# Deuterium-induced Carbon-13 Isotope Shifts in Halogenomethanes

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One-bond deuterium-induced carbon-13 isotope shifts in several chlorine, bromine and iodine derivatives of methane have been measured and used to construct a new incremental scheme for the calculation of carbon-13 isotope shifts in substituted derivatives of methane.

Replacement of a hydrogen atom bonded to a carbon atom by a deuterium atom usually leads to an increased shielding of the carbon nucleus. For example, careful measurements[1] of a $CH_4$–$CH_3D$ mixture at 275 K give a $^{13}C$ isotope shift, $\delta(CH_3D)-\delta(CH_4)$, of $-200.3 \pm 0.5$ ppb with a slight temperature gradient of $-0.06$ ppb $K^{-1}$. Many other measurements of one-bond $^{13}C$-isotope shifts give qualitatively the same results as discussed in several comprehensive reviews.[2–5]

The main trends of $^{13}C$ isotope shifts, $^1\Delta^{13}C(D/H)$, have been investigated and attributed to net charge, lone pairs, carbon hybridisation and substituents. Günther and coworkers[6] found that successive replacement of hydrogen in methane by methyl or phenyl groups led to a decrease in $^1\Delta^{13}C(D/H)$ of *ca.* 95 and 81 ppb, respectively. Although other data can be found in the literature,[7–10] the general dependence on substituents is not clear. In the present paper we report $^1\Delta^{13}C(D/H)$ values in some halogenomethanes $CH_nD_mHal_{4-n-m}$ where Hal = Cl, Br or I.

All $^{13}C$ NMR spectra were recorded on Bruker AM 250 and WH 400 spectrometers operating at 62.9 and 100.6 MHz, respectively, in the proton-coupled mode. All possible $^{13}C$ chemical shifts and coupling constants, $^1J(^{13}C,H)$ and $^1J(^{13}C,D)$, were measured. The coupling constants will be published at a later date. Here we report isotope shifts for the isotopomeric mixtures listed in Table 1. Most of the isotopomers were purchased from Aldrich, but the mixtures $CH_3Br$–$CD_3Br$ and $CH_2I_2$–$CHDI_2$ were synthesized as indicated below Table 1. $^2D$ NMR lock signals were provided either by the deuteriated species, by solvents or by specially added compounds. Small sweep widths (300–500 Hz) and zero filling up to 64 K memory size were applied in order to obtain digital resolution of at least 0.015 Hz. Several thousand scans with acquisition times in the range 6–10 s were accumulated in each experiment to achieve an accuracy of 0.1–0.2 ppb in isotope shifts.

Two typical spectra are depicted in Fig. 1. With the $CH_2I_2$–$CHDI_2$ mixture a small amount of $CD_3OD$ was added to provide the $^2D$ lock signal. With $CHI_3$–$CDI_3$ the choice of appropriate solvent proved to be a serious problem. Iodoform is a solid at ambient temperatures and has a very limited solubility in most organic solvents[11] except pyridine (solubility 1.7 g in 1 g pyridine). Previous measurements of $^{13}C$ chemical shifts of $CHI_3$ performed by Lichtman and Grant[12] were done in pyridine though there may be rather strong intermolecular effects in the $CHI_3$–pyridine system. We found that in acetone the solubility of iodoform was rather high *ca.* 120 mg in 1 ml of acetone at 25 °C with a noticeable increase up to 350 mg in 1 ml of solvent at 52 °C. However, the recording of $^{13}C$ NMR spectra of even saturated solutions of the mixtures $CHI_3$–$CDI_3$ met additional difficulties as the $^{13}C$ lines were almost always broadened (sometimes even split into several components following lengthy accumulation) due to a very strong temperature dependence of $^{13}C$ chemical shifts of carbons with neighbouring iodine atoms.[13] Note also that the $^{13}C$ chemical shift of $CHI_3$ in acetone is $-154$ ppm ($\delta$ scale), which differs substantially from the value reported in ref. 12 for $CHI_3$ in pyridine ($-140$ ppm). Thus the incremental scheme for calculating $^{13}C$ chemical shifts in substituted methanes proposed in ref. 12 needs reinvestigation.

The data are summarised in Table 1. $^1\Delta^{13}C(D/H)$ values are very dependent on the substituent and for diiodomethane and iodoform they have opposite signs from the other compounds. To our knowledge these are the only examples of positive one-bond isotope shifts. A small non-additivity of isotope shifts

**Table 1** Deuterium-induced isotope shifts in some halogenomethanes (results are in ppb and the signs conform to the $\delta$ scale so that a negative sign denotes increased shielding)

| Sample (v/v ratio) | Other components present | Total isotope shift | Isotope shift per deuterium | Total isotope shift, literature data[a] |
|---|---|---|---|---|
| $CH_2Cl_2$–$CD_2Cl_2$ (1/2.5) | None | −398.3 (±0.2) | −199.15 (±0.1) | −398.8 (±0.5)[10] |
| $CHCl_3$–$CDCl_3$ (1/1) | None | — | — | −202.6 (±0.5)[10] |
| $CH_3Br$–$CD_3Br$[b] (1/5) | $CDCl_3$ (65 mol%) | −474.7 (±0.2) | −158.2 (±0.1) | −430 (±50)[8,c] |
| $CH_2Br_2$–$CD_2Br_2$ (1/2) | None | −189.2 (±0.1) | −94.6 (±0.5) | — |
| $CHBr_3$–$CDBr_3$ (1/2.5) | $CD_3OD$ (26 mol%) | −29.1 (±0.1) | −29.1 (±0.1) | −110 (±50)[8,c] |
| $CH_3I$–$CD_3I$ (1/2.5) | None | −147.6 (±0.1) | −49.3 (±0.03) | −146.9 (±0.1)[10] |
| $CH_2I_2$–$CHDI_2$[d] (1/1) | $CD_3OD$ | 107.3 (±0.5) | 107.3 (±0.5) | — |
| $CHI_3$–$CDI_3$ (1/2.5) | [$^2H_6$]acetone (98 mol%) | 386.3 (±1.0) | 386.3 (±1.0) | 380 (±10)[14] |

[a] The literature data refer to samples which are not identical to those used here. [b] This sample was prepared by the bromination of a mixture of deuteriated isotopomers of silver acetate according to the method of B. Nolin and L. C. Leitch, *Can. J. Chem.*, 1953, **231**, 153. The sample contained the isotopomers as follows: $CH_3Br$ (10%), $CH_2DBr$ (30%), $CHD_2Br$ (40%) and $CD_3Br$ (20%). [c] The probable error here is estimated by us. [d] This sample was prepared by the reduction of $CDI_3$ with $NaBH_4$ according to M. M. Nad and K. A. Kocheshkov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1957, 1122.

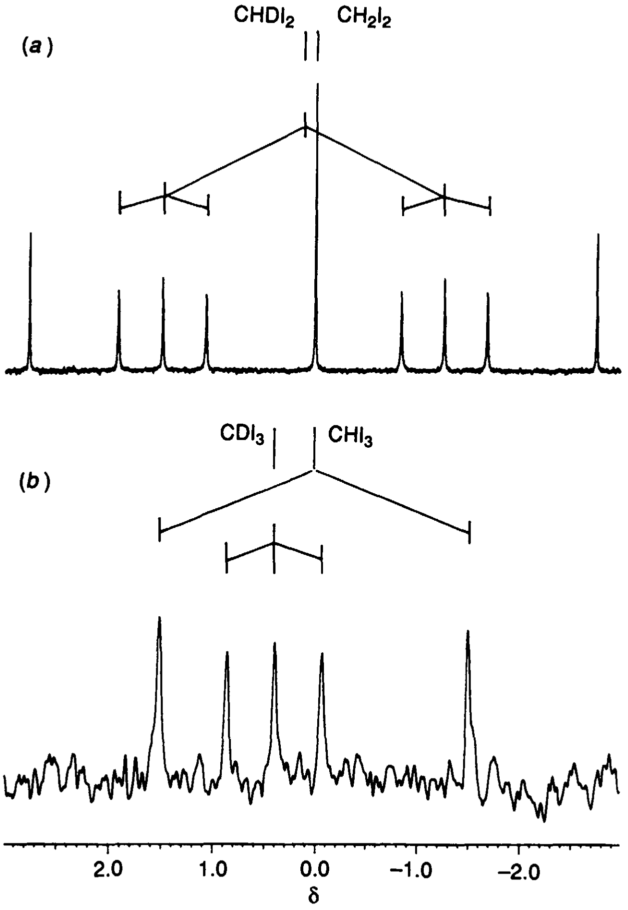

**Fig. 1** Proton-coupled $^{13}C$ NMR spectra of (*a*) diiodomethane and (*b*) iodoform. The spectra were obtained at ambient temperature with a frequency of 62.89 MHz. The downfield displacements of the signals of the deuteriated isotopomers are indicated above the spectra. The poorer signal-to-noise ratio in (*b*) is caused by the limited solubility of iodoform in acetone (see text).

upon successive D/H replacements (up to 5%) and solvent effects (up to 15%) dependent on the nature of the halogen were observed and will be discussed separately.

We now consider the dependence of $^1\Delta^{13}C(D/H)$ upon the number of halogens at the carbon atom. The results for methane (see above) and for $CH_2Cl_2$ and $CHCl_3$ (see first two entries of Table 1) are almost the same (198–203 ppb), showing that chlorine has no effect. However, for bromine and especially iodine the $^1\Delta^{13}C(D/H)$ values increase substantially with the number of halogens.

**Table 2** Incremental parameters (in ppb) for the calculation of $^1\Delta^{13}C(D/H)$ in substituted methanes

| $X^i$ | $\delta\Delta(X^i)$ | Ref. |
|---|---|---|
| Bu$^t$ | −114 | 6 |
| $CH_3$ | −95 | 6 |
| OH | −85 | 10 |
| Ph | −81 | 6 |
| $NO_2$ | −30 | 10 |
| Cl | 0 | [a] |
| Br | 50 | [a] |
| CN | 50 | 10 |
| I | 150 | [a] |

[a] This work.

Although equilibrium isotope effects may contribute to the observable $^{13}C$ isotope shifts (especially for $CHI_3$, for which solvent effects on $^{13}C$ chemical shifts have been already mentioned) it is possible using the present and other data[14,15] to construct an incremental scheme for the empirical calculation of isotope shifts for the $HCX^1X^2X^3$ system where $X^i$ are substituents with increments $\delta\Delta(X^i)$, $i = 1–3$. Thus, eqn. (1)

$$^1\Delta^{13}C(D/H) = -200 + \Sigma\delta\Delta(X^i) \qquad (1)$$

(in ppb) gives values accurate to ±10 ppb with the parameters $\delta\Delta(X^i)$ listed in Table 2. The range covered by these parameters is very wide: −114 ppb to +150 ppb. Their ordering does not follow any obvious trend, although there is a tendency for highly electronegative groups and heavy atoms to possess more positive values of $\delta\Delta(X^i)$. It would be desirable to have results for substituents such as F and $NH_2$ and the scheme could be further tested with mixed isotopomers.

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