nmr spectral effects including: (a) the well known differentiation of cis and trans 1,2-vinyl protons by their J_HH coupling constants wherein J_{trans} > J_{cis}; (b) a downfield shift for H₂ when cis to phosphate (and little or no effect for a trans H₂) in the presence of BF₃Et₂O due to coordination of the BF₃ with PO and a resultant decrease of negative charge on the oxygen and (c) an upfield shift for trans H₂ (and little or no effect for cis H₂) in changing solvent from CCl₄ to C₆D₆ due to "collision complex" formation.

Relevant data is given in Table I. The conclusive case is the reaction of 22 to give 23, proven to be the trans-isomer: H₂ J_{trans} 12 H₂:

"BF₃ shift" -0.26 ppm; "C₆D₆ shift" minimal (-0.06 ppm). The presence of vinyl halogen as in 25, 26 causes both isomers to give "BF₃ shifts", presumably because the halogen also co-ordinates with BF₃. The major isomer is trans 25, contrary to previous work. The assignment of the H₂ and H₂ protons in 23, 25, 26 and the prediction of all of the vinyl proton nmr absorptions in vinyl phosphates was done by our application of method of Tobey with the following assigned values: -1.39 to -1.44 ppm for geminal-phosphate (or phosphinate), +0.30 ppm for cis phosphate and +0.50 for trans phosphate. These values are all about 2/3 of those reported for -OCOCH₃.


October 12, 1970

I.J. Borowitz
Belfer Graduate School of Science
Yeshiva University
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\delta_{\text{Et}_2\text{O}}$ (ppm)</th>
<th>$\Delta_{\text{Et}_2\text{O}}$</th>
<th>$\delta_{\text{CCl}_4}$</th>
<th>$\Delta_{\text{CCl}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H} - \text{Cl}$ TEP $\rightarrow$ single isomer</td>
<td>6.22</td>
<td>-0.185</td>
<td>6.19</td>
<td>-0.045</td>
</tr>
<tr>
<td>$\text{H} - \text{Br}$ TEP $\rightarrow$ single isomer</td>
<td>6.37</td>
<td>-0.26</td>
<td>6.32</td>
<td>-0.06</td>
</tr>
<tr>
<td>$\text{H}_B \delta 6.32 \text{ (d, J = 12 Hz)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_A \delta 7.08 \text{ (d, J = 11.5 Hz)}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>6.26</td>
<td>-0.23</td>
<td>6.14</td>
<td>+0.185</td>
</tr>
<tr>
<td>23</td>
<td>5.70</td>
<td>-0.30</td>
<td>5.605</td>
<td>+0.435</td>
</tr>
</tbody>
</table>

**Table I**

The Stereochemistry of Enol Phosphate Formation
Dear Barry,

we have extended the program for oriented spin-systems LAOCOONOR (Mol.Phys.15, 333, 1968) for use in cases with groups of fully equivalent nuclei (total spin formalism).

The capacity of the new program LEQUOR is limited to cases which do not exceed 7 groups of fully equivalent nuclei and 16 spin-combinations with 13 submatrices for each combination. The dimension of a submatrix should not exceed 52.

LEQUOR is consequently applicable to any problem of 7 spins or fewer, to 8-spin systems such as ABC D E F G2 and e.g. to 11-spin-systems such as ABC3 D3 E3.

Descriptions of the program and listings are available upon request.

Sincerely yours,

P. Diehl  H.P. Kellerhals  W. Niederberger
November 17, 1970

Dear Barry:

RELAXATION TIMES IN PHOSPHORUS COMPOUNDS

Your threats of expulsion have finally succeeded.

We are applying the Fourier transform technique of measuring relaxation times (1) to a number of problems involving P3. Irv Salmeen, who has been a post-doctoral fellow with me and will be leaving for the Ford Scientific Labs at the beginning of December, has been measuring $T_1$ and $T_2$ for phosphorus-containing molecules. Quite naturally, adenosine tri-phosphate (ATP) has been examined. He has observed a pH dependence of the $T_1$ for each of the three phosphates which exhibit titration-like curves. The chemical shifts of these three phosphates are known to exhibit a pH dependence (2) and it is natural to invoke an interaction common to both the relaxation and chemical shift mechanisms to account for these parallel results. In the absence of a better choice we are inclined to attribute these results to the spin-rotation interaction. The temperature dependence of the relaxation rates should help us establish the contribution of this interaction to the relaxation rates.

We have been using a modification of the Fourier $T_1$ relaxation method to measure the $T_2$'s of the individual lines in complex spectra. A Carr-Purcell, Meiboom-Gill sequence is established. This, of course, evokes a series of echoes which after Fourier transformation yield the partly (transversally) relaxed spectra. If the interval between the π pulses is shorter than the time required for the echoes' to decay into the noise, the decays are artificially truncated. Two effects arise as a consequence of the interruptions; 1) the transformed spectra will contain lines artificially broadened and 2) a number of artifactual features or satellites will appear in the spectra.

These undesirable features are circumvented by terminating the pulse sequence at the pulse which evokes the echo to be examined thus allowing it to decay completely. The trailing half of this terminal echo is accumulated with as many identical passes as are required to achieve adequate signal-to-noise ratios. The timing is switched to accumulate the next echo in the sequence, etc.

Although it may be surprising to some, the spectra resulting from these half-echoes are strikingly similar to those resulting from the transformation of simple free-decays following a single pulse.

For simple molecules such as $\text{PO}_4^3^-$, $\text{P}_4\text{O}_6^-$ and $\text{P} (\text{OCH}_3)_3$, $T_1 = T_2$ while for more complex molecules, including ATP, this equality is not found. The extension to additional systems and the interpretation of these findings will, obviously, receive much of our attention for the immediate future.

Sincerely,

Melvin P. Klein

Dear Barry:

We are using Fourier Transform $^{13}$C nmr techniques in the analysis of the microstructure of polymers. Fourier transforms have been obtained of the noise-decoupled, natural abundance, 22.6-MHz $^{13}$C nmr free induction decays of a half dozen different polyelectrolytes, of polyacrylonitrile, of styrene-acrylonitrile copolymers, and of some highly cross-linked polymers. The latter were in the form of semi-rigid gels rather than true solutions. These polymer systems are not amenable to study by $^1H$ nmr. However, the wide range of $^{13}$C chemical shifts, the easy removal of all spin-spin interactions by heteronuclear decoupling, and the absence of severe dipolar broadening of the polymer lines, permit a detailed $^{13}$C nmr analysis of both the structural and steric configurations of the chains. (Details of these studies will appear in the January-February issue of Macromolecules.)

Our spectrometer consists of a Bruker HPX-Fabri-Tek 1074-PDP-8/I combination. The spectrometer has four independent, simultaneously available rf channels, namely the $^{13}$C analytical channel, the $^{19}$F lock channel, and two irradiation channels which are presently tuned to $^1H$ and $^{14}$N. All of the rf frequencies are phase-locked. The $^{13}$C rf drives a transmitter capable of producing ~60-watt (into 50 ohms), square-wave pulse with a width variable between 20 and 200 µsec. Wider pulse widths are used when only a portion of the $^{13}$C nmr spectrum is to be investigated. The pulse sequence timing is provided by the trigger output of the Fabri-Tek 1074. Only identical pulses with equal spacing are produced generating repetitive free induction decays. Delays between pulses ranging from 0.1 to 20 seconds have been used. Very short pulse spacings can be used in obtaining polymer $^{13}$C nmr spectra because of the small effective $T_2$ values involved. The 1074 is used to sample the receiver output after completion of the irradiating pulse. The frequency sweep width is changed by varying the 1074 data sampling rate. A tunable filter between the receiver and 1074 removes undesired high-frequency components from the free induction decay. The PDP-8/I is directly interfaced to the 1074 and calculates the Fourier transform using a program written by Fabri-Tek. Either the amplitude spectrum (the square root of the sum of the squares of the absorption and dispersion spectra) or the pure absorption spectrum can be calculated, the latter calculation including a linear phase correction. Line positions in the transformed spectra are read
as channel locations in the 1074 by means of a CRT display.

The optimum sensitivity of the Bruker spectrometer operating in the pulsed mode is between two and three orders of magnitude greater than when operating in the CW mode, while the sensitivity of the CW mode is about five times greater than what I was able to achieve using an HA-100 in CW 13C nmr studies of polymers two years ago.

An example of the kind of noise-decoupled, natural abundance 13C nmr spectra of small molecules obtained with the Bruker spectrometer is shown in the first figure. Here, we are illustrating lineshape and resolution rather than sensitivity. This is an amplitude spectrum in which no phase correction has been made. The free induction decay from the methyl carbon of the propylene glycol has been removed by filtering and so is not folded back into the narrow width of the transformed spectrum. The 13C nmr spectra of a 10% (wt/vol) DMSO solution of polymethacrylonitrile is shown in the second figure. Detailed interpretations have not yet been completed. However, the indicated line assignments in the wide sweep-width spectrum are clear on the basis of off-resonance decoupling experiments. (The very intense peak is due to the solvent, and is many times off scale.) The free induction decay was accumulated in 4 minutes, and the transform required 30 seconds. In a separate experiment, the high-field methyl-carbon region was expanded yielding the second spectrum of this figure. The increased resolution was obtained at a cost of about a factor of 30 in the time of data accumulation. Other lines were removed from the spectrum by filtering before the transform was performed. (Both of these spectra are amplitude spectra.) The many lines in the methyl-carbon region of the spectrum of polymethacrylonitrile can be interpreted in terms of the various steric pentads present in different concentrations in the chain. That is, the resonance of each methyl carbon is sensitive to the steric configuration of nearest and next-nearest monomer neighbors in the chain. This kind of detailed information is not available from the 1H nmr spectrum of polymethacrylonitrile.

Please credit this contribution to the Monsanto subscription.

Sincerely,

Jacob Schaefer

Title: Fourier Transform 13C NMR Studies of Polymers
Data accumulation time

1 Sec.

2 Sec.

10 Sec.

Fourier transform of 10 Sec accumulation of free induction decay

$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

$13.4 \text{ Hz} \times \frac{1}{0.0754} \text{ Sec.}$
Dear Dr. Shapiro:

Thank you for the reminder. As a payment on our subscription, here are a few notes on a study of long-range fluorine-proton coupling. In the NMR spectrum of compound $1$ the signal of the trimethylsilyl group appears as a doublet which is due to five-bond coupling with the ortho-fluorine. A similar coupling has been observed by C. Tamborsky and E. J. Sokolski (J. Organometal. Chem., 1969, 12, 185) in compounds $2$, $3$, and $4$.

\[
\begin{align*}
J_{F-Me} & = 1.5 \text{ Hz} \\
J_{F-Me} & = 1 \text{ Hz} \\
J_{F-Me} & = 1 \text{ Hz} \\
J_{F-Me} & = 1.5 \text{ Hz}
\end{align*}
\]

In order to check the generality of the phenomenon, we have examined a series of compounds of the type $5$:

It occurred to us that the size of coupling constant could depend on the presence on the heteroatom of free electron pairs, or low-lying empty-d orbitals (like 3d orbitals of silicon atom) available for extended conjugation with the phenyl ring. Two different cases are to be considered: pentfluorophenyl compounds (SF) and simple o-fluorophenyl compounds (IF). Our results are given in the table, together with data from the literature. The compounds are listed in order of increasing $J_{F-Me}$ coupling. The "five bond" or "through space" F-Me coupling is larger in the SF than in the IF series. Moreover, it is clear from compounds 1,9 and 10 that for a given heteroatom, conjugation increases the coupling constant. In the IF series a long-range coupling is observed when $X$ is able to enter conjugation with the ring, but does not occur with any of the other compounds. This observation is in favour of p-ds bonding in trimethylsilyl aromatic compounds. Further investigations are on the way.

Sincerely yours,
<table>
<thead>
<tr>
<th>Y</th>
<th>J=</th>
<th>Y</th>
<th>J=</th>
</tr>
</thead>
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<tr>
<td>Et</td>
<td>0</td>
<td>-CH(_2)-CH(_3)</td>
<td>0</td>
</tr>
<tr>
<td>-SnMe(_3)</td>
<td>0.4</td>
<td>-CH(CH(_3))(_2)</td>
<td>0</td>
</tr>
<tr>
<td>-SnClMe(_2)</td>
<td>0.4</td>
<td>-t-Bu</td>
<td>0</td>
</tr>
<tr>
<td>SnMe(_2)</td>
<td>0.4 (1)</td>
<td>-SnMe(_3)</td>
<td>0</td>
</tr>
<tr>
<td>-SMe</td>
<td>0.7 (2)</td>
<td>-SnMe(_3)</td>
<td>0</td>
</tr>
<tr>
<td>-PbMe(_3)</td>
<td>1 (3)</td>
<td>-SnMe(_3)</td>
<td>0</td>
</tr>
<tr>
<td>-OMe</td>
<td>1.1 (4)</td>
<td>-SnMe(_3)</td>
<td>0</td>
</tr>
<tr>
<td>-PMe(_2)</td>
<td>1.2 (5)</td>
<td>-SnMe(_3)</td>
<td>1.5</td>
</tr>
<tr>
<td>CH(_2)=C-Me</td>
<td>1.2 (5)</td>
<td>-SnMe(_3)</td>
<td>1.2</td>
</tr>
<tr>
<td>-C-CH(_3)</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMe(_2)</td>
<td>1.9 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-NHMe</td>
<td>2.6 (1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(3) L. H. Sutcliffe, unpublished result.
(6) Y. Vignollet - unpublished result.
Professor Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

Dear Professor Shapiro:

The title for our initial contribution to the TAMU NMR Newsletter is Rotational Isomerism in α,β-Unsaturated Acyl Fluorides. Koster studied the temperature dependence of the $^1H$ nmr spectrum of acryloyl fluoride at temperatures above $-95^\circ$ and concluded from the changes in the three-bond HF coupling constant that the enthalpy difference between s-cis and s-trans conformations was $800 \pm 250$ cal/mole, with the latter conformation having the lower energy. Subsequently, infrared and microwave studies have confirmed that the energy difference between the two forms is small. This is in contrast to the behavior of most α,β-unsaturated carbonyl compounds, which generally have a strong preference for the s-trans conformation. We have found that, at very low temperatures, interconversion of the two conformations is stopped on the nmr time scale. The s-trans and s-cis forms are present in a ratio of 76:24 at $-161^\circ$.

\[
\begin{array}{c}
\text{s-trans} \\
76\% \\
\end{array}
\quad \leftrightarrow \quad \begin{array}{c}
\text{s-cis} \\
24\% \\
\end{array}
\]

This ratio corresponds to a free energy difference of $0.25$ kcal/mole. The values of $E_a$ and $\Delta G^\circ$ for rotation about the C-C bond were $6.06 \pm 0.07$ and $5.66 \pm 0.07$ kcal/mole.

The $^{19}F$ chemical shifts at 94.1 MHz were 3623 and 1548 Hz downfield from fluorotrichloromethane, the internal standard, for the s-cis and s-trans conformations, respectively. The fluorine of the s-trans conformation is coupled ($^3J_{HF} = 19.2$ Hz) to the proton separated by three bonds; the corresponding coupling constant for the s-cis form was calculated to be $-7.5$ Hz, assuming the ground-state energy difference between these two forms is invariant with temperature. Crotonyl fluoride, cinnamoyl fluoride, and p-methoxycinnamoyl fluoride also exhibit cis-trans...
isomerism, and the free energy differences and barriers to rotation have been determined for these compounds.

Sincerely yours,

Frank F. S. Lin

Kenneth L. Servis
Associate Professor of Chemistry

References:
November 23, 1970

Professor B. L. Shapiro,
Department of Chemistry,
Texas A and M University,
College Station, Texas 78843,
U. S. A.

Substituent Effects on Geminal Couplings
in Allylic Methylene Groups

Dear Barry:

I thought it worthwhile to describe some work just completed by Bruce Raby for his M.Sc. degree since it will be several months before it appears in the literature.

Bruce synthesized ten members of the series of general formula I for the purpose of studying substituent effects on the geminal coupling constant $J_{AB}$ in the allylic methylene groups.

\[ \text{I} \]

The nmr spectra were measured at 100 MHz during simultaneous irradiation of the deuterons, and the spectra, which were first order, gave the parameters listed in Table I.
Prof. B.L. Shapiro

November 23, 1970

Table I

Coupling Constants in I (in Hz)

<table>
<thead>
<tr>
<th>Compound</th>
<th>-J_{AB}</th>
<th>-J_{CD}</th>
<th>-J_{AB}</th>
<th>-J_{CD}</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=Cl</td>
<td>17.4</td>
<td>13.3</td>
<td>R=COOH₂</td>
<td>18.8</td>
</tr>
<tr>
<td>OCOCH₃</td>
<td>17.3</td>
<td>13.3</td>
<td>OCH₃</td>
<td>16.4</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>18.1</td>
<td>13.2</td>
<td>H</td>
<td>17.5</td>
</tr>
<tr>
<td>CN</td>
<td>19.3</td>
<td>13.4</td>
<td>SC₆H₅</td>
<td>17.2ᵃ</td>
</tr>
<tr>
<td>COOCH₃</td>
<td>19.2</td>
<td>13.3</td>
<td>-N-</td>
<td>16.8</td>
</tr>
</tbody>
</table>

ᵃ estimated from undeuterated derivative of I.

It can be seen that J_{AB} varies by almost three Hz as R is varied. Changes in J_{AB} do not correlate well with Hammett σ_p values for the R substituents but correlate better when increased weight is given to the resonance effect of the substituents.

These results show J_{Gem} to be more susceptible to the R substituent in this series than in the benzylic system, para-R-C₆H₅-C-X. HA HB

In this latter system a large conformational influence of the orientation of the benzene ring in determining substituent effects on J_{Gem} has been observed (R. R. Fraser and R. N. Renaud, Can. J. Chem. in press) and it seems very likely that the substituent effects in allylic CH₂'s are also conformationally dependent and those in the table represent the maximum values. (In the cyclohexene ring the π-orbitals of the double bond are within 9° of the geometry required for maximum overlap with the antisymmetric M.O. of the methylene group). Work towards establishing the conformational influence on J_{Gem} in allylic systems is continuing.

Yours sincerely,

Robert R. Fraser

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

Dear Professor Shapiro:

Subject: Checking performance of Pulse-Gate for FID

We are trying to get approval for FID-FT gear for protons at 100 MHz initially and, after increasing our know-how, for C\textsuperscript{13} at 25 MHz. Judging by the experience of other workers, there are problems related to proper evaluation of the pulse gear as electronic components. The supplying companies rely almost wholly on computer output. We may be driven to using the central computer on a real-time basis to perform these experiments and need some method of evaluating the pulse gear on its own.

A number of properties have been suggested as criteria, but the method of making the necessary measurements is not clear.

Among the properties which should affect performance are: accurate pulse durations to 1% in the 1 to 10 microsecond range; sharp, square cut-off of the pulse (To what standard?); reproducible phase relation of pulse to carrier (To what standard?); and broad band-pass for the system including the detector.

These seem to be the important considerations but most of them are not easily measured.

We should be happy to receive any comments on this problem from readers.

With best regards.

Sincerely,

David Weisleder, Chemist  
Physical-Chemical Properties Investigations  
Cereal Properties Laboratory

Curtis A. Glass, Chemist  
Physical-Chemical Properties Investigations  
Cereal Properties Laboratory
Dr. B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843

A. High Current Connections in Varian Power Supplies  
B. Fabri-Tek 1074

Dear Barry:

Recently, while trying to locate the source of extreme field instability in our broadline magnet system (9" magnet, V-2503 power supply and Mark 1 Fieldial), we attempted to adjust the Fieldial following the procedure described in the Varian manual. We located the instability at the step in which the field must be reversed, because at this point the field reversing switch jammed when it was activated. When we disassembled the switch we found several of the plastic parts charred and the main assembly broken. We also found that the current carrying cables were quite stiff near the lugs and the insulation starting to crack. The switch and cables (all 7) had to be replaced. This overheating can arise from loose connections, as mentioned in the Varian manual, but in our case may more likely have been due to increased resistance caused by corrosion of the high-current connections since the connections appeared to be quite tight.

We recommend that, in addition to checking the nuts and bolts for tightness, the lugs should be checked for corrosion as evidenced by discoloration. If the current cables have to be replaced, the lugs should be soldered on instead of just crimped.

We have received a Fabri-Tek 1074 signal averaging system. In a preliminary arrangement we have used the voltage ramp of the Fabri-Tek to drive a Wavetek 134 sweep generator whose output is used as an external sweep frequency for our HA-100 system. We read out on either the HA-100 recorder or an x-y recorder. This setup has been reasonably successful and will be developed further.

Sincerely,

W. B. Momiz, Head  
NMR Spectroscopy Section

C. F. Poranski, Jr.  
NMR Spectroscopy Section  
Chemistry Division
Dear Barry,

We apparently went through the entire spectrum of your reminders, as the footnote on the far-infrapink letter shows. The present contribution, we hope, will reach you before you cut us off.

This is a sequel to our recently published note [1], part of which was presented at the Aachen NMR Colloquium last April. We think it gives strong evidence that all $J_{HH}$'s as well as ortho- and meta-$J_{HF}$'s in benzenes are "absolutely" positive, if one piece of theory is taken as "absolutely" true, that is, that $J_{CH}$'s are absolutely positive. Two other groups of investigators [2,3], working in the area of oriented molecules, have reached the same conclusion; their auxiliary hypothesis has been one on the orientation of benzene rings in a strong magnetic field.

We related signs of coupling constants to each other by heteronuclear tickling. Mr. E. P. Ragelis of our laboratory synthesized a molecule simple enough to do the necessary tickling experiments, namely, 2-bromo-3-chloro-5,6-difluorobenzene. Mr. R. Tschudin of Varian Associates constructed a frequency multiplier for us so that the 5 MHz standard frequency from the GR frequency synthesizer could be used to provide a 50 MHz source for driving the doubler stage of the V-4311 rf unit of the HA-100 [4]. We gratefully acknowledge the assistance of both gentlemen.

To get oriented in "F-space", that is, to establish an absolutely relative scale of the F spectrum with respect to H (how was that again?), we tickled the two AX systems of cis- and trans-1,2-dichlorofluoroethylene (the "guide" compound mentioned below) and noted at what F frequency the H lines of these two molecules exhibited the cleanest tickling patterns. This "guide for the blind" may not be original and fortunately will not be necessary for those who use spectrometers of the last generation, where all frequencies are derived from one master oscillator.

Spectra were taken of a 50% solution of 2-bromo-3-chloro-5,6-difluorobenzene in a 3:1:1 mixture of CCl$_3$CF$_3$, TMS and our guide compound (see above). The parameters of the Table have an r.m.s. error of 0.01 Hz and were obtained by refinement of experimental data through two iterations.
The Larmor frequencies $w_i$ are referred to arbitrary zeros which correspond approximately to the first lines of the H and F spectra respectively.

The absolute character of the signs is based on the fact that ortho-$J_{FF}$'s are absolutely negative [1]. That the relative signs are

$$0_{J_{FF}}^+, p_{J_{FF}}^+, 0_{J_{HF}}^+, m_{J_{HF}}^+, 0_{J_{HH}}^+, m_{J_{HH}}^+, p_{J_{HH}}^+,$$

has already been established by spectral analysis [5] and by tickling experiments [6].

It would, of course, be desirable to do an experiment similar to ours with a molecule which contains two H's ortho or meta to each other: there is an outside chance that in our particular molecule para-$J_{HH}$ is negative, because para-$J_{HH}$'s can be close to zero.


Best wishes and regards.

Sincerely,

E. Lustig
BF-115

E. A. Hansen
December 2, 1970

AIRMAIL--SPECIAL DELIVERY

Professor Barry Shapiro
1101 Merry Oaks
College Station, Texas 77840

Subject: 12th ENC to be held at University of Florida, Gainesville, from February 18 to 20, 1971

Dear Barry:

I hope this announcement will serve to reinstate my delinquent subscription to the NMR Newsletter.

The 12th Experimental NMR Conference will be held on the campus of the University of Florida, Gainesville, from Thursday, February 18, through Saturday noon, February 20, 1971. This conference is devoted to new developments in instrumentation and experimental techniques. It is not intended as a vehicle for the presentation of results obtained by routine NMR methods.

Sessions will consist almost entirely of invited papers, but a limited number of contributed papers can be accepted. Anyone wishing to present a paper in one of the currently scheduled sessions should communicate directly with the chairman of the appropriate session. Session chairmen will assign the lengths of all presentations.

The following sessions are currently being planned by the indicated chairmen:

User experiences with new generation high resolution spectrometers
P. Bender
Department of Chemistry
University of Wisconsin
Madison, Wisconsin 53706

Structure coding and pattern recognition of NMR spectra
T. Lusebrink
IBM Research K06-025
Monterey and Cottle Roads
San Jose, California 95114
Fourier transform techniques
A. Allerhand
Department of Chemistry
Indiana University
Bloomington, Indiana 47401

Applications of paramagnetic shift reagents in high resolution NMR
P. Demarco
Lilly Research Laboratories
Eli Lilly and Company
Indianapolis, Indiana 46206

Developments in $^{13}$C NMR
J. Stothers
Department of Chemistry
University of W. Ontario
London, Ontario, Canada

Progress in superconducting high resolution spectrometers
A. Bothner-By
Department of Chemistry
Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Topics other than those listed here may be included, with both invited and contributed papers. Anyone wishing to suggest additional topics or to present a paper unrelated to the scheduled sessions should communicate with the conference chairman as soon as possible. The chairman will assign the lengths of these papers.

Additional information and an application to attend may be obtained from the ENC Secretary: Professor Jay Martin Anderson, Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010.

Yours sincerely,

R. E. Lundin
Chairman, 12th ENC
November 30, 1970

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

Dear Barry:

Recently Mrs. Ying-Hseh Chen has been preparing a number of substituted benzyllithiums by addition of t-butyllithium with tetramethyl-ethylenediamine (1:1) to the appropriate α-methylstyrene in isooctane.

The benzyllithiums have proton shifts, see below, very similar to benzyllithium itself from which we conclude that the species look like conjugated anions, I.

At 0°C all the ring hydrogens are magnetically non-equivalent indicating slow rotation about the C(α) - C(benzyl) bond. The nmr parameters for the unsubstituted system are: Shifts, τ scale, H5, 5.03; H6, 3.91; Hα, 2.27; Hα, 4.01; H2, 3.37. Coupling constants, Hz: 2,3: 9.2; 2,4: -1.31; 2,5: -0.1; 2,6: -2.83; 3,4: -6.48; 3,5: -2.33; 3,6: -0.28; 4,6: -1.22; 5,6: 9.02. We are quite certain about the relative signs but not sure what they mean.

Above 0°C the spectrum undergoes line-broadening and averaging and changes with increasing temperature from ABCDE to ABB'C'C'. The complexity of a five spin system allows the rates responsible for this exchange process to be fitted with good accuracy using Binsch's program DNMK. The resulting activation parameters are Ea 19.4 kcal/mole and Aν is 0.3±1 kcal/mole. The kinetic order in contained reagent is 1.4±0.5.

The process responsible for these exchanges clearly involves rotation about the ring benzyl bond. Whether we have measured the barrier to rotation in the anion or whether rotation is chemically assisted by the lithium is a matter which has to be cleared up with more experiments now in progress.

With best regards.

Sincerely yours,

Gideon Fraenkel
Professor of Chemistry
Long range coupling in alkylvinyl ethers and -thioethers.

Dear Professor Shapiro,

In June we acquired a Varian XL 100/15 nmr-spectrometer. It soon turned out that the resolving power of this instrument, in the internal $^1$H lock mode, was very good indeed. We obtained for instance in the centerlines of the o-dichlorobenzene multiplet (Varian sample 943346-26) a line-width at half height of 0.06 Hz. Since it was known (1,2) that in vinyl ethers and vinylthioethers some coupling occurs over the heteroatom and we had a large number of these compounds at hand, we decided to try to obtain more accurate values of these coupling constants with the XL 100.

The nmr-parameters of the methyl- and ethylvinyl ethers and thioethers (20.0% v/v in CCl$_4$, degassed) are given in the table. The vinyl-parts of the spectra were analysed as ABX-systems, treating the long range coupling constants as first-order perturbations. As it is very easy, though of discutable practical utility, to obtain accurate chemical shifts with the XL 100 spectrometer, which operates in a digital frequency-swept mode, most of the reported chemical shifts are accurate within 0.003 ppm.

From these data and from the data on a number of other systems we studied also, we found that $J_{\text{ad}}$ is very sensitive to the nature of the alkyl-substituent. It could be that the orientation of the alkyl-group with respect to the double bond is the determining factor for this coupling.
Furthermore, we found \(|^5J_{ad}| > |^5J_{bd}|\) in all cases studied so far. This observation could be of use in determining the configuration around the double bond. Finally we would like to draw attention to the coupling of the protons in the methyl group in the ethyl derivatives with the ethylenic protons. This coupling is illustrated in figure 2, which shows on an expanded scale one of the four lines of proton a in ethyl-vinyl thioether. Figure 1 gives the observed spectrum of the methoxylprotons in methyl-vinylether.

A detailed account of this work on a larger number of compounds will be published.

Table 1

<table>
<thead>
<tr>
<th>X</th>
<th>R = H</th>
<th>CH₃</th>
<th>S</th>
<th>S</th>
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<td>3.651</td>
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<td>5.117</td>
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<td>4.060</td>
<td>4.035</td>
<td>4.870</td>
<td>5.002</td>
</tr>
<tr>
<td>Hₐ</td>
<td>3.471</td>
<td>3.675</td>
<td>2.189</td>
<td>2.67 ± 0.01</td>
</tr>
<tr>
<td>H₉</td>
<td>1.256</td>
<td>-</td>
<td>1.30 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>³J_ab</td>
<td>+6.85 ± 0.03</td>
<td>+6.90 ± 0.03</td>
<td>+10.06 ± 0.03</td>
<td>+10.10 ± 0.05</td>
</tr>
<tr>
<td>³J_ac</td>
<td>+14.26 ± 0.03</td>
<td>+14.37 ± 0.03</td>
<td>+16.52 ± 0.03</td>
<td>+16.70 ± 0.05</td>
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<tr>
<td>³J_ad</td>
<td>0.40 ± 0.02</td>
<td>0.53 ± 0.02</td>
<td>0.00 ± 0.02</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>³J_ac</td>
<td>0.19 ± 0.02</td>
<td>-</td>
<td>0.18 ± 0.02</td>
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<tr>
<td>³J_ac</td>
<td>-2.13 ± 0.02</td>
<td>-1.85 ± 0.02</td>
<td>-1.06 ± 0.02</td>
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<tr>
<td>³J_ab</td>
<td>0.20 ± 0.02</td>
<td>0.17 ± 0.02</td>
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<tr>
<td>³J_ac</td>
<td>0.17 ± 0.02</td>
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<td>-</td>
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<tr>
<td>³J_ac</td>
<td>0.31 ± 0.02</td>
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<tr>
<td>³J_ac</td>
<td>0.12 ± 0.02</td>
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<tr>
<td>³J_de</td>
<td>7.0 ± 0.1</td>
<td>-</td>
<td>7.3 ± 0.1</td>
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</table>
With best regards,

Yours sincerely,

[Signature]

J.F.C.M. van Donk

The assignment of the lines in an ABX system.

Dear Dr. Shapiro,

The assignment of the lines of an ABX system to A, B, X, and combined transitions, given by Pople\(^1\), is incomplete insofar as it is valid only for the case in which \(v_A - v_B > \frac{1}{2}(J_{AX} - J_{BX})\). With this condition, \(\cos 2\phi_-\) is positive and \(\phi_- > \sin \phi_-\). Consequently the basic wave function \(5(\psi\phi)\) predominates in the mixed wave function \(5'(\cos \phi_- (\psi\phi) + \sin \phi_- (\phi\psi))\), and so does the basic wave function \(6(\phi\psi)\) in the mixed wave function \(6'(-\sin \phi_- (\psi\phi) + \cos \phi_- (\phi\psi))\). Therefore the transitions \(8((\psi\phi) \rightarrow 5'(\phi\psi))\) and \(6'((\phi\psi) \rightarrow 2(\phi\psi))\) may be regarded as being A-lines, the transitions \(8(\phi\psi) \rightarrow 6'((\psi\phi))\) and \(5'(\phi\psi) \rightarrow 2(\phi\psi)\) as B-lines, the transitions \(5'(\phi\psi) \rightarrow 3'((\psi\phi))\) and \(6'((\phi\psi) \rightarrow 4'((\psi\phi))\) as X-lines, and the transitions \(5'(\psi\phi) \rightarrow 4'(\phi\psi)\) and \(6'((\phi\psi) \rightarrow 3'(\phi\psi))\) as combination lines. However, if \(v_A - v_B < \frac{1}{2}(J_{AX} - J_{BX})\), which is the condition for the other ABX solution with the same line positions, \(\cos 2\phi_-\) is negative, hence \(\cos \phi_- < \sin \phi_-\), and then the basic wave function \(6(\phi\psi)\) predominates in the mixed wave function \(5'\), and so does the basic wave function \(5\) in the mixed wave function \(6'\). Therefore the assignment of all the transitions connected to the levels of the mixed wave functions \(5'\) and \(6'\) must be interchanged, i.e. the above-mentioned A-lines must be interchanged with the B-lines, and the X-lines must be interchanged with the combination lines. Based upon these considerations two different assignments ought to be taken into account in a list of transitions for an ABX system (Table 1).

\* The same notation and the same assumptions as those of Pople are used, i.e. \(v_A > v_B\) and \(D_+ > D_-\) (viz. \(J_{AX} > J_{BX}\)).
The correctness of the two assignments may be verified easily: for A- and B-lines, if we consider the two possible combinations of the effective Larmor frequencies of the two sub-AB systems leading to the two solutions; for the X- and combination lines, if we consider the intensities in the X part at a steadily increasing value of \( V_A - V_B \): the relative intensities of X-lines will increase to unity, while the intensities of the combination lines will decrease to zero.

Yours sincerely,

N.V. PHILIPS-DUPHAR Research Laboratories
Dept. 30

F.W. van Deursen

N.V. PHILIPS Research Laboratories

J. Bakker


<table>
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<th>Transition</th>
<th>Origin</th>
<th>Energy</th>
<th>Relative intensity</th>
</tr>
</thead>
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<tr>
<td>1. 8 → 6'</td>
<td>B : A</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 - sin 2( \theta )</td>
</tr>
<tr>
<td>2. 7 → 4'</td>
<td>B : B</td>
<td>( V_{ab} + \frac{1}{4}J_{ab} )</td>
<td>1 - sin 2( \theta )</td>
</tr>
<tr>
<td>3. 5' → 2</td>
<td>B : A</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 + sin 2( \theta )</td>
</tr>
<tr>
<td>4. 3' → 1</td>
<td>B : B</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 + sin 2( \theta )</td>
</tr>
<tr>
<td>5. 8 → 5'</td>
<td>A : B</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 - sin 2( \theta )</td>
</tr>
<tr>
<td>6. 7 → 3'</td>
<td>A : A</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 - sin 2( \theta )</td>
</tr>
<tr>
<td>7. 6' → 2</td>
<td>A : D</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 + sin 2( \theta )</td>
</tr>
<tr>
<td>8. 4' → 1</td>
<td>A : A</td>
<td>( V_{ab} + \frac{1}{4}(2J_{ab} - J_{ax} - J_{bx}) )</td>
<td>1 + sin 2( \theta )</td>
</tr>
<tr>
<td>9. 8 → 7</td>
<td>X : X</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>1</td>
</tr>
<tr>
<td>10. 5' → 3'</td>
<td>X : Comb.</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>( \cos^2(\theta) )</td>
</tr>
<tr>
<td>11. 6' → 4'</td>
<td>X : Comb.</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>( \cos^2(\theta) )</td>
</tr>
<tr>
<td>12. 2 → 1</td>
<td>X : X</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>1</td>
</tr>
<tr>
<td>13. 7 → 2</td>
<td>Comb. : Comb.</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>0</td>
</tr>
<tr>
<td>14. 5' → 4'</td>
<td>Comb. : X</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>( \sin^2(\theta) )</td>
</tr>
<tr>
<td>15. 6' → 3'</td>
<td>Comb. : X</td>
<td>( V_{x} + \frac{1}{4}(J_{ax} + J_{bx}) )</td>
<td>( \sin^2(\theta) )</td>
</tr>
</tbody>
</table>

I for \( V_A - V_B > \frac{1}{4}(J_{ax} - J_{bx}) \)
II for \( V_A - V_B < \frac{1}{4}(J_{ax} - J_{bx}) \)
Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

December 2, 1970

Dear Barry:

I have long wondered what your blue letters actually look like--and now I know. I hope to avoid learning about the pink ones with this contribution which may interest people involved in $^{13}$C work.

Fourteen years ago, McConnell and Holm (1) stated that the $^{13}$C spin-lattice relaxation time in $^{13}$CS$_2$ is short compared with $T_1$ in $^{13}$CCl$_4$, since chemical shift anisotropy provided a relaxation mechanism in $^{13}$CS$_2$. No results were quoted, but recent preliminary measurements in our laboratory indicate that chemical shift anisotropy is indeed important in $^{13}$CS$_2$.

The results obtained for degassed 60% enriched $^{13}$CS$_2$ at 25° C and 15.08 MHz were:

$$T_1 = 44 \text{ sec}$$
$$T_2 = 38 \text{ sec}$$

$T_1$ was obtained from a series of 90°-T-90° pulse sequences, and $T_2$ by the usual Meiboom-Gill modified Carr-Purcell technique. We used the pulse spectrometer at NBS.

The interesting thing about the $T_1$ and $T_2$ values is, of course, that $T_1/T_2 = 7/6$, which is the value theoretically predicted from the expressions for relaxation by chemical shift anisotropy. (2)

These results do not agree particularly well with $T_1$'s quoted by Lippmaa (3), who obtained by adiabatic rapid passage at 28° C: $T_1 = 30$ sec at 15 MHz and $T_1 = 42$ sec at 10 MHz. His conclusion was that chemical shift anisotropy is important, but not dominant, whereas our ratio of $T_1/T_2 \sim 7/6$ indicates chemical shift anisotropy to be the only mechanism. The explanation for this discrepancy is presumably that we used sample tubes which were constricted with a 1-1/2" long capillary below the surface of
the \(^{13}\text{CS}_2\). This restricts interchange between the liquid and gas phases, and thereby reduces spin-rotation contributions to the relaxation rate from molecules in the gas phase.

Considering the experimental uncertainty (possibly ± 2 sec) I hesitate to make too firm conclusions on the basis of two numbers, but we are about to do relaxation time measurements as a function of temperature and field strength. Otherwise, we are at present very excited about \(^{13}\text{C} \ T_2\) measurements which are short due to scalar \(^{13}\text{CH}\) couplings and we will have a report on that soon.

Sincerely yours,

\[\text{\textit{Gitte}}\]

Regitze R. Shoup
Laboratory of Physical Biology
National Institute of Arthritis
and Metabolic Diseases

New assignment for Ethyl pyridine

Dear Barry,

One of the great strengths of your informal newsletter is the opportunity it provides for friendly criticism; an attempt to make the same point in the formal literature too often degenerates into undesirable polemics.

Charlie Reilly (TAMU NR 146, 31) has pointed out that our assignment of the carbon resonances C3 and C5 of 2-ethyl pyridine on the basis of spin-lattice relaxation times is contradicted by his recent selective proton decoupling experiments. We have confirmed Charlie's result by studying the undecoupled Fourier transform carbon-13 spectrum, arguing that the low field resonance must be from C3 since it shows an additional multiplicity ascribed to coupling to the methylene protons (Figure 1). Selective irradiation of the methylene protons restores the C3 resonance to a doublet of doublets of doublets (with some incidental partial coalescence). We feel that this is perhaps a more direct method of assignment, since Charlie's experiment relies on selective irradiation within the rather complex carbon-13 satellite spectrum of the ring protons.

The new assignment would appear to make the relaxation results even more interesting. Ring carbons C3, C4 and C6 have essentially equal spin-lattice relaxation times (22 ± 1 sec) whereas C5 has a much shorter relaxation time (15 sec). Why is C5 singled out in this way? It is tempting to ascribe this to stacking of pyridine rings parallel to one another with their dipoles opposed:

![Diagram](image)

The methyl protons then approach the ring carbons C5 quite closely. Similar considerations would apply if several rings were stacked together. Preliminary experiments seem to indicate that when the methyl protons are weakly irradiated there is a perceptible increase in the integrated

intensity of the C5 resonance, suggesting an intermolecular Overhauser effect. We are also planning to remeasure the spin-lattice relaxation times of a dilute sample, since if stacking is the correct explanation, the differences in $T_1$ should disappear at low concentrations.

Best wishes,

Ray

Ray Freeman Howard Hill

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

December 3, 1970

Dear Barry:

The estimation of small splittings (especially those which lie near or below the limits of resolution of most spectrometers) has always been a problem. The elegant methods developed by Freeman, Hoffman, Lusebrink, etc., are sufficiently involved and tedious as to discourage all but the most persistent spectroscopists. I'd like to describe a simple, accurate method which can be used by anyone who has access to a decoupler.

At slow sweep speeds, NMR lines are Lorentzian in shape, so that it is possible to construct a shape function for any multiplet, e.g., for a doublet,

$$\Gamma(v) = \frac{1}{b^2 + [(\delta v) - 1/2\Delta]^2} + \frac{1}{b^2 + [(\delta v) + 1/2\Delta]^2}$$

where $2b$ is the width at half-height of a simple line, $\Delta$ is the line spacing, and $\delta v$ is the displacement from the center of the pattern. When $\Delta = 0$, $\Gamma(v_0) = 2/b^2$, whereas $\Gamma(v_0) = 0$ as $\Delta \to \infty$. Hence one can construct a series of curves relating $\Delta$ to percent maximum intensity at $(\delta v) = 0$ for various linewidths. To read $\Delta$ directly from the curves, one needs to know the intensity of the broadened absorption, the intensity of the same absorption when $\Delta = 0$, and the linewidth of a simple sharp peak. The latter two numbers can be obtained by careful decoupling of the appropriate proton, the former by direct measurement at identical instrument settings, but with the decoupler set at an irrelevant frequency.
The method has been tested for a number of cases, of which several are summarized below:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Our Method</th>
<th>Literature</th>
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<tr>
<td>3-methyl-2-butanone</td>
<td>0.35 ± 0.02</td>
<td>0.35</td>
</tr>
<tr>
<td>p-nitrobenzaldehyde</td>
<td>0.38 ± 0.02</td>
<td>0.40</td>
</tr>
<tr>
<td>methyl acetate</td>
<td>0.23 ± 0.02</td>
<td>0.22</td>
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</table>

and a manuscript is in preparation. I would particularly like to test it on the 0.05 Hz coupling in 3-bromothiophen-2-aldehyde, but haven't been able to persuade any of my organic friends to make some. If one of your readers could spare 40-100 mg, I'd greatly appreciate receiving it.

Regards to all!

Sincerely,

D. J. Sardella
Assistant Professor

DJS/cp

Short title: Estimation of Unresolved Splittings
Dear Dr. Shapiro,

One problem with using a hi-fi audio amplifier such as the Dyna Mark III to drive modulation coils is that at very low modulation levels, the 60 cps hum from the amplifier may be noticeable. One way to circumvent the problem is to run the amplifier at higher power and use a fixed, high-power attenuator pad across the output of the amplifier to reduce both the hum and the desired signal. In order to boost the level of the reference frequency available from our PAR HR-8 to the 1.5V necessary, we are using the circuit shown below which uses one inexpensive operational amplifier (Analog Devices Model 118A).

The good news here is that we finally have a new magnet which works, a Varian 12", after three tries with a lower bidder; we hope to have some science instead of electronics for the next contribution.

Sincerely yours,

Gerald Ray Miller

C.F. Porsanski
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