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^{81}Br/^{79}Br-Induced ^{13}C Isotope Shifts and Line Broadening in the ^{13}C NMR Spectrum of Methyl Bromide

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NMR studies of the ^{13}C isotope shift between $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ and of the linewidths of the two resolved resonances were carried out as part of a wider study of the NMR properties of methyl halide molecules. The isotope shift of 1.12 ppb can be readily accounted for in terms of the very slight shortening of the C—Br bond (0.000 008 Å) which occurs upon replacing ^{79}Br by ^{81}Br. From the isotope shift it is shown that the C—Br bond length derivative of the carbon-13 shielding is -140 ppm Å^{-1}. There is no need to involve the change in bromine nuclear quadrupole moment to explain the isotope shift. The linewidths are influenced by scalar relaxation of the second kind and, from the observed values of 0.084 and 0.100 Hz for $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$, respectively, it is possible to deduce that $J(^{13}C\,^{79}Br) = 48$ Hz and $J(^{13}C\,^{81}Br)$ is 45 Hz. These results are in accordance with extrapolation from previously measured results for CBr_4, $CHBr_3$ and CH_2Br_2. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Isotope shifts are often very easy to detect in NMR and many thousands of them have now been measured.[1–3] Most measurements involve D/H isotopic substitution although there are many others involving substitutions such as ^{13}C/^{12}C, ^{15}N/^{14}N and ^{18}O/^{16}O. As one moves to elements of greater atomic mass, the magnitudes of isotope shifts diminish since the proportionate changes in mass upon isotopic substitution diminish. Recently, we succeeded in resolving the ^{13}C signals from the various ^{37}Cl/^{35}Cl isotopomers occurring naturally in the chlorinated methanes.[4] It was found that the principal reason why the ^{13}C NMR signals of the standard solvents CH_2Cl_2, $CHCl_3$ and CCl_4 were observed as singlets over so many years of NMR work is that the scalar broadening of the ^{13}C signals due to spin–spin coupling of the ^{13}C and ^{37}Cl (or ^{35}Cl) nuclei is affected by the ^{37}Cl (or ^{35}Cl) quadrupole spin–lattice relaxation. Line broadening is roughly proportional to the number of chlorine atoms at the carbon under study and in many cases it can reach values of 2–3 Hz. In this paper we report data on ^{81}Br/^{79}Br-induced ^{13}C isotope shifts in methyl bromide.

RESULTS

^{13}C NMR spectra in both proton-coupled and decoupled modes were obtained with a UNITYplus-500 spectrometer at the Varian Applications Laboratory in Darmstadt. The operating frequency was 125.69 MHz. The sample was a 10 vol.% solution of methyl bromide in tetramethylsilane-d_{12}. The spectra were obtained with acquisition times of 16 s and the number of points acquired was 32K. To achieve high resolution, the selective excitation technique first proposed by Bax and Freeman[5] was applied with a 5 mm triple resonance PFG probe. Selective excitation experiments were performed using the excitation pulse $\pi/2$ E-BURP-1 as described by Geen and Freeman.[6] FIDs were zero-filled to 512K and no weighting function was used in processing in order to avoid lineshape distortion. The ^{13}C NMR signal of one of the inner components of the proton coupled spectrum is given in Fig. 1 (lower trace). One can clearly see the double structure of the spectrum revealing the ^{79}Br/^{81}Br isotope effect. The high-field component of the spectrum can be confidently assigned to the ^{81}Br isotopomer, although the very clear difference in the amplitudes of the two components was unexpected as the two bromine isotopomers have almost equal natural abundance. To gain more insight into the cause of this difference, we employed the deconvolution procedure with the standard Varian software

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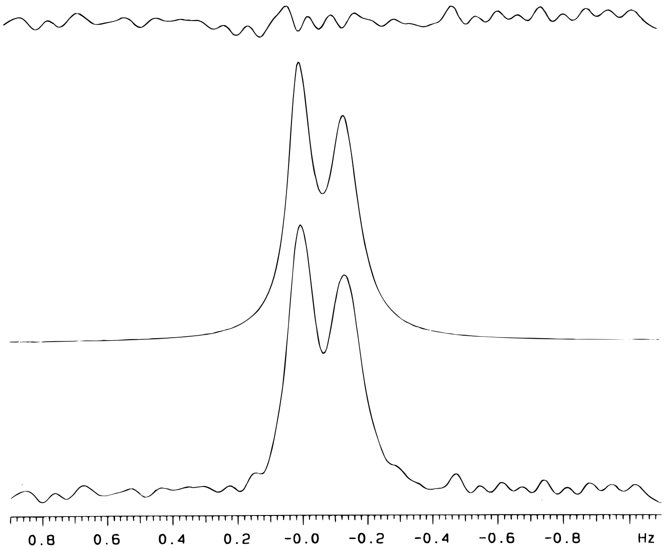

Figure 1. An inner component of the 1 : 3 : 3 : 1 quartet of the proton-coupled ^{13}C NMR spectrum of CH_3Br at 303 K. The experimental signals shown in the lower trace were obtained without weighting. The signals from $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ are clearly resolved with the high-field component having lower peak intensity. The line separation is 0.139 Hz (1.11 ppb). The deconvoluted spectrum (middle trace) was obtained using standard Varian software with 525 iterations. The number of iterations was 65–67 in two runs. The upper trace is the difference spectrum.

using Lorentzian functions and confirmed the existence of the isotope effect in two independent experiments with slightly different parameters (1.11 and 1.13 ppb) obtained after deconvolution. The deconvolution process is illustrated in Fig. 1, where the final iterated spectrum is shown in the middle and the difference spectrum is also shown as the upper trace. Henceforth, we take the isotope shift to be 1.12 ppb.

Linewidths

The difference in the linewidths of the two components is striking. The linewidths are 0.084 and 0.100 Hz (± 0.02 Hz) for low- and high-field components, respectively. The total linewidth is a sum of two contributions:

$$(\Delta\nu_{1/2}) = (\Delta\nu_{1/2})_{ns} + (\Delta\nu_{1/2})_{s} \qquad (1)$$

where $(\Delta\nu_{1/2})_{ns}$ is the non-specific (nonscalar) broadening (mainly due to field inhomogeneity) and $(\Delta\nu_{1/2})_{s}$ is a specific (scalar) broadening due to spin–spin coupling between ^{13}C and ^{79}Br (or ^{81}Br).

For a bromide isotopomer with $I(Br) = 3/2$, one has[4]

$$(\Delta\nu_{1/2})_{s} = (R_2/\pi) = 5\pi[J(CBr)]^2 T_1(Br) \qquad (2)$$

Although neither the coupling constants J(CBr) nor the spin–lattice relaxation time T_1(Br) are known at present, one can easily estimate the ratio ρ of the two scalar linewidths. Thus,

$$\begin{aligned}\rho &= (\Delta\nu_{1/2})_{s}(^{79}Br)/(\Delta\nu_{1/2})_{s}(^{81}Br)\\ &= [J^2(13/79)/J^2(13/81)][T_1(79)/T_1(81)] \qquad (3)\end{aligned}$$

where $J(13/79)$ and $J(13/81)$ are abbreviations for the coupling constants $J(^{13}C\,^{79}Br)$ and $J(^{13}C\,^{81}Br)$ and $T_1(79)$ and $T_1(81)$ denote the corresponding bromine spin–lattice relaxation times. Since coupling constants are proportional to the corresponding magnetogyric ratios, the first factor in Eqn (3) is 0.86. Further, according to the estimates performed by Akitt,[7]

$$T_1(79)/T_1(81) = (\Delta\nu_{1/2})(^{81}Br)/(\Delta\nu_{1/2})(^{79}Br) = 0.67$$

assuming that $T_1 = T_2$ for both isotopes and considering the linewidths in the case of bromine isotopes to be completely determined by the quadrupole relaxation mechanism. As a result, ρ can be estimated to be 0.58.

Now, using Eqn (1), assuming the same non-scalar inhomogeneity terms for both isotopomers and the ratio of the two scalar linewidths estimated above, one obtains values of 0.022, 0.038 and 0.0633 Hz for $(\Delta\nu_{1/2})_{s}(^{79}Br)$, $(\Delta\nu_{1/2})_{s}(^{81}Br)$ and $(\Delta\nu_{1/2})_{ns}$, respectively. Thus, the high-field component should indeed be additionally broadened. It is worth noting that this additional broadening is very small and has been often ignored in measurements of ^{13}C NMR spectra of brominated organic compounds.

Isotope shift

The isotope shift can be explained in terms of the slight changes in the mean bond lengths and bond angles brought about by isotopic substitution.[8] Calculations of these geometrical changes require a full and accurate knowledge of the molecular force field, including harmonic and anharmonic force constants.

Schneider and Thiel[9] calculated the quadratic and cubic force field for a number of alkyl and silyl halides including CH_3Br at the self-consistent field (SCF) level. Using this force field, we calculated that the C—Br bond length in $CH_3{}^{81}Br$ is shorter by 0.000 008 1 Å than that in $CH_3{}^{79}Br$. We can attribute the isotope shift of 1.12 ppb observed in the experiments described above almost entirely to this reduction in C—Br bond length. Other geometrical deformations possible with heavy isotope substitution such as the changes in C—H bond lengths and HCCl interbond angles were shown in the case of CH_3Cl to be too small to contribute significantly to the ^{13}C isotope shift.[4] Assuming a proportionality between the C—Br bond length reduction and the isotope shift (i.e. neglecting second-order effects and changes in the other geometrical parameters), we calculate that the derivative of the carbon-13 shielding with respect to the C—Br bond length is -140 ppm Å^{-1}, which is very close to an *ab initio* value of -152 ppm Å^{-1} calculated[10] with a large basis set wavefunction at the SCF level. This confirms the notion that it is the small change of molecular geometry due to isotopic substitution which produces the isotope effect. A useful working equation for the nuclear radius r is[11]

$$r = 1.18A^{(1/3)} - 0.48 \qquad (4)$$

where r is in fermi (10^{-15} m) and A is the mass of the nucleus (in atomic mass units). This gives a radius for a bromine nucleus of about 0.000 046 Å, which is almost six times greater than the C—Br bond length change detected by resolution of the isotopomeric signals. Even the radius of the proton, 0.000 010 Å, is larger.[12] It should be noted that the change in bond length detected by the resolution of the resonances is much smaller than the error in the equilibrium C—Br bond length: according to Graner,[13] this length is 1.9340 ($\pm 0.0002/3$) Å.

Although, as shown, the change in geometry is sufficient to explain the isotope shift, there is the possibility that a small contribution to it could arise from the change of nuclear quadrupole moment which occurs on replacing ^{79}Br by ^{81}Br. A change in the magnitude of this moment will alter the interaction with the field gradient and so, conceivably, have a small effect on the bond length and hence on the isotope shift.

The potential energy felt by the nuclei of the C—Br bond in the axially symmetric situation is

$$V(r) = \tfrac{1}{2}k(r - r_e)^2 - \tfrac{1}{2}e^2Qq \tag{5}$$

where $r - r_e$ is a small displacement from the equilibrium bond length r_e in the absence of nuclear quadrupole coupling and k is the harmonic force constant of the bond. In the presence of the coupling there will be a new minimum in $V(r)$ shifted by r_0 from r_e. Upon changing the bromine nucleus the change in this new minimum is

$$\Delta r_0 = \frac{e^2 \Delta Q}{2k} q' \tag{6}$$

where $e\Delta Q$ is the change in the nuclear quadrupole moment and eq' is the derivative of the field gradient at the nucleus. All the quantities in the Eqn (6) are available or can be calculated. Raghaven[14] gives $Q(^{79}\text{Br}) = 33.1 \times 10^{-30}$ m^2 and $Q(^{81}\text{Br}) = 27.6 \times 10^{-30}$ m^{-2}, so that $e\Delta Q = -9.6 \times 10^{-49}$ C m^2. An SCF calculation of Schneider and Thiel[9] gives $k = 309.7$ J m^{-2} for the (unscaled) C—Br stretching force field constant. At present there is no literature value for the field gradient derivative at the bromine nucleus. We calculate[10] a value $eq' = -1.59$ a.u. or -29.2×10^{31} V m^{-3}. This gives $\Delta r_0 = 45 \times 10^{-10}$ Å, corresponding to a contribution to the isotope shift of $-0.000\,67$ ppb on replacement of ^{79}Br by ^{81}Br. This change is in the opposite direction to that observed experimentally and about 30 times smaller than the experimental error of ± 0.02 ppb. Hence it can be ignored at the present level of experimental error.

Spin–spin coupling

We now return to the values of the product J^2T_1. To estimate T_1 we use the data of Akitt,[7] who gives 1 ms for $T_1(^{81}\text{Br})$ for dilute aqueous solutions. From the known values of the scalar linewidths, one can estimate $J(^{13}\text{C}\,^{81}\text{Br})$ to be 48 Hz and $J(^{13}\text{C}\,^{79}\text{Br})$ to be 44.5 Hz. Previously values of J(CBr) were estimated for CBr$_4$, CHBr$_3$ and CH$_2$Br$_2$ from the analysis of different mechanisms for the spin–lattice relaxation of ^{79}Br. The data thus obtained (151, 127 and 95 Hz for CBr$_4$, CHBr$_3$ and CH$_2$Br$_2$, respectively[15]) are in reasonable agreement with the estimate of 45 Hz for CH$_3$Br and reveal a strong dependence of ^{13}C—Br coupling constants on the number of bromine atoms present.

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