Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 60

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DEADLINE FOR NEXT ISSUE
24 October 1963
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

The 1,4-diynes constitute an unusual class of compounds. However, 5-phenylpenta-1,4-diyn shows normal 60 Mc acetylenic (triplet) and propargyl (doublet) proton resonances at -130.5 c.p.s and -199.5 c.p.s. respectively from TMS in the pure liquid. The compound is interesting in that it serves as an example of long-range spin-spin coupling observed in acetylenic hydrocarbons, for example by Professor Roberts and coworkers (J. Am. Chem. Soc., 84, 1582, 2004 (1962); Angew. Chem. internat. Edit., 2, 53 (1963)). We observe (using the notation of papers cited) \[|J_{13}| = 2.9 \pm 0.2\text{ c.p.s.}\] This value is quite large considering that coupling takes place through four chemical bonds, but is typical for acetylenes of this type.

Sincerely,

[Signature]
Sheldon H. Marcus
Hiroshi Taniguchi

SM: mc
Dr. B.L. Shapiro  
Kellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania  

Dear Dr. Shapiro:  

In high-resolution nmr-spectroscopy the question has arisen whether the correspondence between the parameters of the hamiltonian:

\[ H = \sum_{i} A_i I_{iz} + \sum_{i,k} J_{ik} I_i I_k = Z + S \]  

\( Z = \) Zeeman term, \( S = \) spin-spin coupling term  

and the experimental spectrum is a one-to-one correspondence or not. This correspondence has been examined in the case of spin-\( \frac{1}{2} \)-particles.

The determination of the hamiltonian from the experimental spectrum is composed in a natural way of two parts. One of them deals with the correspondence between the experimental spectrum and the scheme of transitions. This correspondence has been examined by applying the theory of graphs and the following statement could be proved:

Statement 1  

If one associates the absorption lines with the transitions in such a way that the intensity rules:

\[ \sum_i I_{ik}^{m-1} - \sum_j I_{kj}^m = 2m \quad m= \text{magnetic quantum number} \]  

and the cycle conditions for the absorption frequencies:

\[ \nu_{ik}^m - \nu_{ip}^m = \nu_{jp}^{m+1} - \nu_{kj}^{m+1} \]

\[ \nu_{ik}^m - \nu_{ip}^m = \nu_{jk}^m - \nu_{jp}^m \]

are satisfied, there exist in general only two possible associations differing in the common sign of all frequencies.  

Thereby \( \nu_{ik}^m \) and \( I_{ik}^m \) denote frequency and intensity of an absorption line belonging to a transition of type \( m \leftrightarrow m+1 \).
The number of independent equations is \(2^n - 1\) for those of type (2) and \({n \choose n-1} - 2^n + 1\) for those of type (3), where \(n\) means the number of protons, the system under consideration is composed of.

The second part consists in the determination of the Hamiltonian from the energy spectrum. In this connection the following statement could be proved:

**Statement 2**

The only transformations which turn a Hamiltonian of the form (1) again in a Hamiltonian of this form possessing the same energy spectrum are the permutations of the protons and the time inversion.

Without regard to the permutations, there exist therefore in general only two Hamiltonians which define the same energy spectrum. We can summarize the above statements with aid of the following graphical representation:

```
   experimental spectrum
     |
     |
   +---------------------------> - energy spectrum
     | inversion of the
     | sign of all energy terms
     |<--------------------------|
     |<--------------------------|
H_1 = Z+S  time inversion  H_2 = -Z+S  H_3 = Z-S  time inversion  H_4 = -Z-S
```

or in words:

**Theorem**

The usual method of calculating the (idealized) experimental spectrum is in general only in four ways invertable: The selective inversions of the sign of the Zeeman- and the spin-spin coupling term are the only transformations of the Hamiltonian (1) which turn it in a Hamiltonian defining the same spectrum as the operator (1).

The explicite proof of the above statements will be published in the Helvetica Physica Acta as soon as possible.

Sincerely yours

H. Kummer

H. Kummer
Dear Dr. Shapiro:

This is our second contribution to your excellent news letter. We are very sorry that you had to remind and finally punish us. A heavy teaching load is one of our excuses. Now we trust that you consider a few month without MelloNMR sufficient punishment and that you put us again on the mailing list.

The NMR-spectra of pteridines, a biologically important class of compounds have only very scarcely been investigated. We have now studied about 70 compounds in this series and wish to report some results in condensed form. 2-amino-4-hydroxypteridines, the most important because naturally occurring pteridines are difficult to dissolve. We have found that CF₃COOH and conc. H₂SO₄ are suitable solvents and in some cases CD₃SOCD₃ may be used. Chemical shifts of relevant protons in the 2-amino-4-hydroxy-, 2-amino-4,6-dihydroxy- and 2-amino-4,7-dihydroxypteridine series are summarized in table 1. In the spectra of all compounds one observes a broad and temperature dependent peak for 2 protons between 7.7 and 8.8 ppm which must be assigned to the NH₂-group at C-2 as follows from the spectra of mono- and dialkylamino-derivatives. All the other NH protons at N-1, N-3, N-5 and N-8 exchange with CF₃COOH. From the chemical shift of the NH₂-protons in CF₃COOH, H₂SO₄ and CD₃SOCD₃ it can be concluded that protonation of all these compounds takes place in position 1 of the pyrimidine ring.
7-acetonylxanthopterine (I) and the red butterfly pigment (II) erythropterine do not show NH$_2$-absorption in acid. The spectra exhibit very sharp singlet vinylproton absorption. The spectra of I and II-methylester in CD$_3$SOCD$_3$ are shown in fig. 1 and 2.

The spectra are thus in full agreement with structures Ia and IIa. The very strong intramolecular hydrogen bond in CD$_3$SOCD$_3$ solution is nicely demonstrated by the chemical shift of the lowest field NH-absorptions and by the fact that these hydrogens do not easily exchange on addition of traces of CF$_3$COOH like all the other NH-protons. Since there is no coupling of the vinyl and methyl protons in I in both CF$_3$COOH and CD$_3$SOCD$_3$ solutions a possible enol structure for the side chain can be ruled out. This also follows from other spectroscopic evidence.

Finally we would like to warn everybody not to use Varian's otherwise excellent microcells for CF$_3$COOH solutions. We found that they are more soluble than some of our pteridines and disintegrate after a few hours.

We shall very much appreciate some of the 1963 issues, if still available.

Sincerely yours,

W. von Philipsborn
<table>
<thead>
<tr>
<th></th>
<th>Vinyl -H C-6, C-7</th>
<th>Methyl- C-6, C-7</th>
<th>N(1)-CH₃</th>
<th>N(3)-CH₃</th>
<th>N(8)-CH₃ N(5)-CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8.90-9.10</td>
<td>2.88-2.90</td>
<td>8.50-8.75</td>
<td>4.15</td>
<td>3.79-3.86</td>
</tr>
<tr>
<td>II</td>
<td>8.55-8.70</td>
<td>2.78</td>
<td>7.95-8.25</td>
<td>--</td>
<td>3.73-3.87</td>
</tr>
<tr>
<td></td>
<td>9.27-9.35**</td>
<td>3.05**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>8.25-8.37</td>
<td>2.82</td>
<td>7.70-8.10</td>
<td>--</td>
<td>3.72-3.86</td>
</tr>
<tr>
<td></td>
<td>8.57-8.65**</td>
<td>3.02**</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1.**

I = derivatives of 2-amino-4-hydroxypteridine

II = -//- 2-amino-4,6-dihydroxypteridine

III = -//- 2-amino-4,7-dihydroxypteridine

*) If not otherwise specified chemical shifts are for CF₃COOH solutions (5-10%) in ppm relative to TMS as internal standard.

**) In conc. H₂SO₄ solution, TMS in CC₁₄ as standard in a separate tube.


2) W. Pfleiderer, Ber. deutsch. chem. Ges. 95, 2195 (1962).
fig. 1

fig. 2
Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Dr. Shapiro:

With the usual tardiness I should like to report on some observations concerning 

6β-substituted steroids.

As is now well known the chemical shifts of the 18- and 19-
hydrogen atoms (tertiary methyl groups) of steroids may easily
be calculated. Each substituent at a certain position of the
steroid frame makes a distinct contribution to their chemical
shifts. Summing-up these contributions, provided they are known,
one obtains the total chemical shift of the 18- and 19-hydrogen
atoms. Until now it has been successfully assumed that the con-
tributions to the chemical shift of the 19-hydrogen atoms of
substituents at rings B, C and D are independent of the con-
figuration at C-5, i.e. that for these substituents it does
not matter if rings A and B are cis or trans linked.

Prompted by a paper of Y. Kawazoe, Y. Sato, M. Natsume,
Pharm. Soc. Japan 10, 338 (1962), we have taken a second look
at this problem. These authors found for 3,17-dioxo-6β-hydroxy-
Δ4-androstene and 3,20-dioxo-6β-hydroxy-Δ4-pregnene and the
respective acetoxy steroids smaller values for the additional
chemical shifts of the 19-hydrogen atoms due to the 6β-substi-

Therefore the PMR spectra of 15 6β-hydroxy- and 6β-acetoxy-
steroids with 5α- or 5β-configuration or a double bond Δ4 have
been recorded and the additional chemical shifts due to the
6β-substituents have been determined. The result is surprising:

<table>
<thead>
<tr>
<th></th>
<th>19-H</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cps</td>
</tr>
<tr>
<td>6β-OH with 5α-steroids</td>
<td>13.5</td>
</tr>
<tr>
<td>6β-OH with 5β- or Δ4-steroids</td>
<td>11.5</td>
</tr>
<tr>
<td>6β-OAc with 5α-steroids</td>
<td>11.0</td>
</tr>
<tr>
<td>6β-OAc with 5β- or Δ4-steroids</td>
<td>5.5</td>
</tr>
</tbody>
</table>

*cps at 60 Mcps
Two possible explanations for these rather large differences are envisaged:

1. The 1,3-diaxial interaction between the C-19 methyl group and the 6β-substituent leads to different deformations of the rings according to the configuration at C-5.

2. The rotation of the hydroxy and acetoxy groups is hindered differently for the several configurations.

A repulsion between the C-19 methyl group and the 6β-substituent leads, in the case of 5α-configuration, to a conformation in which the substituent is eclipsed with the 4-CH₃ group while in the case of 5β-configuration it is eclipsed with the 5α-hydrogen atom, the latter being energetically favored. Therefore a deformation of ring B should be more easily possible for 5β-configuration. Symmetry considerations of the type discussed earlier (Helv. Chim. Acta, loc. cit. and Mellomnr Nr. 36) show the contribution of the 6β-substituent in the case of 5α-configuration to be of the "normal" magnitude, i.e. about equal to those of the 2α- and 4α-substituents. The 8β- and 11β-analogs are not exactly comparable as they experience a double 1,3-diaxial repulsion (due to the C-19 and C-18 methyl groups).

Nevertheless, we do not believe that the relatively big difference in the contributions of 6β-substituents is merely a consequence of the different ring deformations. If such deformations were so easily possible and if they could cause such large differences in the contributions of substituents, then much greater deviations between the calculated and the measured chemical shifts of the 18- and 19-hydrogen atoms would be expected than are actually found.

In a forthcoming paper (Helv. Chim. Acta, fasc. VI, 1963) on the chemical shifts of the 18- and 19-hydrogen atoms of 265 steroids and their dependence upon substituents the question of the different contributions of the 6β-substituents is discussed more comprehensively. The contributions due to identical functional groups in equivalent positions, i.e. in approximately the same steric relation to one of the tertiary methyl groups, are given and possible reasons for the variation of these contributions within sets of identical functional groups in equivalent positions are discussed.

Sincerely yours,

R. F. Zürcher
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pa.  

Re: Two New Diagonalizing Operators

Dear Barry:

We would like to describe a way of evaluating the effects of certain exponential operators and then a way of using these operators to diagonalize two specific Hamiltonians. We are curious to see if anyone else finds these techniques of interest.

The rotation operators \( \exp(i I_x \theta) \), \( \exp(i I_y \theta) \), and \( \exp(i I_z \theta) \) can be used to diagonalize some Hamiltonians encountered in NMR. For example, Anderson and Freeman have employed a similarity transformation by \( \exp(i I_x^{(x)} \theta) \) to handle a double resonance Hamiltonain. More generally, the

\[
\mathcal{H}_Z = A I_x + B I_y + C I_z
\]  

(1)
Hamiltonian is made diagonal on the $I_z$ basis set via a transformation by $\exp(i I_\phi) \times \exp(i I_\theta)$ when $\theta = \tan^{-1}(\frac{B_\phi}{B_\theta})$ and $\phi = \tan^{-1}(\sqrt{B_\phi^2 + B_\theta^2})$. Unfortunately, this trick won't work for more complicated Hamiltonians such as those for a quadrupolar nucleus exposed to a non-zero electric field gradient or for an AB system.

For two special cases, however, the Hamiltonian can be diagonalized by using a more general form of these rotation operators: $\exp(i \sigma \theta)$, where $\sigma$ is any Hermitian operator. Unless $\sigma$ is Hermitian, the inverse of $\exp(\pm i \sigma \theta)$ will not be $\exp(-i \sigma \theta)$. To find the effect of a transformation by $\exp(i \sigma \theta)$, successive derivatives of the transformed operand are taken — just as is done to calculate the effect of the rotation operators. These derivatives in turn involve commutators of $\sigma$ with various angular momentum operators. The important point to note is this: for a given spin basis set, only a limited number of possible operators exist that can arise for a given commutator. For example, consider $[I_+ J_z, I_+ J_-] = I_+ [J_z, J_-] = I_+ [J_-, J_-]$. Now, on the $\frac{1}{2} - \frac{1}{2}$ basis set, $I_+^2$ is a null matrix, so that this particular commutator on this particular basis set equals zero instead of $2 I_+^2 J_z$

The way to take advantage of such simplifications for a single-spin basis set is to express all operators as combinations of "irreducible tensor components" $T^\gamma_{\ell}$ where $\ell$ is the rank of the tensor and $\gamma$ denotes the component ($\gamma = -\ell, -\ell + 1, \ldots +\ell$). On a spin-one basis set, $T^\gamma_{\ell} = \frac{1}{2} I_+^\ell$, $T^\gamma_{-\ell} = \frac{1}{2} I_-^\ell$, and $T^0_{\ell} = \frac{1}{\ell + 1} \{3 I_+^\ell - 2 I_-^\ell\}$. These tensors are used because their commutators are readily calculable from a formula.

given by Judd in terms of 3-j and


6-j symbols:

\[
\left[ \mathbf{T}_{l}^{A_{1}}, \mathbf{T}_{l}^{A_{2}} \right] = \sum_{A_{3}, \mathbf{p}_{3}} (-1)^{A_{1} \mathbf{p}_{3}} (-1)^{A_{2} \mathbf{p}_{3}} \sqrt{2A_{1}+1} \sqrt{2A_{2}+1} \sqrt{2A_{3}+1}
\]

\[
\times \left( \mathbf{q}_{1} \mathbf{q}_{2} \mathbf{q}_{3} \right) \left\{ \begin{array}{ccc}
A_{1} & A_{2} & A_{3} \\
I & I & I
\end{array} \right\} \mathbf{T}_{l}^{A_{3}}
\]

where the underlined expression is the 3-j symbol and the expression in curly brackets is the 6-j symbol. Note that the commutator depends on I, the spin angular momentum. These 3-j and 6-j symbols automatically take care of the fact that only a limited number of operators need to be considered for a given basis set. An example of the restrictions imposed by formula (2) is the fact that the 6-j symbol is always zero for \( A \geq 2I_l \), so tensors of rank higher than \( 2I \) need not be considered. The transformations in Table IA were calculated by taking derivatives of the transformed operands and then by simplifying with the commutation formula. From these results it can be seen that the quadrupole Hamiltonian

\[
\mathcal{H}_{Q} = A I_{x}^{2} + B (I_{x}^{2} - I_{y}^{2}) + C
\]

or in tensor notation

\[
\mathcal{H}_{Q} = \alpha T_{0}^{2} + \beta (T_{x}^{2} + T_{y}^{2})
\]

is diagonalized on the spin-one basis set by transformation with the operator \( \exp(i\mathbf{T}_{1}^{2} - \mathbf{T}_{3}^{2}) \), which is independent of \( A \) and \( B \) and \( C \) or \( \alpha \) and \( \beta \). To handle the more complicated case of an AB system, which involves two spins, the would-be diagonalizer must resort to double tensors \( \mathbf{W}_{A B}^{A B} \), where the \( \mathbf{W} \)'s are just shorthand notation for terms like \( I_{x}^{2} J_{x}^{2}, I_{+} J_{-}^{2} \), etc. Table II
### TABLE IA

<table>
<thead>
<tr>
<th>( \sigma )</th>
<th>operand ( \mathcal{M} )</th>
<th>transformed operand</th>
<th>basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{T_2^2 - T_2^2}{m i} )</td>
<td>( T_0^2 )</td>
<td>( T_0^2 )</td>
<td>( I )</td>
</tr>
<tr>
<td>( \frac{T_2^2 - T_2^2}{m i} )</td>
<td>( T_2^2 + T_2^2 )</td>
<td>( (T_2^2 + T_2^2) \cos \left( \frac{2 \theta}{m} \right) ) ( + \frac{1}{m} T_0^2 \sin \left( \frac{2 \theta}{m} \right) )</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE IB

<table>
<thead>
<tr>
<th>( \sigma )</th>
<th>operand ( \mathcal{M} )</th>
<th>transformed operand</th>
<th>basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{W_{i-1}'' - W_{i-1}'''}{i} )</td>
<td>( W_{00}^{11} )</td>
<td>( W_{00}^{11} )</td>
<td>( \frac{1}{R} - \frac{1}{2} )</td>
</tr>
<tr>
<td>( \frac{W_{i-1}'' - W_{i-1}'''}{i} )</td>
<td>( W_{i-1}'' + W_{i-1}'' )</td>
<td>( \left( W_{i-1}'' + W_{i-1}'' \right) \cos 2 \theta ) ( + \left( W_{00}^{11} - W_{00}^{10} \right) \sin 2 \theta )</td>
<td></td>
</tr>
<tr>
<td>( \frac{W_{i-1}'' - W_{i-1}'''}{i} )</td>
<td>( W_{00}^{10} )</td>
<td>( - \frac{1}{R} \left( W_{i-1}'' + W_{i-1}'' \right) \sin 2 \theta ) ( + \frac{1}{2} \left( W_{00}^{10} - W_{00}^{11} \right) \cos 2 \theta ) ( - \frac{1}{2} \left( W_{00}^{10} - W_{00}^{11} \right) + W_{00}^{10} )</td>
<td></td>
</tr>
<tr>
<td>( \frac{W_{i-1}'' - W_{i-1}'''}{i} )</td>
<td>( W_{00}^{11} )</td>
<td>( \frac{1}{R} \left( W_{i-1}'' + W_{i-1}'' \right) \sin 2 \theta ) ( - \frac{1}{2} \left( W_{00}^{10} - W_{00}^{11} \right) \cos 2 \theta ) ( - \frac{1}{2} \left( W_{00}^{10} - W_{00}^{11} \right) + W_{00}^{11} )</td>
<td></td>
</tr>
</tbody>
</table>

When the operand \( \mathcal{M} \) in the second column is operated on the left by \( \exp(i \sigma \theta) \) and simultaneously on the right by \( \exp(-i \sigma \theta) \), the result is the transformed operand given in the third column. \( \mathcal{M} \) is any real constant, not zero.
TABLE II

Translation of double tensors $\mathcal{W}_{A,B}^{A,B}$ on the $\frac{1}{2} - \frac{1}{2}$ basis set into equivalent expressions as the products of angular momentum operators.

<table>
<thead>
<tr>
<th>A</th>
<th>a</th>
<th>B</th>
<th>b</th>
<th>operator representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>+ $I_+ J_+$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>- $\sqrt{2} I_+ J_z$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>- $I_+ J_-$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>- $\sqrt{2} I_z J_+$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>+ $2 I_x J_z$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>+ $\sqrt{2} I_x J_+$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>- $I_1 J_1$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>- $\sqrt{2} I_1 J_z$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>+ $I_1 J_1$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>- $\sqrt{2} I_z J_1$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>+ $I_1 J_1$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>- $\sqrt{2} I_z J_1$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>- $\frac{1}{2} I^+ I_1$</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>+ $\frac{1}{2} I^+ I_1$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>+ $\frac{1}{2} I^+ I_1$</td>
</tr>
</tbody>
</table>
translates these \( \mathcal{W} \)'s on the \( \frac{1}{2} - \frac{3}{2} \) basis set into regular operator language. From a commutation formula similar to (2)^4, the transformations listed in Table IB were calculated. By use of these tabulated relations, it can be seen that the Hamiltonian \( \mathcal{H}_{AB} \) for an AB system

\[
\mathcal{H}_{AB} = A\mathcal{W}_{00} + B\mathcal{W}_{00} + \frac{1}{2} \mathcal{W}_{00} - \frac{1}{2} (\mathcal{W}_{01} + \mathcal{W}_{10})
\]

(4)

on the \( \frac{1}{2} - \frac{3}{2} \) basis set is diagonalized by the operator \( \exp(i\mathcal{W}_{11} X) \) when \( \theta = \tan^{-1}(\frac{\theta}{\mathcal{A}}) \).

Right now these generalized rotation operators don't appear very practical. Perhaps they could be used to make more convenient some first order perturbation calculations: perform the transformation on the perturbing operator and take diagonal matrix elements on the \( I_z \) or \( I_z J_z \) basis set. Anyhow, we think they're interesting.

Yours very truly,
Richard H. Albert
John D. Baldeschwieler

\( /ms \)
Dr. B. L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pennsylvania.
U.S.A.

Dear Barry,

In collaboration with Dr. D. W. A. Sharp and Mr. J. Winfield we have recently run $^{19}$F spectra of several highly substituted chlorofluorobenzenes (e.g. $C_4ClF_5$, $C_5Cl_2F_4$ isomers, $C_6Cl_3F_3$ isomers). The chemical shifts and coupling constants are broadly in agreement with other peoples figures and can be summarised:

Chemical shifts in $R_o$

\[
\begin{array}{ccccccc}
   & F,F & F,F & F,Cl & F,Cl & Cl,Cl & Cl,Cl \\
R_0 & & & & & & \\
\end{array}
\]

\[
\begin{array}{ccccccc}
   & F & Cl & F & Cl & F & Cl \\
R_p & & & & & & \\
\end{array}
\]

\[
\begin{array}{ccccccc}
   & 161.5 & 155.5 & 138.2 & 133.2 & 116.4 & 112.6 \\
\phi & & & & & & \\
\end{array}
\]

No. of examples

\[
\begin{array}{ccccccc}
   & 3 & 4 & 4 & 5 & 4 & 2 \\
\end{array}
\]

Range of values (p.p.m.)

\[
\begin{array}{ccccccc}
   & 1.7 & 1.5 & 5.0 & 5.6 & 4.1 & 0.1 \\
\end{array}
\]

Notes

\[\phi \equiv \text{p.p.m from } CCl_3F \text{ as internal standard.}\]

Spectra were run on 30% solution in $CCl_4$ on a Perkin Elmer instrument at 37.65 Mc/s.

The predominant effect of ortho and para substituents is noticed. The nature of meta substituents had very little effect.
The effects of OH and H as substituents in the ortho and para positions resembled those of F and Cl respectively (to within 1 p.p.m.).

\[ \text{F}^{19} - \text{F}^{19} \text{ Coupling constants} \]

<table>
<thead>
<tr>
<th></th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>20.4</td>
<td>2.3</td>
<td>8.4</td>
</tr>
<tr>
<td>No. of Examples</td>
<td>11</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>Range of values</td>
<td>2.0</td>
<td>4.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Two compounds which had second order spectra were C\(_6\)Cl\(_6\)F\(_5\) and \(\sigma\)-C\(_6\)Cl\(_2\)F\(_4\). From these spectra we got the results:

\[
\begin{align*}
J_{12} &= \pm 20.5; \quad J_{13} = \mp 2.5; \\
J_{13} &= \mp 19.1; \quad J_{14} = 7.4 \text{ c.p.s} \\
|J_{13}| &= 19.1; \quad |J_{14}| = 7.4 \text{ c.p.s} \\
|J_{23}| &= 19.6; \quad |J_{15}| = 5.3 \\
J_{23} &= \mp 6.4; \quad |J_{24}| = 2.0 \text{ c.p.s.}
\end{align*}
\]

The signs of \(J_{\text{para}}\) and \(J_{\text{meta}}\) are thus opposite to that of \(J_{\text{ortho}}\), confirming Evans’ findings by the double resonance approach \([\text{Mol. Phys.} 6, 179 (1963)]\). I wonder whether \(J_{\text{meta}}\) always has an opposite sign to that of \(J_{\text{ortho}}\), we had some very small \(J_{\text{meta}}\) couplings of indeterminate sign and it is possible the values lie either side of zero (any comments?).

Yours sincerely,

Peter Bladon.
Dear Barry:

I trust the following material on recent work in our laboratories will serve to extend our subscription to your very valuable Newsletter. Rather than present material at length, it has seemed appropriate to give some information concerning papers which are being submitted and we hope eventually will be published.

NUCLEAR MAGNETIC RESONANCE STUDIES OF ADSORPTION OF THORIUM OXIDE, Wallace S. Brey, Jr., and Kenneth D. Lawson. To be submitted to J. Phy. Chem. Preprints are available.

Abstract and Introduction: Nuclear magnetic resonance line widths and relaxation times have been measured for water, methyl alcohol, ethyl alcohol, and butylamine adsorbed on thorium oxide. The source of the thorium oxide and the conditions of its activation influence the relaxation times of the adsorbate. Temperature dependence studies of the relaxation times of adsorbed water permit an estimate of the activation energy for the motions producing relaxation of the adsorbed molecules. Similar studies of the organic molecules lead to a quite different sort of information: it is possible to see in the line width thermal transitions corresponding to the successive loss of motional freedom of various parts of the molecule. Line width behavior seems also to be related to the ratio of molecular diameter to pore size.

A number of measurements have been reported in the literature of line widths or relaxation times for various systems. However, it has not been in general possible to differentiate between the behavior of various portions of the adsorbed molecule. For hydrogen atoms, the usual range of chemical shifts is 500 to 1000 cycles at 60 megacycles, and the line widths of interest are of the order of several hundred to several thousand cycles, so that the absorption peaks of nuclei of different chemical shifts overlap one another. Furthermore, not much attention has been paid to the relationship between the history and structure of the adsorbent and the n.m.r. parameters of adsorbates on its surface.

In the present work, temperature dependence studies have led to results which can only be interpreted in terms of varying behaviors of different parts of the adsorbate molecule. Line width measurements for methanol, ethanol, and n-butylamine adsorbed on thorium oxide, carried out over the range from room temperature down to -100° C, show that restriction of motion of part of the molecule, presumably the polar group attached to the surface, occurs not far below room temperature, while a narrow absorption band continues to appear at very much lower temperature. The latter must be associated with persistence of the free motion of the alkyl portions of the molecules at the lower temperatures.
Samples of thorium oxide prepared by dehydration of the hydroxide have also been compared with those obtained by thermal decomposition of the solid oxalate. As it will be shown below, not only does this difference in origin make a considerable difference in the behavior of the adsorbate, but also conditions of activation of the material from any one source, such as the temperature, modify the n.m.r. behavior of the adsorbate.


Abstract: NMR spectral parameters of the compounds CF₂=CFY in which Y is CF₃, CF₂Cl, CF₂Br, CF₂I, or COF have been measured at room temperature and spin-spin coupling constants in four of these molecules have been investigated in the range of temperature from -100° to +100° C. Some aspects of the temperature dependence of the coupling constants can be related to changing equilibria between cis-trans or rotational isomers, but there is an intrinsic temperature dependence, aside from these effects, which is attributed to excitation of molecular vibrations. Particular J values which change magnitude in one direction with increasing temperature are found to change magnitude in the opposite direction in regular fashion as one goes through the series of halogen-substituted compounds from fluorine to iodine. Chemical shifts observed at room temperature are discussed in terms of the effects of substituents.


Abstract: The sydnone ring system is an unusual one, for it can not be represented satisfactorily by any canonical structure which does not place formal charges somewhere in the ring. The conventional formulation of a 3-substituted sydnone is:

\[
\begin{align*}
\text{CH} & \text{C}^\ominus \\
| & \ominus \\
R & \ominus \text{N} \text{N}
\end{align*}
\]

The chemical and spectroscopic properties of molecules containing the sydnone ring have been interpreted to indicate a six-electron aromatic system, delocalized over the five atoms of the ring. Proton resonance spectra of five 3-alkyl sydrones and 3-phenyl sydnone have been determined in acetone and in chloroform solution. The ring hydrogen chemical shifts in chloroform solution are strongly concentration-dependent in a manner which indicates that the chloroform solvent is breaking down aggregates of solute molecules. The resonances of the hydrogens in the substituent group which are alpha to the sydnone ring fall strikingly far downfield, indicating an unshielding by the aromatic ring current as well as by the electronegative effect of the nitrogen atom in the ring.

Cordially yours,

Wallace S. Brey, Jr.
Associate Professor of Chemistry
We have recently investigated the behavior of polycrystalline succinonitrile at temperatures below the melting point using wide line NMR. Early dielectric constant and other measurements had indicated a rotational transition in solid (CNCH\textsubscript{2})\textsubscript{2}, but at the same time they had underscored its peculiarity. The transition occurs at about 230°C, and it was thought to be probably a combination of intermolecular and intramolecular rotations. Below this temperature the solid exists entirely in the C\textsubscript{2} (gauche) rather than C\textsubscript{2h} (trans) configuration.

Spectra were recorded on a Varian DP-60 spectrometer at 15.9 Mc/s using a gas-flow type cryostat. At low temperatures the spectrum is a doublet characteristic of close-lying pairs of nuclei. The IBM 7090 at the University of Maryland Computer Center was programmed and experimental second moments calculated.

The second moment has a value of 17.7 gauss\textsuperscript{2} and remains constant up to 229\textdegree K, at which point it drops to 0.7 gauss\textsuperscript{2}. The low temperature value is in good agreement with the theoretical second moment, although it cannot be used to establish the low-temperature configuration of the molecules. The sharp drop in second moment at 229\textdegree K indicates the onset of rotation in agreement with infrared and other observations. In addition, the NMR data clearly indicate that the transition is a general isotropic reorientation involving the whole molecule and not a simple rotation or oscillation about the C-C bond. X-ray results have shown...
that the crystal lattice is too small to accommodate freely rotating succinonitrile molecules; therefore, the rotation is probably not completely free, but as it has been suggested, coupled to the rotation of neighboring molecules with two rotating molecules in a cell penetrating into their mutual rotation ranges.

There is a further reduction in second moment between 240° and 280°K. This is explained by postulating self-diffusion in the crystal lattice. This is corroborated by the close agreement between the lattice energy and the calculated energy required to form a vacancy in the lattice by removal of one molecule and the activation energy required to move an adjacent molecule into this vacancy.

This work was done at the University of Maryland, and it will appear shortly in J. Chem. Phys. in greater detail.

I have recently joined the Du Pont Company Experimental Station, and I will appreciate receiving my copies of the NMR newsletter here.

Sincerely yours,

NYLON TECHNICAL DIVISION

Leon Petrakis

LP:mb
MELLON INSTITUTE
4400 FIFTH AVENUE
PITTSBURGH 13, PA.

6 September 1963

Proton NMR Studies of CHDO and CH₂O

B. L. Shapiro, R. M. Kopchik and S. J. Ebersole

We have measured |J₇HD| in CHDO in various solvents, and from the values so obtained, have deduced the corresponding |J₉HH| in CH₂O. We have also measured the chemical shifts of CHDO and CH₂O in the various solvents and the differences between these shifts. Our results are summarized in Table I.

To the best of our knowledge, these are by far the largest |J₇HD| (gem) and |J₉HH| (gem) values which have been reported. In fact, they appear to be the largest H-D and H-H couplings known with the exception of the value obtained for the HD molecule. Analogous, even larger solvent dependences of |J₉HH| (gem)'s have also been observed in other systems.

Also noteworthy are the ∆r's observed, other reported values being < 0.017 ± 0.002 ppm per D-for-H substitution.

A fuller account and discussion of these and other aspects of the spectra will appear in due course.

*Submitted for publication in J. Chem. Phys.

1Part II of the series "NMR Spectral Studies of sp²-type CH₂ Systems", for Part I, see B. L. Shapiro, S. J. Ebersole and R. M. Kopchik, J. Mol. Spectry., In Press.
2Prepared by pyrolysis of eu-(CHDO)₁, supplied by Merck, Sharp and Dohme of Canada, Ltd.
3Using the relationship |J₉HH| = \( \gamma_H \cdot |J_{7HD}| / \gamma_D \), the value of \( \gamma_H / \gamma_D \) used is that derived from B. Smaller, E. Yasaitis and H. L. Anderson, Phys. Rev., 81, 896 (1951).
6The apparently real solvent dependence of ∆r is intriguing, but not as yet to be taken as firmly established.
### TABLE I. NMR Spectral Data† on CHDO and CH₂O

| Solvent        | $|J_{HD}|^a$ (c/s) | $|J_{HH}|^b$ (c/s) | $\tau^{c}$_{CHDO} | $\tau^{d}$_{CH₂O} | $\Delta^{d}$(ppm) |
|---------------|------------------|------------------|-------------------|-------------------|-------------------|
| Tetramethylsilane | 6.52             | 42.42            | 0.427             | 0.398             | 0.029             |
| Tetrahydrofuran   | 6.26             | 40.70            | 0.440             | 0.417             | 0.023             |
| Acetonitrile       | 6.18             | 40.22            | 0.417             | 0.391             | 0.026             |

†All data obtained on dilute (< 5%) solutions, using a carefully calibrated Varian Associates A-60 NMR spectrometer operating at 60 mc/sec. Sample temperature 37 ± 1°C.

$^a$P.E.: ± 0.02 c/s.

$^b$Calculated as described in Ref. 3; P.E.: ± 0.13 cps.


$^d$P.E.: 0.002 ppm or less.
Dear Dr. Shapiro:

We have recently investigated a group of metabolites from Actinomycetes called rifamycins. Extensive degradative and spectroscopic studies lead eventually to the unusual structure I for rifamycin S. In the n.m.r. spectrum of this compound (Figure 1) 4 doublets a-d (J ~ 7 cps) corresponding to four CH$_3$-(CH)-groups (C-31; C-32; C-33 and C-34) are easily recognizable. Noteworthy is the position of two of these doublets at $\delta$ = 0.22 and 0.67 ppm (Varian A 60, CDCl$_3$). The occurrence of the methyl proton signals at such high magnetic fields is evidently due to the long range shielding of methyl protons located above the plane of the naphthoquinone nucleus by the magnetic field of aromatic \*F-electrons. This shielding becomes much stronger when the compound is reduced to the naphthalene derivative II. The signal of the one of the methyl groups in the n.m.r. spectrum of II lies at $\delta$ = -0.59 ppm and can be easily overlooked in routine work. Similar results have been obtained in the course of our work with many other derivatives of rifamycins.

The unusual position of the methyl protons at high magnetic fields helped considerably to recognize at a very early stage of our work that the aromatic system in rifamycins must be bridged by a long aliphatic chain, as in cyclophanes [cf. J.S. Waugh and R.W. Fessenden, JACS 79, 846 (1957)] and other so called ansa-compounds.
When the aliphatic bridge in rifamycins is open on one side, as in degradation product III, the signals of all four CH₃-(CH)-groups (Figure 3) almost coincide and have the normal 6-value around 1.

We think that these results may be of interest not only to natural product chemists who use n.m.r. as a tool for structure elucidation, but that they also deserve further study with simpler model compounds.

With apologies for delay in "paying" our subscription and with best personal regards,

Sincerely yours,

W. v. Oppolzer and V. Prelog
High-resolution NMR-Spectra of Orientated Molecules

Since about three years we have been interested in the proton magnetic resonance (PMR) spectra of liquid crystals, especially of the so-called nematic type. We have obtained some interesting results which we should like to discuss here briefly.

In the nematic phase the long-shaped molecules are aligned essentially parallel to each other. This direction is the optical axis of the anisotropic melt, turning parallel to the external magnetic field in NMR experiments. Despite their ordering, the molecules are highly mobile (no regular arrangement of the centers of the molecules, low viscosity), and therefore the intermolecular direct dipole-dipole interaction is reduced practically to zero as in isotropic liquids. On the other hand, the reduction of the intramolecular dipole-dipole interaction is less complete because of the molecular orientation. The re-orientation of the molecules, however, is at least in some cases very rapid as can be shown from dielectric measurements with p-azoxyanisole (PAA; R-C₆H₄-N=N-C₆H₄-O-R=CH₃; mp 117°C, clearing point 136°C). We expected therefore that the PMR-spectrum of this compound in the nematic phase should consist of a large number of sharp lines.

The spectrum of PAA has been extensively studied by several authors and has been described as a broad diffuse triplet. In contrast to these earlier observations we have found a very detailed fine structure of the signal of the nematic phase in agreement with our expectation (fig. 1). With improved resolution even more details are to be expected.

If the methyl groups are replaced by larger groups (R = CₙH₂n+1, n = 2 to 7) the spectra become more and more quasi-continuous due to the strongly increasing number of lines.

A very sharp line superimposed on a much broader signal has been observed in the spectra of nematic p-butoxybenzolic acid (C₄H₉OC₆H₄CO₂H) and similar compounds. The sharp line is assigned to the acidic protons rapidly exchanging between different molecules.

Upon heating above the clearing point (isotropic phase) all compounds gave normal high-resolution spectra with chemical
shifts and J-couplings close to those observed in solutions. We have extended our PNR investigations to solutions of organic molecules (not possessing liquid crystalline properties) in nematic phases. By this matrix method a partial orientation of the dissolved molecules can be achieved, the degree of ordering being much higher than that attainable in electric fields (Mc Leachlan and Waugh, MELLONMR 54).

Using normal high-resolution technique we have taken spectra of "isolated" n-spin systems (n=1 to 6), some examples are given in fig. 2 and 3. The spectra consist of sharp lines (some cps) with an overall splitting up to several kcps depending on the number of interacting protons, internuclear distances and the orientation and degree of ordering of the molecules. The broad signal of the nematic matrix is lost in the background.

The following applications are possible:

1) Measurement of relative internuclear distances.
2) Determination of arrangement and degree of ordering; study of the intermolecular forces.
3) Measurement of the anisotropy of the chemical shift, including isotropic contributions of neighbouring groups.
4) Determination of the absolute sign and perhaps of the anisotropic part of the indirect spin-spin-coupling.
5) Investigation of the quadrupole interactions.

Some of our results may be mentioned here:

1) Benzene dissolved in the nematic melt of 4,4-di-n-hexyloxyazoxylbenzene (R=C6H13): Degree of ordering (depending on concentration and temperature) S=\(3 \cos^2 \theta - 1\) / 2 = -0.099

(\(\theta = \angle C_6\)-axis and optical axis)

Chemical shift: 420.7 ± 0.4 cps (nematic) below TMS

432.1 ± 0.3 cps (isotropic) "

The anisotropy of the screening constant turns out to be

\[ \Delta G = G_z - \frac{1}{2}(G_x + G_y) = -2.88 \times 10^{-6} \] 

(z-axis parallel C6)

The J-coupling is observable in the spectrum of the nematic solution in spite of the strong direct dipole-dipole interaction.

2) 1,3,5-Trichloro-benzene in the same nematic matrix:

\[ S = -0.14 ; \Delta G = -5.0 \times 10^{-6} \]

The anisotropy is considerably stronger because of the influence of the chlorine atoms.

3) We have also investigated the spectra of tetrachloro-substituted anisoles and of 2,3,5,6-tetrachloro-toluene. For the latter compound we obtained for the ratio of proton distances:

\[ \frac{r(H_4-H_{CH_3})}{r(H_{CH_3}-H_{CH_3})} = 3.225 \pm 0.025 \]

Finally we should like to point out that solutions of stable free radicals in nematic melts are very easily obtained in small concentrations sufficient for ESR-experiments. This might be of interest to those, who would like to investigate the anisotropic part of the nucleus-electron spin-spin interaction.

Sincerely yours,

Alfred Saupe

Gerhard Engler
Fig. 1. p-azoxyanisol, spectrum of the nematic phase (derivative curve).

Fig. 2. Benzene, spectrum in nematic solution.

References


Fig. 3. 1,3,5-trichloro-benzene, spectrum in nematic solution.
Dr. B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13,
Pennsylvania,
U.S.A.

Dear Dr. Shapiro,

pH-Dependence of Coupling Constants
in Aspartic Acid

In the course of an investigation of the NMR-spectra of
certain α-amino acids, we found a strong pH-dependence of the coupling
constants. A detailed study of aspartic acid showed a direct relation
between the geminal coupling constant and the degree of dissociation
of the amino group. Using the dissociation constant

\[
\frac{[\text{RNH}_2^-] \cdot [\text{H}^+]}{[\text{RNH}_3^+]} = 9.842
\]

(with \(R = (\text{CO}_2^-)\text{CH} = \text{CH} (\text{CO}_2^-)\)), we calculated the percentage of \(\text{RNH}_2^-\)
at a given pH and plotted the coupling constants against these
values (Figure 1). The relationship is almost linear. The deviation
from linearity may well be due to systematic errors in the correction
of the pH-values as the pH, as well as the \(\text{Na}^+\) concentration, were rather
high.

An interpretation of these findings may be attempted in the
light of Barfield and Grant's recent calculations of the angle dependence
of the \(\pi\)-electron enhancement of geminal coupling constants. Aspartic
acid anhydride with a planar five-ring structure has a geminal coupling
constant of 18.0 c/sec. The \(\pi\)-electron contribution should be 4.5 c/sec
giving a basic value of 13.5 c/sec. The lowest value (at high pH)
measured for aspartic acid is 15.2 c/sec with a relative increase of
1.7 c/sec which corresponds roughly with the average enhancement by a freely
rotating \(\beta-\pi\)-electron. Decreasing the pH means increasing the cationic
form of the aspartic acid (\(\text{RNH}_3^+\)) allowing for electrostatic interaction
between amino group and \(\beta\)-carboxyl group favouring a locked position of
the carboxyl group with an increased \(\pi\)-electron contribution to the geminal
coupling/...
coupling constant by maximal 3.9 c/sec compared with the basic value.

As nice as this sounds, serine and cystine with no \( \pi-\pi \)-electrons in respect to the methylene group also show an increase of the geminal coupling constant with decreasing pH which cannot be explained on the same basis.

Yours sincerely,

\[ \text{Signature} \]

K. Pachler  
RESEARCH OFFICER  
CHEMICAL PHYSICS GROUP  
NATIONAL CHEMICAL RESEARCH LABORATORY

c.c. Dr. Herbstein  
Dr. Abraham  
KP/CV

REFERENCES

FIGURE 1

\[ \text{Graph showing the relationship between } \% \text{RNH}_2 \text{ and } J_{\text{gem}}. \]
Dr. Bernard L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pa.

Dear Dr. Shapiro:

We would like to add some further observations to our previous letter in MELLOMFR No. 57.

(1) The apparent singlets of the dimethylthiepin If in carbon tetrachloride and of the diketone IIIe in deuteriochloroform are not resolved \(^1\) even at 100 Mc.! Other solvents which give apparent singlets (peak width at half-height: 1.5-2.1 c.p.s., 60 Mc.) for those two compounds: carbon disulfide, pyridine, nitrobenzene. The unique position of benzene is heavily underscored by these additional findings. In the same vein, the separation of diastereomeric oxepin (b-series) and aepine (c-series) proton resonances \(\Delta \tau\) (leaving aside cases of magnetic equivalence due to conformational interconversion) increases with dielectric constant except for benzene solutions in which \(\Delta \tau\) is abnormally small. Conversely, in the thlepins (f-series) \(\Delta \tau\) appears to decrease with increasing dielectric constant except again for the benzene solutions which exhibit the largest values of \(\Delta \tau\) (for If, the only measurable values!). This behavior can no doubt be related to the large diamagnetic anisotropy of benzene molecules in suitable orientations \(^2\), but the complete ineffectiveness of the other solvents in revealing the AB pattern of If and IIIe is really rather startling. Our studies are continuing and we shall report to MELLOMFR again.

(2) Concerning the average position of the diastereomeric methylene protons \(\bar{\tau}\) \(= (\tau^A + \tau^B)/2\), we note that (a) \(\bar{\tau}\) has its lowest value in pyridine solutions, (b) \(\bar{\tau}\) of the b- and c-series has its highest values in carbon disulfide solutions, whereas \(\bar{\tau}\) of the e- and f-series has its
highest values in benzene solutions. Furthermore, $\tilde{r}$ of the I-series is invariably higher than $\tilde{r}$ of the II- and III-series (for a given $X$ and a given solvent) and, with a few exceptions, $\tilde{r}$ of the II-series is similarly higher than $\tilde{r}$ of the III series. We interpret these results in terms of shielding by the distal benzene ring and conclude that, for a given $X$, the biphenyl angle of torsion $\theta$ decreases in the order $I : II > III$. We have completely independent evidence of the same order in the u.v. spectra, which, for a given $X$, show a progressive red shift of the conjugation band, in the order $\lambda_{\text{max}}^\text{III} < \lambda_{\text{max}}^\text{II} < \lambda_{\text{max}}^\text{I}$. This change in angle within each "horizontal series" (i.e. the three oxepins) is of course not revealed by the Dreiding models, which only respond to gross changes in angle strain and bond stretching, but which are insensitive to torsional and nonbonded strain.

3. The $J_{AB}$ values are characteristic for each horizontal series, as shown in the Table. For any one compound in each series, $J_{AB}$ is solvent-independent. This result is in sharp contrast with the findings of Snyder$^4$ who has claimed a solvent dependence of diastereomeric methylene proton coupling constants in non-rigid systems. Within each series, compounds III have $J_{AB}$ values which are larger than those of the corresponding compounds I by 0.3-0.4 c.p.s. These results may be rationalized as follows: the characteristic range of values reflects the nature of the substituent attached to the methylene carbon (e.g. oxygen or sulfur) while the small variation within each range reflects the change in $\theta$, which may in turn affect the magnitude of the HCH angle$^3$.

4. In the series of dimethylbiphenyls I, the C-methyl proton signal is a sensitive function of $\theta$. In the Figure are plotted (circles) the methyl proton $\tau$-values against the values of $\theta$ calculated from normal molecular dimensions. For $\theta = 90^\circ$ the $\tau$-value of $2,2',6,6'$-tetramethylbiphenyl ($\tau 8.12$) was selected. A theoretical estimate of the change in shielding values with geometry$^5$ (curve, Figure) fits the semi-experimental points rather well, and the $\tau$-value of 7.75 found for 9,10-dihydro-4,5-dimethylphenanthrene, which is a good deal above the calculated value of 7.48, suggests out-of-plane bending and extra shielding of the methyl groups.
Nevertheless it must be pointed out that the general usefulness of the function plotted in the Figure is severely limited, as revealed by the fact that 4-methylbiphenyl, 2-methylbiphenyl and 2,2'-dimethylbiphenyl, with estimated (from u.v.) \( \theta \)-values of 55\(^\circ\), 58\(^\circ\) and 70\(^\circ\), have \( \tau \)-values of 7.62, 7.72 and 7.92, respectively. This is not really surprising in view of the crudeness of our theoretical treatment.

(5) Kurland has reported in MELLONMR No. 59 that \( E_{\text{act}} \)-values for the racemization of oxepin IIb and thiopin III\(^\circ\) are 9.6 \pm 0.6 and 16.2 \pm 0.3 \text{ kcal./mole}, respectively, and that these n.m.r.-derived activation energies agree rather well with those estimated by halving our calculated \( E_{\text{act}} \)-values for III (11 and 18.5 \text{ kcal./mole}, respectively). Actually the agreement is even better than that, since for IIb and III\(^\circ\) proper we had calculated 9 and 17 \text{ kcal./mole}, respectively! However, we are the first to admit that this agreement is probably largely fortuitous: so many assumptions had to be plugged into our computations that we must be dealing with much cancellation of errors. - We thank Dr. Kurland for stimulating discussions.

Sincerely yours,

Kurt Mislow

[Signature]

KM:GD

P.S. I am aghast at finding a letter to MELLONMR referred to in the open literature\(^6\), and I believe that a clarification would be in order.

Kurt Mislow

Clarification (?):

Aksel Bothner-By and I are also both aghast at finding a reference to MELLONMR in the open literature. Despite our repeated requests, warnings, statements, etc. about this, every once in a while a felony of this kind occurs - and not always by individuals outside of or on the periphery of the MELLONMR family. In each case which we come across (including that to which you refer), we write a pointed letter to the individual concerned giving him The Word. So far, we have at least had no repeat offenders and there have been less than a half dozen instances all together in nearly five years, so we have been fairly successful in this. MELLONMR participants can help this situation by not only observing the rules themselves, but also by trying to make sure that all those who come in contact with their particular copy of MELLONMR are aware of those rules.

Barry Shapiro
The measurements were kindly performed by Dr. N. S. Bhacca, Varian Associates, Palo Alto, Calif.

A. A. Bothner-By and R. E. Glick, J. Chem. Phys., 26, 1651 (1957) and subsequent papers by W. H. Schneider and others.


E. I. Snyder, J. Am. Chem. Soc., 85, 2624 (1963). We are grateful to Dr. Snyder for informing us of his results prior to publication.

J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc., 79, 846 (1957); C. E. Johnson, Jr., and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958). In the present computations an "average proton" was taken at the midpoint of the triangle defined by the three methyl protons.

Methyl Proton Chemical Shifts, p.p.m. (γ-scale)

Dihedral Angle ϕ
Dr. Bernard L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh 13, Pennsylvania  

Dear Dr. Shapiro:

In connection with a comparison that we are making between oxazole and thiazole and between oxazolium ions and thiazolium ions because of the importance of the thiazole system in biological catalysis, we have noted some interesting H-H and C\textsuperscript{13}-H coupling constants which are tabulated below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>J\textsubscript{ab}</th>
<th>J\textsubscript{bc}</th>
<th>J\textsubscript{ac}</th>
<th>J\textsubscript{c-H\textsubscript{a}}</th>
<th>J\textsubscript{c-H\textsubscript{b}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>neat</td>
<td>1.86</td>
<td>1.00</td>
<td>0.28</td>
<td>209</td>
<td>187</td>
</tr>
<tr>
<td>B</td>
<td>neat</td>
<td>1.01</td>
<td>1.28</td>
<td>0.45</td>
<td>231</td>
<td>209</td>
</tr>
<tr>
<td>C</td>
<td>CF\textsubscript{3}CO\textsubscript{2}H</td>
<td>2.39</td>
<td>0.69</td>
<td>218</td>
<td>247</td>
<td>224</td>
</tr>
<tr>
<td>D</td>
<td>CF\textsubscript{3}CO\textsubscript{2}H</td>
<td>1.15</td>
<td>0.45</td>
<td>231</td>
<td>209</td>
<td>200</td>
</tr>
</tbody>
</table>

Note that although J\textsubscript{ab} is larger in the thiazole, J\textsubscript{ac} is larger in the oxazole. This long range coupling constant was resolved for both A and B and although our values may be slightly inaccurate, there's no question but that J\textsubscript{ac} is larger in B. The large C\textsuperscript{13}-H coupling constants, especially for the 2-hydrogens, are of considerable interest because of the unusual acidity of thiazolium ions. The results suggest that oxazolium ions should be even more acidic than thiazolium ions and our preliminary results.
on rates of exchange of the 2-hydrogen indicate that this is correct.

Although thiazolium ions, C, have customarily been written with the positive charge on nitrogen, our M. O. results (using a variety of models for the participation of sulfur in the pi system of thiazole) and those of Pullman indicate that the majority of the charge in the ring is on sulfur and structure C is a more appropriate single representation of the structure. Qualitative reasoning based on electronegativities suggests the same conclusion.

Walter B. Miller
Paul Haake

References:

Dr B.L. Shapiro,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh 13, Penn.
U.S.A.

Dear Dr Shapiro,

Spectra of Platinum-alkyls

During our study of the N.M.R. spectra of square-planar platinum-alkyls, we have noticed that the Pt-H coupling constants depend on the group present in the trans-position. For example, in the compound

\[
\text{Pt} - X (I)
\]

This coupling constant increases from 48 to 71 when changing X from Br to CN. When CN is substituted for Br in I the signal moves upfield from 9.03 to 9.49 ppm. Initial indications are that the coupling constant increases as the "trans-effect" of the trans-substituent increases; in addition the position of the resonance moves upfield. Relevant results, obtained using a Varian A60 instrument, are summarised in the following table:
FROM: D.T. Thompson.
TO: Dr. B.L. Shapiro.

DATE: 12.9.63

<table>
<thead>
<tr>
<th>Compound</th>
<th>Central triplet of methyl resonance (r)</th>
<th>$J_{PH}$ (c/sec.)</th>
<th>$J_{PtH}$ (c/sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEts$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me - Pt - Br</td>
<td>9.03</td>
<td>6.5</td>
<td>48</td>
</tr>
<tr>
<td>PEts$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me - Pt - PEts$_3$</td>
<td>9.00</td>
<td>6.5</td>
<td>48</td>
</tr>
<tr>
<td>PEts$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me - Pt - PEts$_3$</td>
<td>9.11</td>
<td>7.0</td>
<td>62</td>
</tr>
<tr>
<td>CH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEts$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me - Pt - CN</td>
<td>9.19</td>
<td>6.5</td>
<td>71</td>
</tr>
<tr>
<td>PEts$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Yours sincerely,

(D.T. Thompson)

---

1See, e.g., (i) Chatt, Duncanson, and Venanzi, J., 1955, 44, 56.
   1927, 5, 118.
Dr. B. L. Shapiro,
Mellon Institute,
4400, Fifth Avenue,
Pittsburgh, 13,
Pennsylvania, U.S.A.

Dear Barry,

$^1H$ spectra of stannylamines.

We have been investigating the 60 Mc/s $^1H$ spectra of compounds containing a Sn-N bond. The results of our spectral analysis are given in Table 1. With one exception (as indicated in the Table), the materials were studied as neat liquids. Some of these were rather impure, but there was no difficulty in recognising the impurity bands. Below are some of the significant features in the results.

A. Chemical Shifts

1. In group I, the Sn-CH$_3$ shielding order is NMe$_2$ > N(H)Ø > Nø$_2$. This is sensibly interpreted in terms of (a) the order of positive inductive effect (electron donation: Me$_2$ > Ø, H > Ø, and (b) the possibility of delocalisation of nitrogen lone-pair electrons into the aromatic $\pi$-system. Either mechanism which facilitates electron transfer to the nitrogen substituents would (i) assist the inductive transfer Sn -> N, and (ii) diminish any possibility of a migration of the nitrogen lone pair into an Np$\pi$ - Sn$d\pi$ orbital.

2. A comparison of the average shieldings for phenyl attached to nitrogen and to tin (groups I and II) shows a higher value for the former. This is probably associated with the possibility of nitrogen lone-pair delocalisation and the absence of an analogous situation with Sn - Ø.

contd/
B. Coupling Constants

1. $J_{CH}$ is slightly greater in a methyl group bonded to nitrogen than in one bonded to tin. This is compatible with (a) greater electron attraction from CH$_3$ by the more electronegative nitrogen (especially if this atom may reduce its $\pi$-electron density by donation to N-Sn) causing an increased s character in the carbon hybrids used for C-H bonding, and (b) a higher steric effect with Sn causing a reduction of HCH, i.e. a decreased s character of the hybrids.

2. $^{117}\text{Sn-H}$ and $^{119}\text{Sn-H}$ coupling constants are not quite in the ratio of magnetogyric ratios ($\gamma_{117}/\gamma_{119}=0.9556$) indicating a coupling constant isotope effect.

3. Sn - H couplings, Sn - N - CH$_3$, may be compared with "corresponding" values in $^{29}\text{Si} - N - \text{CH}_3$ and $^{31}\text{P} - N - \text{CH}_3$ systems. This comparison, made for both the coupling constants as such and "nuclear-free" coupling constants (to use Norman Sheppard's nomenclature - MELLONMR No. 25, P11) is given in Table 2. Whichever form we adopt, an increase with increasing atomic number of the hetero-atom is indicated.

Table 2.

<table>
<thead>
<tr>
<th>X</th>
<th>J$_{X-H}$</th>
<th>J$_{X-H}$</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{29}\text{Si}$</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>$^{31}\text{P}$</td>
<td>$\sim 14$</td>
<td>$\sim 35$</td>
<td></td>
</tr>
<tr>
<td>$^{117}\text{Sn}$</td>
<td>35-44</td>
<td>98-124</td>
<td></td>
</tr>
<tr>
<td>$^{119}\text{Sn}$</td>
<td>36-46</td>
<td>97-123</td>
<td></td>
</tr>
</tbody>
</table>

* Not previously reported but probably very small since $J_{^{29}\text{Si} - \text{CH}_3} \sim 6c/s$
Table 1.

<table>
<thead>
<tr>
<th>CHEMICAL SHIFTS c</th>
<th>COUPLING CONSTANTS (c/s).</th>
</tr>
</thead>
<tbody>
<tr>
<td>(γ VALUES)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sn-H</td>
</tr>
<tr>
<td></td>
<td>Sn-CH₃</td>
</tr>
<tr>
<td></td>
<td>NCH₃-SnCH₃</td>
</tr>
<tr>
<td>MeSn</td>
<td>Me₂N</td>
</tr>
<tr>
<td>9.76</td>
<td>3.13</td>
</tr>
<tr>
<td>Me₃SnN(Ph)</td>
<td></td>
</tr>
<tr>
<td>Me₃SnNMe₂</td>
<td>9.83</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Φ₃SnNMe₂</td>
<td>7.85</td>
</tr>
<tr>
<td>Φ₂Sn(NMe₂)₂</td>
<td>7.10</td>
</tr>
<tr>
<td>ΦSn(NMe₂)₃</td>
<td>7.18</td>
</tr>
<tr>
<td>nBu₃SnNMe₂</td>
<td>7.35</td>
</tr>
<tr>
<td>nBu₂Sn(NMe₂)₂</td>
<td>7.30</td>
</tr>
<tr>
<td>nBuSn(NMe₂)₃</td>
<td>7.32</td>
</tr>
</tbody>
</table>

a. Ratio of coupling constant 117Sn/119Sn.

b. Butyl absorption; complex structure but two main regions, one with greater intensity than other; first figure gives position of most intense region, second figure gives "average position of whole absorption.

c. ± 0.03

d. In CCl₄ solution; γ-values may need "solvent correction"; solution too dilute for observation of satellites.

e. Satellites not observed.

f. Phenyl absorption complex and not yet analysed.
Dear Dr. Shapiro,

In connection with our work on nuclear relaxation in HF\textsuperscript{1} an apparatus has been constructed for spin decoupling of hydrogen and fluorine. The spin coupling constant in HF (521 c/s) required the stirring field to be large (>450 mG). For Mellonmr readers who are interested in proton-fluorine decoupling we give the following details.

Our spin decoupler is used in conjunction with the Varian HR 40 instrument. The stirring frequencies (42.5 M c/s or 37.6 M c/s) are obtained by tripling crystal-controlled oscillators. The crystals have been shunted by small capacitors (40 pF) to allow frequency variation over 20 kc/s.

The Varian nmr probe can be used in these experiments, provided some minor modifications are made. The transmitting coil in the probe is normally connected to two small capacitors. These should be removed and the coil should be directly connected to the power input plug P 100, which in its turn is plugged to a matching box. Three of these matching boxes are in use: for stirring at 42.5 M c/s and at 37.6 M c/s, respectively, and the third one for normal high-resolution work. In the last case the matching box contains the above-mentioned capacitors only. The two other matching boxes contain the following circuitry, which has resonance peaks both at the measuring (40 M c/s) and the stirring frequency (37.6 or 42.5 M c/s).

\[
\begin{array}{|c|c|c|}
\hline
& 40 \text{ and } 37.6 & 40 \text{ and } 42.5 \\
\hline
L & 2.1 \mu\text{H} & 2.0 \mu\text{H} \\
C_1 & 100 \text{ pF} & 100 \text{ pF} \\
C_2 & 12.5 \text{ pF} & 12 \text{ pF} \\
C_T & 14 \text{ pF} & 12 \text{ pF} \\
\hline
\end{array}
\]

The inductances (L) are made of 10 to 15 turns of copper wire ("Povin" 0.25 mm enamelled) on a 7-mm rod. By stretching the coil one can adjust L to the correct value. The variable capacitors \(C_T\) and \(C_2\) are of the flat ceramic type (3-15 pF).
The amplifying stages in the transmitter are conventional. The power tube is type PE 1/100. The maximum attainable stirring field has a peak amplitude of about 700 mØ.

When doing quantitative Overhauser experiments one should be certain that the characteristics of the receiver are not modified by leakage of the r.f. power of the transmitter. Although the circuits are highly selective this has proved to be impossible at high power levels unless the spectra are recorded using a nearly perfect probe balance. Base-line independence of the amount of stirring power can thus be obtained and its influence on the receiver is eliminated. This can be checked by adding to the sample an internal or external reference.

Fig. 1 displays the broadened doublet of HF; the chemical exchange is relatively slow. Stirring the fluorine makes the spectrum collapse into one single line and it is expected that an Overhauser effect will be observed. The exchange rate is too small to have any influence on the magnitude of the Overhauser effect. This is in accordance with the ratio of $3/2$ of the integrals of the spectra.

The line widths of the components of the doublet are determined by lifetime-limiting exchange reactions. This cause of line broadening is removed by double resonance as can be seen from the smaller line width in the collapsed spectrum.

Yours sincerely,

I.A.M. Hesselmann C. MacLean

Reference

T. C. MacLean and E. L. Mackor, Colloque Ampère, Eindhoven 1962 (North Holland Publishing Company, Amsterdam)
SPECTRUM OF HF WITH AND WITHOUT STIRRING
Please address any reply to
THE DIRECTOR
and quote: B.P.A.P.
Your reference:

Department of Scientific and Industrial Research
NATIONAL PHYSICAL LABORATORY
TEDDINGTON, Middlesex

Please address any reply to THE DIRECTOR and quote: B.P.A.P.
Your reference:

20th September, 1963

Dear Barry,

Molecular Orbital Theory of Nuclear Spin Coupling Constants

We believe we have made some progress in the theory of coupling constants between directly bonded atoms which may interest MELLONAR readers.

We consider reduced coupling constants $K_{AB}$ defined as $(2\pi/\hbar) \gamma_A \gamma_B J_{AB}$ where $J_{AB}$ is in $\phi$'s and $\gamma_A, \gamma_B$ are the nuclear magnetogyratic ratios. These $K$-constants (units cm$^{-3}$) are independent of the nuclear isotope and may reasonably be compared along a series of related atoms. According to McConnell's molecular orbital theory of spin coupling $^1$, the contact contribution to $K_{AB}$ is given by

$$K_{AB\text{(cont)}} = \frac{1}{2} \beta^2 (3\Delta E)^{1/2} S_A^{1/2} S_B^{1/2} \sum_{\gamma} \left( \frac{3 \Delta E_{\gamma,2s}}{\gamma} \right) C_{\gamma}^A C_{\gamma}^B$$

(1)

where $3\Delta E$ is a mean triplet state excitation energy, $P_{2s} S_{2s}$ is the molecular orbital bond order between the valence $S$ atomic orbitals $S_A^{2s}$ and $S_B^{2s}$, and $S_A^{1/2}$, $S_B^{1/2}$ are the values of these orbitals at the respective nuclei. According to eqn (1), the contact contribution is positive. However, if the theory is developed without the approximation of using a mean excitation energy (this is an important refinement), (1) has to be replaced by

$$K_{AB\text{(cont)}} = -\frac{1}{2} \beta^2 \sum_{\gamma} \left( \frac{3 \Delta E_{\gamma,2s}}{\gamma} \right) C_{\gamma}^A C_{\gamma}^B$$

(2)

where $3\Delta E_{\gamma,2s}$ is the excitation energy to the triplet state in which an electron is removed from the occupied molecular orbital $\Psi_i$ and placed in the unoccupied one $\Psi_j$. $C_{\gamma}^A$ is the LCAO coefficient of the atomic $S$-orbital $S_A$ in the molecular orbital $\Psi_i$ and the double summation covers all such triplet excited states.

If all the excitation energies $3\Delta E_{\gamma,2s}$ are equal, (2) reduces to (1) and $K_{AB\text{(cont)}}$ is positive. But if they differ widely, the sum in eqn (2) may have either sign. This modification is particularly important if either of the atoms is fluorine, for the 2s-atomic orbital is then very low in energy.

Consider hydrogen fluoride, for example. The valence $\sigma$-molecular orbitals can be constructed from the hydrogen $1s$ function ($h$), the fluorine $2p$-function ($p$) and the fluorine $2s$-function ($s$). The energy level diagram is then roughly:

$$\begin{align*}
\Psi_3 & \quad \xrightarrow{p-h+s} [s] \\
\Psi_2 & \quad \xrightarrow{p+h-s} [s] \\
\Psi_1 & \quad \xrightarrow{s+h} [h]
\end{align*}$$

HF:

contd....
Because of the low energy of $s$, to a first approximation $\psi_1$ is constructed purely from the fluorine $2s$-function, which has something of the character of an inner shell. The other two molecular orbitals $\psi_2$ and $\psi_3$ are bonding and antibonding combinations of fluorine $2p$ and hydrogen $1s$. To a higher approximation, some $h$ is mixed with $s$ to give $\psi_1$ a little bonding character and, at the same time, $\psi_2$ and $\psi_3$ acquire some $s$ to give them some antibonding character between $h$ and $s$ (although $\psi_2$ remains overall bonding between $h$ and $p$). These general characteristics of the MO's are confirmed by more detailed LCAO calculations and by Ransil's accurate SCF work. Since both $\psi_2$ and $\psi_3$ involve $h$ and $s$ with opposite signs, the contribution of the lowest triplet excitation $\psi_2 \rightarrow \psi_3$ to $K_{HF}$ (cont) is negative. Further, the energy of the excitation $\psi_1 \rightarrow \psi_3$ is much larger, so the theory predicts that this term is dominant and that $K_{HF} < 0$, other non-contact contributions being relatively small. A similar argument applies to $K_{HF}$ (where there is experimental evidence for a negative sign), the only modification being the replacement of the hydrogen $1s$ atomic orbital by a carbon tetrahedral hybrid.

We have applied equation (2) to the coupling constants between atoms directly connected by single bonds with reasonable quantitative success. Our (rather tentative) prediction of signs (for $K_{AB}$) is:

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td>B</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td>?</td>
<td>-</td>
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<tr>
<td>N</td>
<td></td>
<td></td>
<td>+</td>
<td>?</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>?</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

References
3. Tiers G.V.D. J. Amer. Chem. Soc. 84, 3972 (1962)

Yours sincerely,

D. P. Santry

Dr. B. L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
Pittsburgh 13, Pa.,
U.S.A.
September 24, 1963

Dr. B. L. Shapiro
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania

Dear Barry:

In our letter of March 22, 1963, which appeared in Mellonmr No. 54, we offered engineering data for an A-60 Cooling System. We now are submitting specifications and parts lists to Mellonmr in the hope that this information will be of use to other A-60 owners.

A unit of this type has been operational in our laboratory for several months, and we have found it to be most satisfactory.

Sincerely,

Frank E. Dickson
Executive Vice-President

P.S. Note that in the attached graph, indicating the performance of the cooler, the upper line is the "magnet out" and the center one is "magnet in". I had hoped that, in reproduction, the red circles on the "magnet in" points would drop out; but our conscientious printer made every effort to get them in.
## WC-60

### PARTS LIST

<table>
<thead>
<tr>
<th>Drawing Reference</th>
<th>Part Description</th>
<th>Manufacturing Data</th>
<th>N.M.R. Specialties Part No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Steel Frame</td>
<td>See Drawing (Frame may be bolted or welded)</td>
<td>WC-101</td>
</tr>
<tr>
<td>B</td>
<td>Water Cooler</td>
<td>Sunroc NM3B NHI or Marchase MCA33-H6</td>
<td>WC-102</td>
</tr>
<tr>
<td>C</td>
<td>Pump</td>
<td>Tuthill WF-60 or Aurora 6319612 B32-AB</td>
<td>WC-103</td>
</tr>
<tr>
<td>C</td>
<td>Motor</td>
<td>Westinghouse, Type FHT 1/3 hp, rpm. 1725</td>
<td>WC-104</td>
</tr>
<tr>
<td>D</td>
<td>Pre-cooler</td>
<td>Marchase, 4 Pass (all copper)</td>
<td>WC-105</td>
</tr>
<tr>
<td>E</td>
<td>Water Tank</td>
<td>Copper Sheet, 15-1/2&quot; x 8-1/2&quot; x 6-1/2&quot;, 16 oz. (per sq. ft.)</td>
<td>WC-106</td>
</tr>
<tr>
<td>F</td>
<td>Water Hammer</td>
<td>Copper Pipe, 1/2&quot; (length about 30&quot;)</td>
<td>WC-107</td>
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<tr>
<td>G</td>
<td>Power Cable</td>
<td>Belden 17408-S, 8'</td>
<td>WC-108</td>
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<tr>
<td>H</td>
<td>Relay Power Cable</td>
<td>Belden 17410-S, 10'</td>
<td>WC-109</td>
</tr>
<tr>
<td>I</td>
<td>Pressure Gauge</td>
<td>U.S. Gauge 98CB - 60 psi.</td>
<td>WC-110</td>
</tr>
<tr>
<td>J</td>
<td>Bypass Valve</td>
<td>Sherman #597 or equivalent</td>
<td>WC-111</td>
</tr>
<tr>
<td>K</td>
<td>Drain Valve</td>
<td>Copper or bronze</td>
<td>WC-112</td>
</tr>
<tr>
<td>L</td>
<td>Control Relay</td>
<td>Potter Brumfield PR7AY, DP3T 230 V.A.C.</td>
<td>WC-113</td>
</tr>
<tr>
<td>M</td>
<td>Fuse Block</td>
<td>Bussman, one each 3742, two each 3743</td>
<td>WC-114</td>
</tr>
<tr>
<td>M</td>
<td>Fuse</td>
<td>Fusetron, 2 each FNM 20</td>
<td>WC-115</td>
</tr>
<tr>
<td>N</td>
<td>Fan</td>
<td>8&quot;, 32° pitch, 525 cfm, 1500 rpm.</td>
<td>WC-116</td>
</tr>
<tr>
<td></td>
<td>Rubber Feet</td>
<td>Fisher Rubber Stoppers #12</td>
<td>WC-117</td>
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<tr>
<td></td>
<td>Pump Mount</td>
<td>For Tuthill WF60 Pump - Tuthill OIAIC Foot Mount</td>
<td>WC-118</td>
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<tr>
<td></td>
<td>Copper Pipe</td>
<td>Soft 3/8&quot;</td>
<td>WC-119</td>
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<td></td>
<td>Solenoid Valve</td>
<td>Hayes Mfg. 2155-2161</td>
<td>WC-120</td>
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<tr>
<td></td>
<td>Thermometer</td>
<td>Rochester 1250</td>
<td>WC-121</td>
</tr>
<tr>
<td></td>
<td>Raw Water Coil</td>
<td>Soft Copper Water Tube, 1/4&quot; 20 - 4&quot; coils</td>
<td>WC-122</td>
</tr>
</tbody>
</table>

Approximate Parts Cost: $550.00
OPERATIONAL DATA

Magnet Temp. In  30°C ± 0.5°C
Magnet Temp. Out 41°C ± 1°C
Circuit Pressure  45 PSI ± 5 PSI
Flow  18 GPM/Minute
Ambient  70°F
A) WELDED FRAME
B) COOLER
C) MOTOR-PUMP
D) PRE-COOLER
E) STORAGE TANK
F) WATER HAMMER
G) POWER CABLE
H) MAGNET CONTROL CABLE
I) PRESSURE GAUGE
J) BYPASS VALVE
K) DRAIN VALVE
L) CONTROL RELAY
M) FUSE BLOCK
N) FAN
NOTES

ALL HOLES TO BE %" DI. (1/16 DRILL)
FOR %"-32 NC BOLTS.

IF FACILITIES PERMIT, ANGLES SHOULD
BE WELDED NOT BOLTED FOR A
MORE RIGID FRAME.
WC - 60 Test
Date 8/4/63
Inst. 246
Raw Water - None
Test Mag. Vavian A - 60
Unit Complete
Pressure From 43.5 - 44.614

- Mag. "In" Temp
- Mag. "out" Temp
- Amb. Temp °C

Time

0 30 60 90 120 150 180 210 240 270 300 330 360 390 420 450 480 510 540 570 600 630 660 690 720 - Minutes
1 2 3 4 5 6 7 8 9 10 11 12 - Hours
Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pennsylvania, 15213  

Dear Barry:  

Recently we reported the synthesis and properties of cis,cis,cis-1,4,7-cyclononatriene (I). We would like to present the results of proton-proton spin decoupling experiments which provide the proof of structure and conformation.

The undecoupled and composite decoupled spectra of I taken at low temperature (ca. -40°C) are shown in Figure I. The methylene pattern at 6.05 τ (Fig. 1a) is assigned to the inner methylene protons (H_A in I). A Dreiding molecular model of I (normal bond distances and angles) clearly shows that any two nuclei of the inner methylene protons would be much closer (ca. 1.6Å) than two hydrogen van der Waal radii (2.4Å). We believe that this considerable compression of the inner proton electronic orbitals would have caused a redistribution of their electron densities in such a way as to reduce the net shielding associated with these protons. This phenomenon would account for their chemical shift at lower field. The observed chemical shift may also be due, in part, to the anisotropy of the double bonds. However, we cannot determine the contribution of this effect, while on the other hand, the magnitude of this shift is consistent with the molecular geometry and other downfield shifts which have been attributed to steric effects. The undecoupled and decoupled spectra of I taken at high temperature (ca. 80°C) are shown in Fig. 2.

These observations demonstrate that the structure and conformation of cis,cis,cis-1,4,7-cyclononatriene are that represented by I. The arguments that lead to this conclusion are as follows: a) in the low temperature spectra, the AB quartet of the decoupled methylene protons verifies that there is only one type of methylene hydrogen pair (the magnitude of J_AB, 12.4 c.p.s., is in
FIG. 1
Low Temperature N.m.r. Spectra of I

FIG. 2
High Temperature N.m.r. Spectra of I
It is also evident from the decoupled spectra that $|J_{AX}|$ is greater than $|J_{BX}|$. The previous assignment of $H_A$ and $H_B$, based on steric considerations, is supported by this result. If one assumes that the dependence of the olefin-aliphatic coupling constants is given qualitatively by a curve such as that of H. Conroy, one can say that dihedral angles for $H_A$-$C$-$C$-$H_X$ less than ca. 135° and for $H_B$-$C$-$C$-$H_X$ less than ca. 20° would be required if $|J_{AX}|$ were to be less than $|J_{BX}|$. The dihedral angles estimated from a Dreiding molecular model are ca. 165° for $H_A$-$C$-$C$-$H_X$ and ca. 45° for $H_B$-$C$-$C$-$H_X$. The actual dihedral angles in the molecule are probably less than these; however it is unlikely that they are less than 135° for $H_A$-$C$-$C$-$H_X$ and 20° for $H_B$-$C$-$C$-$H_X$.

A. A. Bothner-By et al. have presented data which allow for a determination of the vicinal olefin-aliphatic coupling constants for trans and gauche arrangements. Values of 11.6 c.p.s. for $J_{trans}$ and 3.7 c.p.s. for $J_{gauche}$ were cited. The curve, calculated for aliphatic vicinal H-H couplings, would predict 11 and 2 c.p.s. for $J_{trans}$ and $J_{gauche}$, respectively.

Yours sincerely,

K. G. Untch

   (b) K. G. Untch and R. J. Kurland, ibid., 85, 346 (1963).


Dr. B.L. Shapiro,
Mellon Institute,
4400 Fifth Avenue,
PITTSBURGH 13,
Pennsylvania,
U. S. A.

Dear Dr. Shapiro,

Following the letters by Muller and Rose in M.R.L.L.O.N.M.R. nos. 52 and 55 (concerning the association of carboxylic acids in donor solvents) Dr. Allen suggested that I measure molecular weight data on such solutions.

This was accomplished using the Mechrolab Vapour Pressure Osmometer Model 301A. Solutions of benzoic acid in various donor solvents at concentrations up to 0.2M - the maximum possible with this instrument - were studied. Benzoic acid was chosen in preference to acetic acid, since current infra-red investigations lead us to believe that acetic acid behaves somewhat anomalously in its association compared with other carboxylic acids.

Up to 0.2M in solution in acetone and in tetrahydrofuran, the benzoic acid showed no detectable association - the molecular weight of monomeric benzoic acid being obtained throughout. Thus, over this concentration range, complexing of the monomeric acid with these typically donor solvents occurs to a much greater extent than self-association of the acid.

/The
The "controversial" statement by Allen and Caldin\(^1\) quoted by Muller and Rose was only intended to refer to the range of concentrations normally used in molecular weight determinations from colligative properties - up to about 0.2M - and these osmometry results bear out the statement over this concentration range. At higher concentrations of acid, the dimerisation equilibrium competes more effectively with, and eventually predominates over, the monomer-solvation equilibrium.

The N.M.R. results quoted by Muller and Rose\(^2,3\) were at relatively high concentrations, (between 0.3M and pure acid) and over this concentration range it is highly likely that the observed concentration dependence of chemical shift is basically due to the dimerisation of the acid. At lower concentrations where the extent of dimerisation is relatively small, the chemical exchange between the acid proton and water present is an additional factor which causes strong concentration dependence of the chemical shift.

Yours sincerely,

Kenneth H. Webb

(Kenneth H. Webb.)

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