STUDY OF DEUTERIUM ISOTOPE EFFECTS ON SOME CARBON-13 CHEMICAL SHIFTS

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The shift observed in nuclear magnetic resonance spectra following isotopic substitution has been attributed to changes in such parameters as bond hybridization, bond angle, or intramolecular electric fields.[1] Irrespective of the mechanism, the small deuterium isotope effect on proton chemical shifts appear to be related to changes in the diamagnetic term for protons whereas for atoms with intrinsic orbital angular momentum variations in the paramagnetic term are dominant and the isotope shift is usually much larger.[1]

There have been few reports[2-4] concerning deuterium isotope effects on carbon-13 chemical shifts. Because such effects are likely to be much larger for carbon-13 than for protons they may be very useful in developing theories to explain isotope shifts in general. In this note we report deuterium isotope effects on the carbon-13 chemical shifts of some 1-deutero-1-substituted heptanes, 1-deuterohept-1-ene, and 1-deuterohept-1-yne.

The isotope shifts and ^{13}C–D scalar coupling constants measured by recording the proton-decoupled carbon-13 spectra of solutions containing about three parts deuterated compound to one part undeuterated are given in Table 1. Figure 1 shows the ^{13}C resonances of C1 and C2 of hept-1-yne obtained from such a sample. Except for 1-deuterohept-1-ene no difficulties were experienced in observing the sharp bands of the $1:1:1$ triplet of the deuterated carbon and there appeared to be no marked loss of signal intensity relative to the other resonances because of deuterium substitution. For 1-deuterohept-1-ene, the method of preparation will yield a Z–E mixture and we believe the relatively broad resonances observed for C1 and C2 of this compound are due to slight differences in the deuterium isotope effect for different configurations of the deuterium.

Inspection of Table 1 reveals that the deuterium isotope effects on carbon-13 chemical shifts are more than an order of magnitude larger than on proton chemical shifts and all isotope shifts of the deuterated carbons are positive. When resolved, the secondary isotope shifts are positive for all the compounds studied. The values

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[1] Batiz-Hernandez, H., and Bernheim, R. A., *Prog. N.M.R. Spectrosc.*, 1967, **3**, 63; Batiz-Hernandez, H., and Bernheim, R. A., *J. chem. Phys.*, 1966, **45**, 2261.

[2] Maciel, G. E., Ellis, P. D., and Hofer, D. C., *J. phys. Chem.*, 1967, **71**, 2160.

[3] Lebel, G. L., Laposa, J. D., Sayer, B. G., and Bell, R. A., *Analyt. Chem.*, 1971, **43**, 1500.

[4] Bell, R. A., Chan, C. L., and Sayer, B. G., *Chem. Commun.*, 1972, 68.

of $J_{C1,D}$ are consistent with values calculated from the known $^{13}C-^1H$ scalar coupling constants.

TABLE 1

CARBON-13 DEUTERIUM ISOTOPE SHIFTS AND $J_{C,D}$ VALUES FOR THE
1-DEUTERO COMPOUNDS STUDIED

Isotope shifts in p.p.m.; $+$, upfield; unr., unresolved. J in Hz

Compound	C 1 shift	C 2 shift	$J_{C1,D}$
$CH_3(CH_2)_5CH_2D$	$+0\cdot28$	unr.	$19\cdot2$
$CH_3(CH_2)_5CHDCl$	$+0\cdot30$	$+0\cdot11$	$22\cdot6$
$CH_3(CH_2)_5CHDBr$	$+0\cdot41$	$+0\cdot11$	$23\cdot2$
$CH_3(CH_2)_5CHDI$	$+0\cdot11$	unr.	$22\cdot6$
$CH_3(CH_2)_5CHDOH$	$+0\cdot38$	unr.	$21\cdot5$
$CH_3(CH_2)_4CH=CHD$	$+0\cdot21$[a]	unr.[a]	$23\cdot0$[a]
$CH_3(CH_2)_4C{\equiv}CD$	$+0\cdot22$	$+0\cdot50$[b]	$37\cdot6$

[a] Lines broadened, possibly owing to the presence of $Z-E$ isomers.
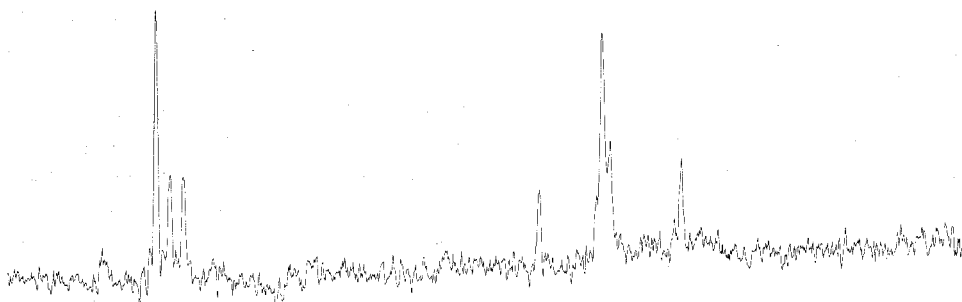[b] $J_{C2,D}$ $7\cdot8$ Hz.

Fig. 1.—Proton-decoupled ^{13}C spectrum for C 1 (upfield) and C 2 of a solution containing 70% 1-deuterohept-1-yne and 30% hept-1-yne (150 scans, 5 Hz/s). A spectral width of 500 Hz is shown.

Batiz-Hernandez and Bernheim[1] have noted that the magnitude of the deuterium isotope effect on proton chemical shifts decreases with an increase in the s character of the carbon atom directly bonded to the deuterium (e.g. for mono-deuteromethane the isotope shift on the proton resonance is $+0\cdot019$ p.p.m. while for monodeuteroethylene it is $+0\cdot0085$ p.p.m.). No such correlation is apparent for the carbon-13 isotope shifts reported in this paper. In fact, the value for 1-deuteroheptane ($+0\cdot28$ p.p.m.) is almost the same as for monodeuterobenzene[4] ($+0\cdot29$ p.p.m.). For the hydrocarbons so far reported the isotope shifts are within the limits $0\cdot25\pm0\cdot04$ p.p.m. Bell, Chan, and Sayer[4] have interpreted their results on substituted monodeuterobenzenes as indicating that in this case the deuterium isotope effect on carbon-13 chemical shifts is composed of two components; the first and largest effect is the result of changes in the normal vibrational modes of the benzene ring upon deuterium substitution, and the second and smaller effect is polar in nature. In our case, however, substituent effects are much larger and difficult to rationalize solely in terms of substituent polarity. Relative to 1-deutero-heptane, a chlorine atom has only a small influence on the carbon-13 isotope shift ($+0\cdot02$ p.p.m.) whereas a bromine atom produces a large change ($+0\cdot13$ p.p.m.).

However, the effect of an iodine atom relative to the other two halogen atoms is very different in that it *decreases* the carbon-13 isotope shift by 0·17 p.p.m. Consequently, deuterium isotope shifts on carbon-13 chemical shifts in general cannot be simply understood in terms of changes in the normal vibrational modes on deuterium substitution and polarity effects.

For the compounds reported here it is possible that bond-length changes on deuteration are an important factor in determining the magnitude of the carbon-13 isotope shifts. Unfortunately, there are no precise data concerning changes in *all* bond lengths on deuteration even for simple model compounds such as the substituted methanes, although it is usually conceded that average bond lengths are decreased upon heavy isotopic substitution.[1] Evidence that bond-length changes on deuteration may be important is provided by 1-deuterohept-1-yne. The *secondary* deuterium isotope shift is more than twice the primary. There is no doubt of the spectral assignments because of the relative positions of the C1 and C2 resonances and the values of the ^{13}C–D scalar coupling constants (Fig. 1). A proton isotope shift of 0·019 p.p.m. on geminal deuterium substitution in methane may be accounted for by bond-length changes of the order of 0·03%.[1] The change in C≡C bond length on deuteration of acetylene is unknown, but the force constant of dideuteroacetylene is substantially larger than that for acetylene.[5] The increase could be due to a shortening of the bond. The shortening of the above order would be below the limit of detection by high-resolution infrared[5] but would have a strong influence on the nuclear shielding through its effect on the wave functions of this polyelectronic bond.

We hope these results will stimulate theoretical research into the mechanisms controlling isotope shifts. The results for 1-deuterohept-1-yne should provide a good test for any chemical shift theory relating variation in molecular wave functions to internuclear distance because this is possibly one case where reductions in bond lengths on deuteration are the only important changes.

Experimental

Proton-decoupled natural-abundance carbon-13 spectra were determined at 15·086 MHz on a Varian HA60IL spectrometer in an experimental configuration to be described in detail later.

1-Deuteroheptan-1-ol was prepared in 75% yield by LiAlD$_4$ reduction of heptan-1-al. Treatment of the alcohol with 48% HBr containing a little conc. H$_2$SO$_4$ gave 1-deutero-1-bromoheptane in 68% yield, which on boiling in acetone containing NaI was converted into 1-deutero-1-iodoheptane in 82% yield. Reduction of the iodide with LiAlH$_4$ resulted in a 70% conversion into 1-deuteroheptane. Heating the alcohol under reflux with SOCl$_2$ gave 1-deutero-1-chloroheptane in 67% yield. Dehydrohalogenation of the bromide in hexamethylphosphoric triamide gave 1-deuterohept-1-ene in 61% yield. Three exchanges of hept-1-yne in NaOD/D$_2$O resulted in 75% incorporation of deuterium.

Acknowledgments

[5] Herzberg, G., "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules." (Van Nostrand: New York 1945); Brown, J. K., and Cox, A. P., *Spectrochim. Acta*, 1961, **17**, 1230; Christensen, M. T., Eaton, D. R., Green, B. A., and Thompson, H. W., *Proc. R. Soc. (A)*, 1957, **238**, 15.