\textbf{1}^1\text{H} \text{ and} \ 2^2\text{H} \text{ Spectra of Ethyl Bromide}

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\textit{\textsuperscript{1}H} NMR spectra of ethyl bromide, \textit{2}\textsuperscript{[\textit{1}H]}—ethyl bromide, \textit{1,2,2-}
\textit{tr}\textsuperscript{[\textit{2}H]}—ethyl bromide have been observed, and the chemical shift and
coupling constants determined. The results were \textit{\textit{J}}(\textit{CH}_3) = -13.1
Hz; \textit{\textit{J}}(\textit{CH}_2\textit{Br}) = -9.3 Hz; \textit{\textit{J}} = 7.2 Hz. \textit{2}^2\text{H} \text{ spectra of the deu-
terated species were recorded and analyzed. The coupling constants and
chemical shifts obtained were in close agreement with the data
obtained from \textit{1}^1\text{H} data.

Geminal and vicinal isotope effects on chemical shift have been
measured in \textit{1}^1\text{H} NMR spectra relative to ethyl bromide as internal
standard. The geminal isotope effect was determined to be \(\sim 14
\times 10^{-2}\) ppm and the vicinal effect \(\sim 7 \times 10^{-2}\) ppm.

In the last few years, a number of papers describing isotope effects on
chemical shifts have been published.\textsuperscript{1} The results refer mainly to \textit{1}^1\text{H}
in geminal position to deuterium. Theoretically, the effect has been ascribed
to changes in vibrational amplitude, and electron distribution.\textsuperscript{1} Vicinal iso-
tope effects originating in deuterium substitution on neighbouring carbon
atoms have recently been reported.\textsuperscript{2} For this effect no theoretical derivation
has yet been given. It may partly be due to the fact that only a few spectro-
scopic data are known for the molecules in which the vicinal isotope effect
was observed. In the present work, geminal and vicinal isotope effects are
reported for ethyl bromide. The gas phase structure of ethyl bromide has been
determined by MW spectroscopy\textsuperscript{4} and the IR spectra have been analyzed.\textsuperscript{5}
We therefore believe that ethyl bromide can provide relevant data for theo-
retical considerations.

Only a few \textit{2}^2\text{H} NMR spectra have been published\textsuperscript{3} and they indicate
that the shielding for various positions in a molecule need not be equal in
protonated and deuterated species.\textsuperscript{3} The original measurements did, in our
opinion, not eliminate all possible solvent and concentration effects. In par-
tially deuterated ethyl bromide constant contributions can be expected due
to solvent and concentration. To obtain accurate spectral parameters it is
important that well resolved lines can be observed. In \textit{1}^1\text{H} NMR spectra of
ethyl bromide the majority of lines can be observed as separate signals, and

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used as basis for calculations. The calculations were performed using a program capable of handling nuclei having spin of 1/2, 1, and 3/2, developed in this laboratory.

EXPERIMENTAL

The preparation of the deuterated ethyl bromides has been described earlier. The samples were the same as those used in the IR investigation, where no evidence of impurities was found. Ethyl bromide was a commercial product, the purity of which was checked by the NMR spectrum.

Samples were prepared by distilling TMS, CDCl₃, and ethyl bromides into an NMR tube. The sealed tubes contained a 25 v/v % solution of ethyl bromides. In order to determine the isotope shifts, the deuterated species were mixed with sufficient ethyl bromide to yield reference signals of comparable intensities. The ¹H spectra were obtained using both Varian A 60 and HA 100 spectrometers, operating at approximately 32°C. The ¹H spectra were obtained on Varian HA 100 spectrometer using a Varian V-4311 frequency unit, operating at 15.361 MHz, and a 5 mm probe V-4333A designed for deuterium resonance.

All HA 100 spectra were obtained in frequency sweep mode using TMS or CDCl₃ as lock signal. The Varian spectro system 100 made possible an expanded sweep of 0.5 Hz/cm as well as digital amplification and resolution enhancement.

In the ¹H spectra, an increased RF power ten times the value used in ¹H spectra was found not to saturate the signals. Under these conditions, the S/N ratio was about the same as found in the ¹H spectra of the same sample.

*Table I. Chemical shift and coupling constants measured in ¹H spectra of partly deuterated ethyl bromides.*

<table>
<thead>
<tr>
<th></th>
<th>CH₃DCH₂Br</th>
<th>CDH₄CHDBr</th>
<th>CH₃CH₂Br</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>δH(1)</td>
<td>3.39 ± 0.005 ppm</td>
<td>3.36 ± 0.005 ppm</td>
<td>3.362 ± 0.001 ppm</td>
<td>9*</td>
</tr>
<tr>
<td>δH(2)</td>
<td>1.64 ± 0.005</td>
<td>1.62 ± 0.005</td>
<td>1.6767 ± 0.0011</td>
<td>9</td>
</tr>
<tr>
<td>Δδ</td>
<td>1.74 ± 0.005</td>
<td>1.74 ± 0.005</td>
<td>1.6895</td>
<td>9</td>
</tr>
<tr>
<td>JH(1)D(1)</td>
<td>-2.02 ± 0.04 Hz</td>
<td>-2.00 ± 0.04 Hz</td>
<td>-13.03 ± 0.26*</td>
<td>9</td>
</tr>
<tr>
<td>JH(1)H(1)</td>
<td>-13.16 ± 0.29*</td>
<td>-13.03 ± 0.26*</td>
<td>7.327 ± 0.049 Hz</td>
<td>9</td>
</tr>
<tr>
<td>JH(2)D(1)</td>
<td>-1.43 ± 0.02</td>
<td>-1.43 ± 0.02</td>
<td>7.25 ± 0.1</td>
<td>8</td>
</tr>
<tr>
<td>JH(2)H(2)</td>
<td>-9.32 ± 0.13*</td>
<td>-9.32 ± 0.13*</td>
<td>7.26 ± 0.2</td>
<td>6</td>
</tr>
<tr>
<td>JH(2)H(1)</td>
<td>7.28 ± 0.12</td>
<td>7.327 ± 0.049 Hz</td>
<td>7.14 ± 0.2</td>
<td>7</td>
</tr>
</tbody>
</table>

*10 % v/v CCl₃.
*Calculated from corresponding HD coupling constants.

*At present, the procedures are the sole property of the Varian Ass. and cannot be released.*

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RESULTS

In Table 1, the $^1$H NMR data obtained earlier for ethyl bromide are presented together with the results of the present investigation. The errors quoted are estimates based on comparison of series of theoretical and experimental spectra. The geminal $^1$H $^1$H coupling constants are calculated from experimental data using the ratio of the gyromagnetic values for hydrogen and deuterium $\gamma_H/\gamma_D = 6.514$. The $^2$H NMR data are listed in Table 2. The isotope

Table 2. Chemical shift and coupling constants measured in $^1$H spectra of deuterated ethyl bromides.

<table>
<thead>
<tr>
<th></th>
<th>$\text{CH}_2\text{D} - \text{CH}_2\text{Br}$</th>
<th>$\text{CHD}_2 - \text{CHD} - \text{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{D(1)}$</td>
<td>$-86.20 \pm 0.15$ Hz</td>
<td>$-59.88 \pm 0.15$ Hz</td>
</tr>
<tr>
<td>$\delta_{D(2)}$</td>
<td>$-5.61 \pm 0.01$ ppm</td>
<td>$-3.90 \pm 0.01$ ppm</td>
</tr>
<tr>
<td>$\Delta \delta$</td>
<td></td>
<td>$-86.77 \pm 0.15$ Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-5.65 \pm 0.01$</td>
</tr>
<tr>
<td>$J_{H(2)D(4)}$</td>
<td>$-2.03 \pm 0.12$ Hz</td>
<td>$1.75 \pm 0.02$ ppm</td>
</tr>
<tr>
<td>$J_{H(2)H(3)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{H(1)D(1)}$</td>
<td>$-13.22 \pm 0.78$ Hz</td>
<td>$-2.05 \pm 0.12$ Hz</td>
</tr>
<tr>
<td>$J_{H(1)H(1)}$</td>
<td></td>
<td>$-13.35 \pm 0.78$ Hz</td>
</tr>
<tr>
<td>$J_{H(1)D(3)}$</td>
<td></td>
<td>$-1.41 \pm 0.12$</td>
</tr>
<tr>
<td>$J_{H(1)H(3)}$</td>
<td></td>
<td>$-9.38 \pm 0.78$ Hz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$1.15 \pm 0.12$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$7.49 \pm 0.78$</td>
</tr>
</tbody>
</table>

$^a$ Measured relative to internal CDCl$_3$.
$^b$ Calculated from corresponding HD coupling constants.

Table 3. Isotope effect on chemical shift by deuterium substitution in ethyl bromide. $\Delta$ (1), the observed effect in the methylene group; $\Delta$ (2), the effect in the methyl group.

<table>
<thead>
<tr>
<th></th>
<th>$\text{CH}_2\text{D} - \text{CH}_2\text{Br}$</th>
<th>$\text{CHD}_2 - \text{CHD} - \text{Br}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$ (1)</td>
<td>$0.77 \pm 0.15$ Hz</td>
<td>$2.79 \pm 0.15$</td>
</tr>
<tr>
<td>$\Delta$ (2)</td>
<td>$1.64 \pm 0.13$</td>
<td>$3.94 \pm 0.13$</td>
</tr>
</tbody>
</table>

Effect on chemical shifts, listed in Table 3, are differences between chemical shift values for ethyl bromide and the deuterated species in the same sample thus eliminating solvent and concentration effects. Isotope effects have only been observed in the $^1$H spectra, since the lower frequency applied for $^2$H reduces the isotope effects to the same size as the experimental error.

DISCUSSION

The chemical shift values, reported in Table 1, are in good agreement with those of Ebersole and Castellano when the solvent and concentration effects are taken into account. The vicinal coupling constant in both deuterated species deviates less than 0.3 Hz from the value given by earlier investigations. A change in value for the vicinal coupling between mono- and tri-deutero ethyl bromide might be expected in principle due to a different rotational averaging favouring either the gauche or trans conformation. The variation in experimental data is too small to give evidence for this effect.

In their study of ²H NMR spectra, Diehl and Leipert noticed that chemical shift differences, when measured in ¹H and ³H resonance spectra, did not necessarily coincide for isotopic species. A variation of about 0.06 ppm was observed but with no definite trend. For partially deuterated ethyl bromides we found no changes in the Δδ value exceeding the experimental error. The difference in experimental technique may be important. While Diehl and Leipert investigated two separate samples, one consisting of fully protonated and one of fully deuterated molecules, we have obtained ¹H and ²H data for the same partly deuterated molecule using the same sample.

The geminal coupling constants can indirectly be determined using the observed ²J HD values. The results obtained in this way are characterized by relatively large experimental uncertainties. A variation in J HD cannot be detected when hydrogen as the third atom is replaced by deuterium. The geminal coupling constants obtained from the ²H spectra (Table 2) coincides within the experimental error with the results obtained from ¹H spectra. The average value of $-13.1 \pm 0.2$ Hz found for the methyl group can be compared with the literature value for methane of $-12.4 \pm 0.6$ Hz. The geminal coupling in the methylene group is determined to be $-9.3 \pm 0.2$ Hz. This value is substantially smaller than the one observed for the CH₃ group, but close to the experimental value of $-10.2 \pm 0.4$ Hz found by Bernstein and Sheppard in bromoform.

Until the recent work of Saur et al. no experimental data on vicinal isotope effects seem to have been published. If we assume that the rule of additivity for isotope effects is valid we can deduce the two geminal and vicinal isotope effects from Table 3.

The geminal isotope effect is $16.4 \times 10^{-6}$ ppm in the methyl groups, and $12.5 \times 10^{-8}$ ppm in the methylene group. For the vicinal isotope effect, a value of $6.6 \times 10^{-8}$ ppm is found for the methyl groups, and $7.7 \times 10^{-8}$ ppm for the methylene groups.

The geminal isotope effects reported earlier in CH₃X systems range from $13 \times 10^{-8}$ ppm to $19 \times 10^{-6}$ ppm when going from CH₃NO₂ to methane. The magnitude of the two calculated geminal isotope effects are within this range, and the electronegativity of bromine makes it plausible that the methylene group has the lowest value. The vicinal values reported earlier range from zero to $8 \times 10^{-3}$ ppm for sp³ hybridized carbon compounds. The two values reported here are within this range.

The sensitivity in ²H NMR is calculated to be approximately one hundred times less than in ¹H NMR. Since the same samples were used in both types of
experiment, we had anticipated rather weak signals to be detected. It can furthermore be expected that the line shape for nuclei of spin 1 are determined mainly by quadrupolar relaxation producing signals with a large half line width compared to proton spectra.

An estimate of the half line width can be obtained from the equations

\[
\frac{1}{T_2} = \frac{3}{8} \left[ \frac{eQ}{\hbar} \frac{d^2V}{dx^2} \right]^2 \tau_c
\]

\[
\tau_c = 4\pi n(a^3/3)kT
\]

Here the value of the quadrupole coupling constant may be taken to be of the order of 240 kHz. For \( n = 0.514 \) cp, and \( a = 5 \) Å, we get a line width

\[
1/\pi T_2 = 0.44 \text{ Hz}
\]

This crude guess is in good agreement with the experimental value of 0.30 Hz.

We found that the S/N ratio obtained in \(^2\text{H}\) NMR spectra was not much different from what we found in \(^1\text{H}\) spectra of the same sample. This may primarily be ascribed to the much higher RF power that can be applied in the former case without saturation. Fig. 1 shows the \(^2\text{H}\) spectrum of \(\text{CH}_2\text{BrCH}_2\text{D}\), and Fig. 2 the spectrum of \(\text{CHDBrCHD}_2\).

Improvement in the experimental spectra could be obtained using resolution enhancement.\(^{12,13}\)

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**Fig. 1.** \(^1\text{H}\) spectrum of \(\text{CH}_2\text{BrCH}_2\text{D}\). The frequency scale is relative to internal CDCl\(_3\).

**Fig. 2.** \(^1\text{H}\) spectrum of \(\text{CHDBrCHD}_2\). The frequency scale is relative to internal CDCl\(_3\).

This method is particularly important when partial overlap of a series of lines occur. It has been shown that the line positions in the enhanced spectrum in such cases will correspond to the true line positions, provided the resolution is carried so far that no overlap any longer exists. Employing this method, calculation of coupling constants and isotope effects were greatly simplified.

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REFERENCES

13. The detailed description of the programming is the property of the Varian Ass. and cannot be released.

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