Deuterium Isotope Effects on ^{13}C Chemical Shifts in Benzene and Substituted Benzenes

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Summary The ^{13}C n.m.r. isotope shifts induced by deuterium in mono-substituted benzenes are shown to be dependent upon vibronic and polar factors; the observed, directly bonded shifts for deuterium in the *ortho* position are suggested as a measure of a Hammett σ_o.

Isotope induced chemical shifts have been frequently observed in high resolution n.m.r. spectra,[1] and much effort has been expended to interpret the shifts in terms of simple structural parameters. Little work has been recorded on deuterium isotope induced shifts in ^{13}C n.m.r. spectra,[2] and, to probe further the origin of the effects, we have examined the ^{13}C isotope shifts in mono-deuteriobenzene and a number of mono-substituted derivatives (see Table).

The spectrum of mono-deuteriobenzene showed that the carbon bearing the deuterium is shifted substantially upfield (0·289 p.p.m.) and the two adjacent carbons are shifted upfield to a smaller extent (0·110 p.p.m.). The ***meta*** carbons showed a pronounced coupling of 1·14 Hz to the deuterium[2b] and are moved upfield by 0·011 p.p.m. Taking the shifts observed for mono-deuteriobenzene as a standard, the data in the Table show that there are sub-

^{13}C *isotope shifts in mono-deuteriobenzenes*

Compound	Isotope shift,[a] p.p.m. 1 atom	Isotope shift,[a] p.p.m. 2 atom
$^{2}H \cdot C_6H_5$	0·289	0·110
o-$^{2}H \cdot C_6H_4 \cdot OMe$	0·338	0·092 (C-3) 0·037 (C-1)
o-$^{2}H \cdot C_6H_4 \cdot Me$	0·321	0·114 (C-3) 0·086 (C-1)
o-$^{2}H \cdot C_6H_4 \cdot Cl$	0·295	0·106 (C-3)
o-$^{2}H \cdot C_6H_4 \cdot CN$	0·243	0·103 (C-1)
m-$^{2}H \cdot C_6H_4 \cdot OMe$	0·284	0·102 (C-2) 0·111 (C-4)
m-$^{2}H \cdot C_6H_4 \cdot Me$	0·295	0·110 (C-2) 0·111 (C-4)
m-$^{2}H \cdot C_6H_4 \cdot Cl$	0·276	0·106 (C-2) 0·101 (C-4)
p-$^{2}H \cdot C_6H_4 \cdot OMe$	0·292	0·118 (C-3, -5)
p-$^{2}H \cdot C_6H_4 \cdot Me$	0·294	0·123 (C-3, -5)
p-$^{2}H \cdot C_6H_4 \cdot Cl$	0·284	0·101 (C-3, -5)
p-$^{2}H \cdot C_6H_4 \cdot CF_3$	0·279	0·113 (C-3, -5)

[a] The chemical shifts of the ring carbons were in substantial agreement with the values reported in ref. 6. The isotope shifts (±0·003 p.p.m.) were measured at 25·143 MHz (Varian Associates) on the neat liquids, containing 20—30% of the fully protio-benzenes as markers.

stituent effects on both the directly bonded isotope shifts and the second atom shifts. The directly bonded shifts for *ortho*-substituted compounds correlate well with Taft's σ_o,[3] while those compounds with *meta* and *para* substituents correlate with σ_m and σ_p, respectively. We interpret this as demonstrating for the first time, that the ^{13}C isotope shift in aromatic rings is dominated by two factors. The first, and larger effect, is the change in the normal vibrational modes of the benzene ring upon deuterium substitution,[4] which is approximated to by the 0·289 p.p.m. shift observed for mono-deuteriobenzene itself, and the second, and smaller, effect (ranging from $-0{\cdot}046$ to $+0{\cdot}032$ p.p.m.) is the electronic demand of the substituent: an increase in electron density at a given carbon (negative σ) being associated with an increased isotope shift.

The problem of measuring the polar effects of a substituent at the *ortho* position is one in which only partial success has been achieved,[3] and, although our preliminary data are limited, we suggest that the ^{13}C *ortho* isotope shift, being a difference between two chemical shifts, has resulted in the cancellation of anisotropic and steric effects, and can be adopted as a useful measure of σ_o. The isotope shift sigma σ_o(Is), if it is to be meaningful value, should be expressable in terms of Swain's $\mathcal{F}$ and $\mathcal{R}$,[5] and work is in progress to test this hypothesis.

The second atom isotope shifts recorded show only small variations about the standard shift of benzene at 0·110 p.p.m. A *para* carbon as second atom shows reasonable agreement with σ_p, but an *ortho* or *meta* carbon show no correlation with any σ_o or σ_p. We consider that the second atom shifts are dominated by the effects of the substituent on the vibrational modes of the ring carbons and that the electronic demands of the substituent are of minor importance.

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