N.M.R. STUDIES OF CONFORMATIONAL EQUILIBRIA IN SUBSTITUTED ETHANES

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INTRODUCTION

Early studies of rotational isomerism employed dielectric constant measurements and vibrational spectra. Most of such results have been summarized by Mizushima. Problems studied include the energy differences and potential barriers between the various molecular configurations and the dependence of these quantities upon factors such as substituents, the solvent and the state of the sample. The basic question, which remains in large part, is the nature of the forces restricting intramolecular motions. Other means of making such studies have been provided by the advent of high resolution nuclear magnetic resonance. The present work deals with the application of N.M.R. techniques to the rotational isomerism of substituted, liquid ethanes. The factors governing the appearance of the N.M.R. spectra of these compounds include the relative energies of the three rotational isomers, the potential barriers to internal rotation about the C—C bond, and the chemical shifts and coupling constants characteristic of the magnetic nuclei in each rotamer. These quantities can be obtained most completely and directly for a compound if the potential barriers are high enough that the spectrum at lower temperatures is a superposition of spectra for the three rotamers.

In the most general case of a substituted ethane, there will be three stable rotational forms, as shown in Figure 1. Each of these forms has a mirror image, not given here, with identical thermodynamic and spectroscopic properties, except for optical rotation. The potential energy of the molecule depends, of course, upon the orientation of one end of the molecule with respect to the other, as shown in Figure 2. One would like to know not only the energy differences between the stable forms, but also the potential barriers hindering rotation of one form into another, as well as the spectrum characteristic of each form. To illustrate what N.M.R. can do, let us consider a simpler case in which two of the forms are identical, as is the case for CHX2CFX2.
The hypothetical, high resolution proton, or fluorine, magnetic resonance spectrum of such a compound is shown in Figure 3 for several widely different temperatures. The rotamers of the compound are the meso form, with the H and F atoms trans, and the \((\pm)\) pair, with the H and F atoms gauche. At temperatures low enough to freeze out averaging by internal rotation \((\text{Figures 3a and 3b})\) the proton, and also the fluorine, spectrum consists of a doublet for each rotamer\(^2\), \(^3\), \(^6\). The centres of the doublets are the chemical shifts \(v_t\) and \(v_g\) in the two types of rotamer, and the splittings are the corresponding H—F coupling constants \(J_t^{HF}\) and \(J_g^{HF}\). It is assumed that the gauche form is more stable, so absorption lines for it are stronger than those for the trans form. Here we find an important advantage of N.M.R. over vibrational spectra. The N.M.R. transition probabilities depend on nuclear properties so that to a very good approximation the relative intensities of the doublets are directly proportional to the relative populations of trans and gauche rotamers. Therefore, their energy difference, \(\Delta E = E_t - E_g\), can be obtained directly from the intensities, without the corrections and uncertainties common in studies of vibrational spectra.

At higher temperatures, the spectra show an increasing fraction of the higher energy trans form. Also, a rotational averaging sets in which first causes the two doublets to broaden and then coalesce to a single doublet with broadened components \((\text{Figures 3c—3e})\). These effects occur when the re-orientation rate, \(k \text{ sec}^{-1}\), is approximately equal to \(|v_t - v_g|\) and to \(|J_t - J_g|\) in \(\text{c/s}\). There are several methods for determining \(k\) from such spectra\(^3\). The temperature dependence of \(k\) gives an activation energy \(E_a\) which is the potential barrier between the trans and gauche rotamers. At still higher temperatures the components of the averaged doublet become sharper and the average shift \(\langle v\rangle\) and average coupling constant \(\langle J\rangle\) exhibit temperature dependences \((\text{Figures 3f—3h})\) which reflect the changing proportions of trans and gauche rotamers. This temperature dependence continues until at
high temperatures the molecules are equally distributed among the two gauche and the one trans form.

TEMPERATURE DEPENDENCE OF SPECTRA AVERAGED BY INTERNAL ROTATION

If the full range of spectra given in Figure 3 is observed, then it is relatively easy to obtain from them the energy differences of the rotamers, the potential barriers between them, and the chemical shifts and coupling constants for each rotational form. But it takes potential barriers greater than $\sim 10$ kcal to prevent the rotational averaging at ordinary temperatures, and since most ethanic barriers are less than this we have to deal mainly with averaged spectra, which are simpler and have less information content. Nonetheless, all the information is still present in the temperature dependence of the averaged spectrum and our main concern is to see how well this information can be extracted.

In ethanes with the symmetry of CHX$_2$CFX$_2$, the experimentally observed average resonance frequency or chemical shift for the $i$th nucleus is given as

$$\langle v_i \rangle = x_t v_{t}^i + x_g v_{g}^i$$

and the coupling constant between nuclei $i$ and $j$, as

$$\langle J_{ij} \rangle = x_t J_{t}^{ij} + x_g J_{g}^{ij}$$

where the $x$'s designate the mole fractions. The ratio of the $x$'s is

$$\frac{x_t}{x_g} = Q'_t \exp \left( \frac{-\Delta E}{RT} \right) : 2Q'_g$$

where $Q'_n$ is the partition function for a particular rotamer $n$, excluding the internal rotation coordinate. $Q'$ will differ for the two rotamers, but to a
good approximation we can set \( Q'_t = Q'_g \) and eliminate them from equation (3). This permits the conversion of equations (1) and (2) to the form

\[
\langle v_t \rangle = \frac{2v_g + v_t \exp (-\Delta E/RT)}{2 + \exp (-\Delta E/RT)} \quad \text{and} \quad \langle J_{ij} \rangle = \frac{2J_g + J_t \exp (-\Delta E/RT)}{2 + \exp (-\Delta E/RT)}
\]

(4)

Similar five-parameter equations apply when one of the carbons is asymmetric and there are three distinguishable rotamers.

Inspection of equation (4) shows that if the temperature dependence of \( \langle v_t \rangle \) and \( \langle J_{ij} \rangle \) results only from changes in the equilibrium proportions of rotamers, then such data determine the three parameters, \( \Delta E \) and the chemical shifts and/or coupling constants characteristic of the trans and gauche rotamers. Unfortunately, the changes in \( \langle v_t \rangle \) and \( \langle J_{ij} \rangle \) for the experimentally useful temperature ranges are modest, particularly for protons. So, it must be borne in mind that the chemical shifts and coupling constants for a particular rotamer may themselves exhibit temperature dependences. The chemical shifts seem sensitive mainly to intermolecular interactions such as solvation, association and hydrogen bonding, while the coupling constants are affected by torsional and other vibrations, although both types of effect can contribute to the temperature dependence of each spectral parameter. Also, it is important to note that the effects of torsional oscillations become increasingly important the smaller the barriers to internal rotation. Therefore, extra care must be taken in the measurements and their analysis to obtain reliable, final results; and even so, the temperature dependence may be too small to determine all of the parameters involved. Moreover, the fitting of the experimental data is time consuming because of the exponentials in the unknown \( \Delta E \), or the two \( \Delta E \)'s in the general case.

So programmes were written to make the appropriate non-linear, least-squares analyses on automatic digital computers. In general, we start with a set of experimental values \( F_k \) versus \( T_k \) and an analytical function \( F = F(x, \beta, \gamma, \ldots) \). We wish to determine values of the unknowns, \( x, \beta, \gamma, \ldots \), such that \( F \) is a "best fit" to the experimental data. In other words, we wish to minimize the auxiliary function

\[
\phi = \sum_k [F_k - F(x, \beta, \gamma, \ldots T_k)]^2
\]

(5)

with respect to \( x, \beta, \gamma, \ldots \). The programmes written start with an initial set of trial parameters \( x, \beta, \gamma \ldots \); they calculate \( F(x, \beta, \gamma \ldots T_k) \), for instance equation (4); and then \( \phi \) according to equation (5). The programmes locate a minimum in \( \phi \) by stepping each of the parameters in turn, in the direction of decreasing \( \phi \), until a complete cycle produces no further decrease. Finally, the probable errors in the best fit parameters are obtained by comparing the uncertainties in the experimental values \( F_k \) with \( \phi_{\text{min}} \).

This approach will not provide the re-orientation rates and thereby the barrier to internal rotation. Nonetheless, the information is present in the rotationally averaged spectrum. Recently, Meiboom has used rf pulse techniques to study the inversion rate of ring systems under conditions of complete motional averaging, at least insofar as steady state experiments are concerned. It appears to me that the method could be extended and used to
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determine the internal rotation rates of substituted ethanes in favourable cases. One such procedure involves the Carr-Purcell sequence of a 90° pulse, followed at a time $\tau_p/2$ by a 180° pulse, and then by a sequence of 180° pulses with a spacing of $\tau_p$. This sequence gives rise to a train of spin echoes, each midway between two of the 180° pulses. If $\tau_p$ is long compared to $T_1$, $T_2$, and the half-life $\tau_a$ of the averaging process, the envelope of the echo maxima is exponential with a decay time of $T_2$, in the absence of diffusional effects. However, if $\tau_p$ is adjusted, and made shorter until it approaches $\tau_a$, the averaging is not completed in the time $\tau_p$ and the echo envelope gives an apparent $T_2$ which is a function of $\tau_a$. This method seems capable of extending the range of N.M.R. rate measurements to $\tau$'s as short as $10^{-4}$ or $10^{-5}$ sec. But it is difficult to analyse the shape of the echo envelope and its dependence upon $\tau_p$ for the general case, because the averaging depends not only upon the rate, i.e. the internal rotation frequency, but also upon the chemical shifts and relative populations of the species involved in the averaging. However, for substituted ethanes, it seems feasible to obtain the chemical shifts and relative populations of the rotamers by the steady state N.M.R. methods described in this report. Thereby, the echo envelope shape analysis would be reduced to the simpler problem of obtaining only the half-life of the averaging process. And, of course, the temperature dependence of the latter is governed by the barriers to internal rotation.

RESULTS AND DISCUSSION

Of the substituted ethanes studied thus far by N.M.R. methods, the results for CHCl$_2$CHCl$_2$ are in many ways the most encouraging. Both $\langle J_{HH} \rangle$ and $\langle H_H \rangle$ have been observed as a function of temperature, at 60 Mc/s, as shown$^8$ in Figure 4. $\langle J_{HH} \rangle$ was obtained from the satellites produced in the proton spectrum by the $^{13}$C—H coupling in the $^{18}$C—$^{12}$C isotopic species$^{10}$. $\langle H_H \rangle$ was obtained from the position of the single line from $^{12}$C—$^{12}$C molecules with respect to that from $\sim 5$ per cent of CHC1$_3$, an internal reference used to minimize hydrogen bonding effects. The curves drawn through the experimental points are the best fit lines obtained by our computer programme. The values found for $\Delta E$ by fitting the experimental points with equation (4) are listed in Table 1, in cal/mole, along with N.M.R. results for other compounds with two equivalent gauche forms. Included in the table are values from vibrational spectra for comparison. The agreement and accuracy are encouraging. Moreover, because of the "asymmetry" in equation (4), the sign of $\Delta E$ is obtained as well as unambiguous assignments to the trans and gauche forms of the spectral parameters, which is very useful in establishing the dependence of the latter upon rotational configuration. The results for CFCl$_2$CHCl$_2$ are an example of what can be done with N.M.R. experiments in favourable instances. In this case it was possible to measure the H—F coupling with exceptionally high accuracy using the "wiggle-beat" method and the parameters obtained from the analysis of $\langle J_{HF} \rangle$ are correspondingly good.

The apparent accuracy of the parameters obtained by this method of data analysis may, however, be somewhat misleading. The difficulty lies in the fact that the function $\phi$, defined by equation 5, may have several more-or-less
broad minima depending upon the accuracy of the data and the "information content" of the observed temperature dependence. For example, if very accurate data for the temperature range in question can be fitted by a straight line, then only two parameters can be determined for the system, corresponding to the slope and intercept of the line. In this case, there will not be a unique fit of the data even by the simplest, three-parameter, forms given in equation 4. Instead, there will be a family of solutions. In less extreme situations, there may still be several local minima in \( \phi \), which do not differ much in value, but which have appreciably different values of the parameters. Thus, the accuracy of the latter depends upon the nature and distribution of the minima in \( \phi \)-space rather than upon the characteristics of a particular minimum. In fact, the \( \phi \)'s for CHCl\(_2\) CHCl\(_2\) and for CFCI\(_2\) CHCl\(_2\) do exhibit several minima, the smaller of which, however, appear to be clustered in one moderately small volume of \( \phi \)-space. Presumably, reliability criteria similar to those used in single crystal X-ray diffraction work can be employed. In any event, further investigation of the matter is needed.

![Figure 4](image_url)

**Figure 4.** The temperature dependence of \( \langle \nu_H \rangle \) and \( \langle J_{HH} \rangle \), in c/s, observed in CHCl\(_2\)-CHCl\(_2\). The best-fit lines drawn through the observed points are eq. (4) with \( v_t = 114 \pm 1.6 \) (upfield), \( v_d = 75 \pm 0.2 \) and \( \Delta \varepsilon = 1100 \) cal, and with \( J_t = 16.35 \pm 0.8 \), \( J_d = 2.01 \pm 0.08 \) and \( \Delta \varepsilon = 1085 \) cal

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_t - E_d )</th>
<th>Source</th>
<th>Compound</th>
<th>( E_t - E_d )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_2)CHCl(_2)</td>
<td>1050 ± 30</td>
<td>( \langle J_{HH} \rangle )</td>
<td>CF(_2)CICFCI(_2)</td>
<td>2760 ± 120</td>
<td>( \langle J_{HH} \rangle )</td>
</tr>
<tr>
<td></td>
<td>1100 ± 35</td>
<td>( \nu_H )</td>
<td>CF(_3)CHCl(_2)</td>
<td>2300 ± 300</td>
<td>( \nu_H )</td>
</tr>
<tr>
<td></td>
<td>1080 ± 40</td>
<td>i.r., R</td>
<td>(Gas)</td>
<td>3500 ± 150</td>
<td>i.r., R</td>
</tr>
<tr>
<td>CHCl(_2)CHCl(_2)</td>
<td>495 ± 40</td>
<td>( \langle J_{HH} \rangle )</td>
<td>CFCI(_2)CHCl(_2)</td>
<td>400 ± 4</td>
<td>( J_{HF} )*</td>
</tr>
<tr>
<td></td>
<td>350 ± 50</td>
<td>i.r.</td>
<td></td>
<td>420 ± 130</td>
<td>i.r.</td>
</tr>
</tbody>
</table>

*See ref. 11.

Table 1. \( \Delta \varepsilon \) for liquid haloethanes with two equivalent gauche forms

Compounds of lower symmetry have also been investigated\(^8\), and complete 5-parameter analyses made, or rather attempted, of the temperature dependences. One such case is CF\(_2\)BrCFBrCl, which has an asymmetric carbon and hence consists of three non-equivalent \((\pm)\) pairs, the rotamers of each pair having identical N.M.R. spectra and thermodynamic properties.
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The asymmetry of the molecule leads to a non-equivalence of the two fluorine atoms in the CF₂Br end of the molecule. Hence, the fluorine spectrum is fairly complex. Moreover, the accuracy of the measurements was relatively poor and the coupling constants and chemical shifts had to be derived indirectly from the measured line positions. Therefore, the quality of the temperature dependence measurements leaves much to be desired as is apparent in Figure 5.

Because of the non-equivalence of the fluorines in the CF₂Br group, three quantities were obtainable from the spectrum, \( \langle J_{aa}^{FF} \rangle \), \( \langle J_{bb}^{FF} \rangle \) and \( \langle \Delta v_F \rangle = |v_a - v_b| \), the subscripts corresponding to the formula CF₃FBrCFBrCl.

![Figure 5. The temperature dependence of the F-F coupling constants \( \langle J_{aa}^{FF} \rangle \) and \( \langle J_{bb}^{FF} \rangle \) observed for CF₃FBrCF₃BrCl, and of the internal chemical shift \( \langle v_a - v_b \rangle \); the parameters corresponding to the best-fit lines drawn through the data are summarized in Table 2; the assignment of particular fluorines as F_a and F_b is uncertain.](image)

The coupling constants exhibit only a small temperature dependence and about all that can be said for them is that form 2 is of highest energy and that \( |J_{gauche}^{FF}| < |J_{trans}^{FF}| \). The numerical results of the one analysis are summarized in Table 2. The temperature dependence of the chemical shift

**Table 2. Results obtained from the five-parameter analyses of the temperature dependence data observed for CF₃FBrCF₃BrCl**

<table>
<thead>
<tr>
<th>Rotamer</th>
<th>( E ) (cal)</th>
<th>( \langle J_{aa}^{FF} \rangle ) (c/s)</th>
<th>( E ) (cal)</th>
<th>( \langle J_{bb}^{FF} \rangle ) (c/s)</th>
<th>( E ) (cal)</th>
<th>( \langle \nu_a^{F} - \nu_b^{F} \rangle ) (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-38.7 ± 0.3</td>
<td>0</td>
<td>+5.3 ± 0.2</td>
<td>0</td>
<td>+178</td>
</tr>
<tr>
<td>2</td>
<td>2695 ± 425*</td>
<td>-12.0 ± 0.3</td>
<td>605 ± 20</td>
<td>-10.5 ± 1.0</td>
<td>645</td>
<td>-273</td>
</tr>
<tr>
<td>3</td>
<td>0 ± 6</td>
<td>-8.9 ± 11.2</td>
<td>230 ± 10</td>
<td>+41.6 ± 0.4</td>
<td>0</td>
<td>+75</td>
</tr>
</tbody>
</table>

* This value is particularly unreliable because \( \langle J_{aa}^{FF} \rangle \) changes by only about 0.5 c/s over a 250°C temperature range, and this small change has to be obtained by indirect methods from the spectra. In rotamer 3, the two bromines are trans, while in rotamer 2, the CF₂Br fluorines are both gauche to the fluorine in CF₂BrCl.
between $F_a$ and $F_b$ is quite large, but it does seem to be affected by intermolecular interactions. Nonetheless, its temperature dependence permits an analysis of the relative importance of population differences and of the CFBrCl group asymmetry in determining the magnetic non-equivalence of $F_a$ and $F_b$ in the CF$_2$Br group.$^{12}$

The coupling constants found for the various conformations in the other compounds, as well as those for CF$_2$BrCFBrCl, are summarized in Table 3. These values are of considerable interest in connection with the theory of the coupling, but this aspect is beyond our present concern. However, it is of importance here that conformation, rather than substituents, appears to be the dominant factor governing the values of the coupling constants. For example, the trans $H--H$ coupling is consistently nearly an order of magnitude larger than the gauche. Because of this, it has been possible to assume that $|J_t| > |J_g|$ and thereby develop approximation methods from equation (4) to obtain $\Delta E$ when the temperature dependence of $(J_{HH})$ is too small to give $J_t$ and $J_g$ as well as $\Delta E$, and such approaches may have considerable utility.$^8$

The difficulties probably inherent in many cases are illustrated by the data, in Figure 6, of Richards and Higman concerning solvent effects upon CHCl$_3$CHClCH$_3$$^{13}$. This is really a 5-parameter problem, for each solvent, but the experimental error and the moderate temperature dependence of $(J_{HH})$ are such that the data can be fitted by a 2- or 3-parameter equation. This is evident from unreasonable values and from different sets of values, each giving equally good minima to equation (5). For example, the two particular "best fit" curves given for the two solutions in Figure 6 yield quite different values of $J_t$ and $J_g$. However, the latter should not be nearly that sensitive to solvent according to all other evidence, and since equally good fits for each solution are obtained with quite different parameters, it is clear that the procedure is at fault.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_t$ (c/s)</th>
<th>$J_g$ (c/s)</th>
<th>$J_{gem}$ (c/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl$_2$CHCl$_2$</td>
<td>$+2.01 \pm 0.08$</td>
<td>$+16.08 \pm 0.8$</td>
<td></td>
</tr>
<tr>
<td>CHCl$_2$CHF$_2$</td>
<td>$+2.01 \pm 0.09$</td>
<td>$+10.25 \pm 0.4$</td>
<td></td>
</tr>
<tr>
<td>CHCl$_2$CHFCI</td>
<td>$+1.63 \pm 0.15$</td>
<td>$+16.5 \pm 0.3$</td>
<td></td>
</tr>
<tr>
<td>CFCl$_2$CHCl$_2$</td>
<td>$+1.00 \pm 0.02$</td>
<td>$+18.2 \pm 0.08$</td>
<td></td>
</tr>
<tr>
<td>CHCl$_2$CHFCI</td>
<td>$+13.2 \pm 0.4$</td>
<td>$+37.3 \pm 0.3$</td>
<td>$+49.1 \pm 0.2$</td>
</tr>
<tr>
<td>CF$_2$ClCFCl$_2$</td>
<td>$-21.17 \pm 0.13$</td>
<td>$+40.03 \pm 0.13$</td>
<td></td>
</tr>
<tr>
<td>CF$_2$BrCFBrCl</td>
<td>$+5.3 \pm 0.2$; $-8.9 \pm 11.2$</td>
<td>$+38.7 \pm 0.3$; $+41.6 \pm 0.4$</td>
<td>$+66.8 \pm 0.5$</td>
</tr>
</tbody>
</table>

* The signs given for the coupling constants are relative within each compound for each pair of nuclear species, and for each set the largest constant was arbitrarily taken to be positive.
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Still it is possible to obtain some semi-quantitative conclusions from the data by introducing appropriate assumptions and approximations. In Figure 6, the data for the pure liquid fall between the two curves given for the solutions, and in fact, all three sets of data fall on virtually identical curves, which differ mainly by displacement along the temperature coordinate. This displacement must result largely from the effect of the solvent upon the relative energies of the rotamers and the change in $\Delta E$, due to the solvent, can be estimated. The appropriate 5-parameter expression for $\langle J_{HH} \rangle$ in CHCl$_2$CHClCH$_3$ is the following

$$
\langle J \rangle = J_g + J_t \exp(-\Delta E_1/RT) + J_t \exp(-\Delta E_2/RT) \\
1 + \exp(-\Delta E_1/RT) + \exp(-\Delta E_2/RT)
$$

(6)

From the results in Table 3, we know that $|J_t| >> |J_g|$ and $J_g \approx J'_g$. Also, since $\langle J \rangle \approx J_g$, we know that one or both of the forms with the protons gauche is quite stable compared to the trans form; that is, $\Delta E_2 >> RT$. Let us assume that $\Delta E_1 >> RT$ (the same final results are obtained if we assume $\Delta E_1 \approx 0$). Then, we have

$$
\langle J \rangle \approx J_g + J_t \exp(-\Delta E/RT)
$$

(7)

where $\Delta E$ is defined as the energy of the trans form less that of the gauche form of lowest energy. Let this value of $\Delta E$ be that for the pure liquid.

Then, in solution, the solvent effects change equation (7) to

$$
\langle J + \delta J \rangle \approx J_g + J_t \exp[(\Delta E + \delta \Delta E)/RT]
$$

(8)
Rearrangement and dividing of equation (8) by equation (7) leads to the relation

\[ 1 + \frac{\langle \delta J \rangle}{\langle J \rangle - J_g} \approx \exp \left( -\frac{\delta \Delta E}{RT} \right) \approx 1 - \frac{\delta \Delta E}{RT} \]  

(9)

For the pure liquid at 300 °K, the observed value of \( \langle J \rangle \) is 3.45 c/s and from Table 3 it appears reasonable to take \( J_g \approx 0 \) c/s. On this basis the experimental change in \( \langle J \rangle \), \( \langle \delta J \rangle \approx 0.05 \) c/s, for the 0.16 M solution in CS\(_2\), gives \( \approx \exp (\) -0.16) c/s. Similarly, for the 50 per cent (by volume) solution in acetone the observed change \( \langle \delta J \rangle \approx -0.25 \) c/s corresponds to a change in \( \Delta E \) of about +50 cal.

For this case, the analysis of the relatively small solvent effects is complicated by the presence of three non-equivalent forms. The same approach should be more reliable for treating more symmetrical ethanes, with two equivalent gauche forms. Even so, the estimate made for the changes in \( \Delta E \) produced by the solvents are accurate probably within a factor of 2, which certainly is an improvement over the usual assumption of no solvent effects in treating vibrational spectra.

In conclusion, it appears that in principle and at least partially in practice, the N.M.R. methods are very powerful. With improved instrumentation and new techniques, better data and a fuller understanding of the factors affecting the results, N.M.R. may well be the best approach for studying rotational isomerism in liquids and perhaps even in gases.

Most of this research was done in collaboration with G. G. Belford and P. E. McMahon, with assistance from the University of Illinois Digital Computer Laboratory and its staff. I am indebted particularly to Dr R. E. Richards and P. Higman for challenging me with their unpublished data on CHCl\(_2\)CHClCH\(_3\) and its solutions. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Also, the work was supported by the Office of Naval Research.

References

13. R. Richards and P. Higman. Unpublished results; for which I thank them.