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^{13}C CHEMICAL SHIFTS OF BRANCHED ALKYLBENZENES. A REINVESTIGATION.

Ludger Ernst

Gesellschaft für Molekularbiologische Forschung mbH

D-3300 Braunschweig-Stöckheim

Mascheroder Weg 1, West Germany

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The ^{13}C NMR chemical shifts of alkylbenzenes had been reported in the early stages of the ^{13}C NMR age[1]. During a recent reinvestigation in this laboratory it was found that there exist some major discrepancies with these early values (see Table).

Table. ^{13}C chemical shifts (δ) of alkylbenzenes as 40% (v:v) solutions in C_6D_6 referenced to internal TMS[a,b,c]

	C-1	C-2	C-3	C-4	C-α	C-β
Toluene	137.80 137.8	129.29 129.3	128.51 128.5	125.66 125.6	21.37 21.3	-- --
Ethylbenzene	144.25 144.1	128.10 128.1	128.60 128.5	125.92 125.9	29.22 29.3	15.80 16.8
i-Propylbenzene	148.82 148.7	126.61 126.6	128.60 128.6	126.06 126.1	34.44 38.9	24.12 24.2
t-Butylbenzene	150.91 149.2	125.35 125.4	128.30 128.4	125.65 125.6	34.57 47.5	31.44 31.7

a) First row for each compound: data from present work, second row: data from ref. 1.

b) Contradictory results underlined.

c) All compounds were also measured as 40% (v:v) solutions in dimethyl sulphoxide-d_6. They showed shifts to higher field by between 0.1 and 0.5 ppm.

While the average agreement between the shifts found in the two studies is better than 0.1 ppm, the underlined values differ by more than 1 ppm. The discrepancies for the α-carbons in both isopropylbenzene (4.5 ppm) and tert-butylbenzene (12.9 ppm) are especially remarkable and are worth comment.

Woolfenden's results[1] have been interpreted in a very popular monograph[2] in terms of a constant increase in shielding of C_α for each additional methyl group; cf. the series 21.3, 29.3, 38.9, 47.5 ppm. If these results were correct they would imply a rather exceptional behaviour of δ_α in the series MePh, EtPh, iPrPh, tBuPh as compared to analogous aliphatic compounds, for it is known that introduction of a methyl group in principle increases the shift of the substituted carbon by ca. 9 ppm. If, however, tertiary or quarternary carbons are being considered, several important correction factors are to be applied (Grant and Paul)[3]. The results of ref. 1 seem not to demand these corrections.

Yet the present findings are in full agreement with what would be expected from a shift prediction according to ref. 3. Taking δ_α = 21.4 for toluene, using an α-effect of +9.1 ppm and the correction factors[3,4] $3^o(2^o)$ = -3.7, $4^o(1^o)$ = -1.5 and $4^o(2^o)$ = -8.4 ppm, one calculates δ_α = 30.5, 35.9 and 35.8 ppm for EtPh, iPrPh and tBuPh, respectively, which compare favourably with the experimental values of 29.2, 34.4 and 34.6 ppm. In short: the chemical ^{13}C shifts of the branched alkylbenzenes do not behave anomalously, but can be predicted by straightforward application of the Grant-Paul approach[3].

Experimental. The alkylbenzenes were obtained from commercial sources in >98% purity. Their authenticity was certified by proton NMR and mass spectra. ^{13}C NMR spectra were run on a Varian XL-100-12 spectrometer at 25.16 MHz in the pulse Fourier transform mode using a single 90^o pulse. 16K data points were accumulated for each spectrum giving an accuracy of the chemical shifts of ±0.024 ppm.

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(1) W.R. Woolfenden, Ph.D. thesis, University of Utah, 1965.

(2) J. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 99.

(3) D.M. Grant and E.G. Paul, J. Amer. Chem. Soc. 86, 2984 (1964)

(4) The correction factor for a tertiary carbon connected to a secondary one is termed $3^o(2^o)$, the other factors correspondingly.