Deuterium Isotope Effect on ^1H Chemical Shift in Pentadeuteriobenzene

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Summary The ^1H n.m.r. spectrum of a mixture of pentadeuteriobenzene and benzene showed that the intermolecular deuterium isotope effect in benzene produces a downfield shift.

^1H N.m.r. spectra of pentadeuteriobenzene (prepared using the method of Renaud and Leitch[1]) were measured on a Hitachi R-22 spectrometer (90 MHz, 35 °C, continuous wave mode) with a probe modified for deuterium spin-decoupling.[2]†

The broad quintet pattern of $[^2H_5]$benzene displayed in Figure (a) is interpreted as being due to complex coupling ($^3J_{HD}$ 1·16 Hz, $^4J_{HD}$ 0·10 Hz, and $^5J_{HD}$ 0·01 Hz). A molar ratio of $[^2H_5]$benzene: benzene of *ca.* 87 : 13 was determined from the integrated intensities of spectra (b) and (c). From Figures (b) and (c) it is clear that the chemical shift of $[^2H_5]$benzene is 0·0032 p.p.m. downfield of that of benzene. This isotopic shift value was determined by averaging the results of 21 measurements. Furthermore, this representative pattern was independent of the variation of the relative concentrations of $[^2H_5]$benzene and benzene. It is known that deuterium substitution causes an upfield shift in both ^1H chemical shifts and ^{13}C chemical shifts for methane,[3,4] ammonia,[5,6] acetone,[7,8] cyclohexane,[9] *etc.* Moreover, deuterium isotopic shifts in the ^{13}C chemical shifts of monodeuteriobenzene[10] and hexadeuteriobenzene[11] are upfield. The downfield shift observed in the present experiment is uncommon and is attributed to the predominant effect of the increased electron density of the carbon skeleton on the π-electron ring current.

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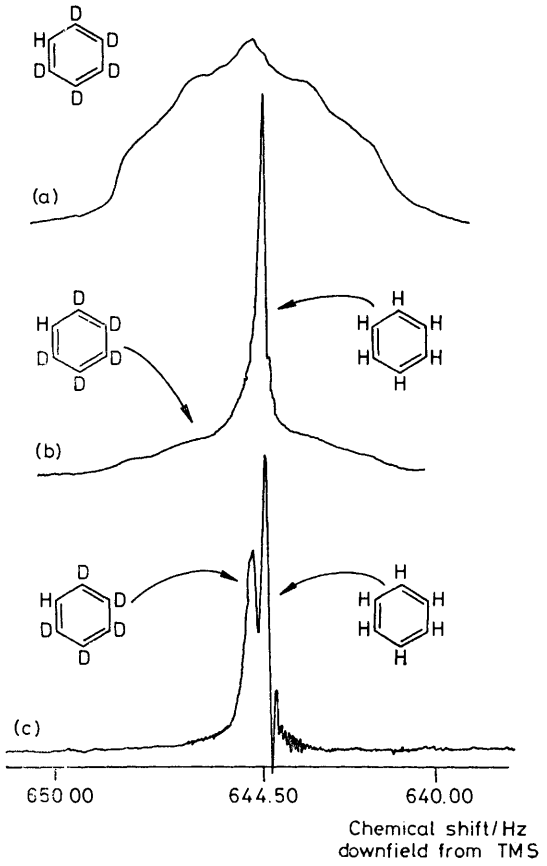

FIGURE. 90 MHz ^1H n.m.r. spectra: (a) $[^2H_5]$benzene, normal spectrum; (b) $[^2H_5]$benzene + benzene mixture (*ca.* 87 : 13 mol. ratio), normal spectrum; (c) as for (b), deuterium spin-decoupled spectrum.

† A mixture of benzene, $[^2H_5]$benzene, and tetramethylsilane (TMS) (as internal reference) was sealed into a 5 mm i.d. Shigemi Standard Joint k.k. 001 tube *in vacuo*. Spectra were recorded at a sweep rate of 0·05 Hz s^{-1}.

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