^{1}H and ^{2}H Spectra of Ethyl Bromide

H. JENSEN* and K. SCHAUMBURG

Department of Chemistry, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

^{1}H NMR spectra of ethyl bromide, 2,[^{2}H] — ethyl bromide, 1,2,2-tri[^{2}H]-ethyl bromide have been observed, and the chemical shift and coupling constants determined. The results were $^2J(CH_3) = -13.1$ Hz; $^2J(CH_2Br) = -9.3$ Hz; $^3J = 7.2$ Hz. ^{2}H spectra of the deuterated species were recorded and analyzed. The coupling constants and chemical shifts obtained were in close agreement with the data obtained from ^{1}H data.

Geminal and vicinal isotope effects on chemical shift have been measured in ^{1}H NMR spectra relative to ethyl bromide as internal standard. The geminal isotope effect was determined to be ~ 14 × 10^{-3} ppm and the vicinal effect ~ 7 × 10^{-3} ppm.

In the last few years, a number of papers describing isotope effects on chemical shifts have been published.[1] The results refer mainly to ^{1}H in geminal position to deuterium. Theoretically, the effect has been ascribed to changes in vibrational amplitude, and electron distribution.[1] Vicinal isotope effects originating in deuterium substitution on neighbouring carbon atoms have recently been reported.[2] For this effect no theoretical derivation has yet been given. It may partly be due to the fact that only a few spectroscopic 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 [4] and the IR spectra have been analyzed.[5] We therefore believe that ethyl bromide can provide relevant data for theoretical considerations.

Only a few ^{2}H NMR spectra have been published [3] and they indicate that the shielding for various positions in a molecule need not be equal in protonated and deuterated species.[3] The original measurements did, in our opinion, not eliminate all possible solvent and concentration effects. In partially 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 ^{2}H NMR spectra of ethyl bromide the majority of lines can be observed as separate signals, and

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* Research student 1968—70.

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.[5] The samples were the same as those used in the IR investigation,[6] 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 ^{1}H spectra were obtained using both Varian A 60 and HA 100 spectrometers, operating at approximately 32°C. The ^{2}H spectra were obtained on Varian HA 100 spectrometer using a Varian V-4311 frequency unit, operating at 15.351 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 ^{2}H spectra, an increased RF power ten times the value used in ^{1}H spectra was found not to saturate the signals. Under these conditions, the S/N ratio was about the same as found in the ^{1}H spectra of the same sample.

Table 1. Chemical shift and coupling constants measured in ^{1}H spectra of partly deuterated ethyl bromides.

$$\begin{array}{c} H(2)H(1) \\ H(2)-C-\ \ C-Br \\ H(2)H(1) \end{array}$$
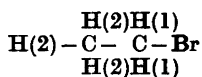
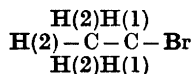|	CH₃DCH₂Br	CDH₂CHDBr	CH₃CH₂Br	Ref.
$\delta_{H(1)}$	3.39_1 ± 0.005 ppm	3.36_9 ± 0.005 ppm	$\{3.3662 \pm 0.0010$ ppm / 3.43	9ᵃ / 6
$\delta_{H(2)}$	1.64_4 ± 0.005	1.62_0 ± 0.005	$\{1.6767 \pm 0.0011$ / 1.69	9 / 6
$\Delta\delta$	1.74_7 ± 0.005	1.74_9 ± 0.005	$\{1.6895$ / 1.74	9 / 6
$^2J_{H(1)D(1)}$	− 2.02 ± 0.04 Hz	− 2.00 ± 0.04 Hz		
$^2J_{H(1)H(1)}$	− 13.16 ± 0.26ᵇ	− 13.03 ± 0.26ᵇ		
$^2J_{H(2)D(2)}$		− 1.43 ± 0.02	7.327 ± 0.049 Hz	9
$^2J_{H(2)H(2)}$		− 9.32 ± 0.13ᵇ	7.25 ± 0.1	8
$^3J_{H(1)H(2)}$	7.28 ± 0.12	7.21 ± 0.15	7.26 ± 0.2	6
			7.14 ± 0.2	7

ᵃ 10 % v/v CCl₄.
ᵇ Calculated from corresponding HD coupling constants.

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

RESULTS

In Table 1, the ¹H 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 ¹H ¹H 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 ²H NMR data are listed in Table 2. The isotope

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

$$\begin{array}{c} H(2)H(1) \\ H(2)-C-C-Br \\ H(2)H(1) \end{array}$$

	CH_2D-CH_2Br	$CHD_2-CHD-Br$
$\delta_{D(1)}$		$\begin{cases} -59.88 \pm 0.15 \text{ Hz} \\ -3.90 \pm 0.01 \text{ ppm} \end{cases}$
$\delta_{D(2)}$	$\begin{cases} -86.20 \pm 0.15 \text{ Hz}^a \\ -5.61_5 \pm 0.01 \text{ ppm} \end{cases}$	$\begin{cases} -86.77 \pm 0.15 \text{ Hz} \\ -5.65_2 \pm 0.01 \end{cases}$
$\Delta\delta$		$1.75_1 \pm 0.02$ ppm
$J_{H(2)D(2)}$	-2.03 ± 0.12 Hz	-2.05 ± 0.12 Hz
$J_{H(2)H(2)}$	-13.22 ± 0.78^b	-13.35 ± 0.78^b
$J_{H(1)D(1)}$		-1.41 ± 0.12
$J_{H(1)H(1)}$		-9.38 ± 0.78^b
$J_{H(1)D(2)}$		1.15 ± 0.12
$J_{H(1)H(2)}$		7.49 ± 0.78^b

a Measured relative to internal CDCl₃.
b Calculated from corresponding HD coupling constants.

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

	CH_2D-CH_2Br	$CHD_2-CHDBr$
Δ (1)	0.77 ± 0.15 Hz	2.79 ± 0.15
Δ (2)	1.64 ± 0.13	3.94 ± 0.13

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 ¹H spectra, since the lower frequency applied for ²H 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 [9] 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.[6-9] A change in value for the vicinal coupling between mono- and tri-deuterio 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 ^{2}H NMR spectra, Diehl and Leipert [3] noticed that chemical shift differences, when measured in ^{1}H and ^{2}H 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 $\Delta\delta$ 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 ^{1}H and ^{2}H 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 be deuterium. The geminal coupling constants obtained from the ^{2}H spectra (Table 2) coincides within the experimental error with the results obtained from ^{1}H spectra. The average value of -13.1 ± 0.2 Hz found for the methyl group can be compared with the literature value for methane [10] of -12.4 ± 0.6 Hz. The geminal coupling in the methylene group is determined to be -9.3 ± 0.2 Hz. This value is substantially smaller than the one observed for the CH_3 group, but close to the experimental value of -10.2 ± 0.4 Hz found by Bernstein and Sheppard [11] in bromoform.

Until the recent work of Saur et al.,[2] no experimental data on vicinial isotope effects seem to have been published. If we assume that the rule of additivity for isotope effects is valid [1] we can deduce the two geminal and vicinal isotope effects from Table 3.

The geminal isotope effect is 16.4×10^{-3} ppm in the methyl groups, and 12.5×10^{-3} ppm in the methylene group. For the vicinal isotope effect, a value of 6.6×10^{-3} ppm is found for the methyl groups, and 7.7×10^{-3} ppm for the methylene groups.

The geminal isotope effects reported earlier [1,3] in CH_3X systems range from 13×10^{-3} ppm to 19×10^{-3} ppm when going from CH_3NO_2 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.[1] The vicinal values reported earlier [3] range from zero to 8×10^{-3} ppm for sp^3 hybridized carbon compounds. The two values reported here are within this range.

The sensitivity in ^{2}H NMR is calculated to be approximately one hundred times less than in ^{1}H 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 [3]

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

$$\tau_c = 4\pi\eta(a^3/3)KT$$

Here the value of the quadrupole coupling constant may be taken [3] to be of the order of 240 kHz. For $\eta = 0.514$ 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 ²H NMR spectra was not much different from what we found in ¹H 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 ²H spectrum of CH_2BrCH_2D, and Fig. 2 the spectrum of $CHDBrCHD_2$.

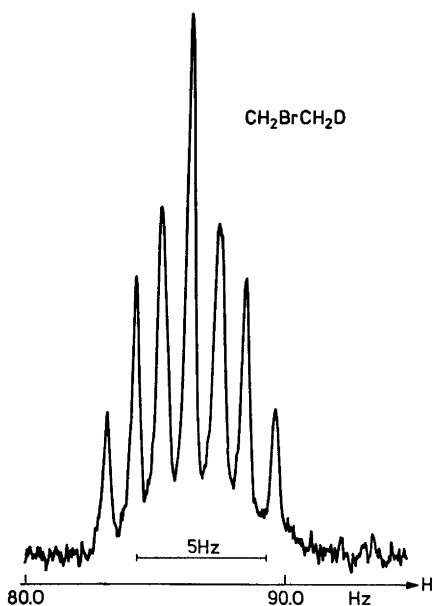Improvement in the experimental spectra could be obtained using resolution enhancement.[12,13]

Fig. 1. ²H spectrum of CH_2BrCH_2D. The frequency scale is relative to internal $CDCl_3$.
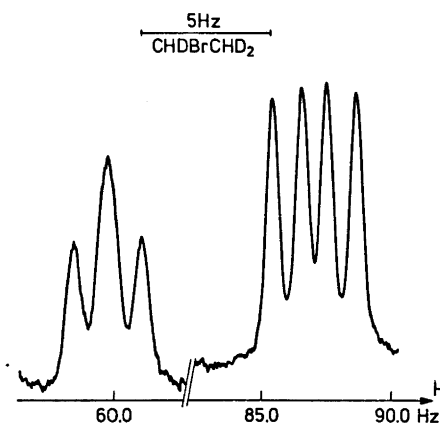
Fig. 2. ²H spectrum of $CHDBrCHD_2$. The frequency scale is relative to internal $CDCl_3$.

This method is particularly important when partial overlap of a series of lines occur. It has been shown [14] 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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