Long-range Deuterium Isotope Effects on Chemical Shifts

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SECONDARY isotope effects have been attributed to diverse origins including inductive, steric, and vibrational effects.[1] The isotope shift in n.m.r., reviewed recently,[2] has been explained variously in terms of electrostatic deformations, differences in bond lengths and angles upon isotopic substitution, and thermal population of excited vibrational states. While there are numerous examples[2] of deuterium isotope shifts involving nuclei separated by two bonds in saturated compounds, or separated by several bonds in unsaturated compounds, reports of deuterium isotope shifts through three saturated bonds are sparse.[3–5] Katz and his co-workers[4] noted an upfield isotope shift involving three bonds in deuteriated ethyl acetates, and very minor three-bond shifts are apparent for deuteriated ethylbenzenes.[3] To determine if the deuterium isotope chemical shift persists over a longer range and to gain information about the origin of the isotope shift, we measured the chemical shifts of a series of deuteriated, saturated hydrocarbons.

An upfield shift is observed for 2, 3, and 4 σ-bond separations, but no shift was found with a 5-bond separation (Table).

Clearly, the deuterium isotope shift is not due to protium and deuterium having different inductive effects. The isotope shift, 0·024 p.p.m., for $CD_3{\cdot}CH_3$ is far greater than would be predicted from a consideration of the value, 0·045 p.p.m., for CD_3H and the normal attenuation of the inductive effect with an increasing number of bonds. Additional evidence against an inductive effect is based on the non-proportionality of the number of deuterium atoms substituted in isobutane and the magnitude of the isotope shift. The isotope shift is 0·009 p.p.m. for $DCMe_3$ and 0·012 p.p.m. for $(CD_3)_3CH$.

1,1,1-Trideuterioethane (from $MeCCl_3$, Zn, and $CH_3{\cdot}CO_2D$),[6] 1-deuterio-1,1-dimethylethane (from Me_3CLi and D_2O), 1,1,1,3,3,3-hexadeuterio-2-trideuteriomethylpropane [from $(CD_3)_3CMgCl$ and HCl], 1,1,1-trideuterio-2,2-dimethylpropane (from Me_3CCl and CD_3MgI in refluxing toluene), and 1,1,1-trideuterio-2,2-bis(trideuteriomethyl)-3,3-dimethylbutane [from $(CD_3)_3CMgCl$ and Me_3CCl in refluxing tetrahydrofuran] were prepared by standard procedures and purified by either vacuum line techniques or gas chromatography.

*Proton chemical shifts of deuteriated compounds**

Compound	δ(p.p.m.)[a]	*J*(H–D) (c./sec.)
CDH_3	0·019[b]	1·91[6]
CD_2H_2	0·027[b]	1·89[6]
CD_3H	0·045[b]	1·91[6]
$CD_3{\cdot}CH_3$	0·024 ± 0·001[e]	1·21
$DCMe_3$	0·009 ± 0·001[b]	1·00
$(CD_3)_3CH$	0·012 ± 0·001	0·99
$CD_3{\cdot}CMe_3$	0·003 ± 0·001	d
$(CD_3)_3C{\cdot}CMe_3$	0·000	d

* Measured in CCl_3 with Varian A-60 and HR 100 Spectrometers.

[a] Upfield relative to protium analogue; [b] R. A. Bernheim and B. J. Lavery, *J. Chem. Phys.*, 1965, **42**, 1464; [c] Measurements were faciliated by homonuclear decoupling of Me_3CH; [d] Not observed; [e] Average error.

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