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SUBSTITUENT EFFECTS IN THE ^{1}H N.M.R. SPECTRA OF 4-SUBSTITUTED N-BENZYLIDENEANILINES

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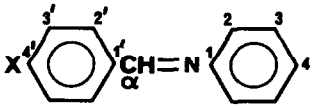
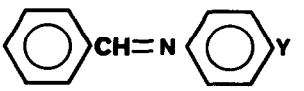
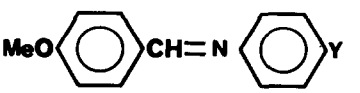
It has been reported[1,2] that the chemical shifts for the α-protons ($\delta_{\alpha-H}$) of the 4'-substituted N-benzylideneanilines (I) correlate with the Hammett σ-constants for the substituents, with a negative value for ρ, our measurements support this correlation. It is further claimed[2] that a correlation exists between $\delta_{\alpha-H}$ and σ for the 4-substituted series (II), but that in this case ρ is positive. In view of the exceptional nature of this claimed correlation[2,3], we have compared our measurements with those reported previously, and we have examined the 4'-methoxy-compounds (III). The results are given in the Table. Clearly, the variation of $\delta_{\alpha-H}$ within each series is very small, even with substituents having widely different electronic effects; the values for the compounds (II) recorded in ref. 2 vary by only 0.05 ppm from the nitro-substituent (σ = + 0.78) to the methoxy-substituent (σ = - 0.27). Moreover, the discrepancies between the values quoted in refs. 1 and 2 suggest that the measurements may not be accurate to within ± 0.01 ppm. The discrepancies may be partly due to the different concentrations used (we find that in carbon tetrachloride, $\delta_{\alpha-H}$ for N-benzylideneaniline is 8.43 ppm at 10% w/v, 8.47 ppm at 5% and 8.48 ppm at 2.5%) but even if an accuracy of ± 0.01 ppm is accepted for the values extrapolated to infinite dilution, we do not believe that the five measurements given in ref. 2 justify the proposed correlation. A further criticism of the earlier results is that solute-solvent interactions may not be insignificant in deuteriochloroform[4]. However, our measurements in carbon tetrachloride do not reveal any correlation between $\delta_{\alpha-H}$ and σ for the series (II) or (III), ($\delta_{\alpha-H}$ for some 2'- and 4'-hydroxy-N-benzylideneanilines



I



II



III

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in dimethyl sulphoxide also varies very little for different 4-substituents)[5].

Table $\delta_{\alpha-H}$[a] for some substituted N-benzylideneanilines

		Compound			
			(II)		(III)[e]
Y	σ_p[b]	(a)[c]	(b)[d]	(c)[e]	
NO_2	0.78	8.43		8.45	8.44
Br	0.23		8.40	8.42	8.34
Cl	0.23	8.43	8.39	8.43	8.37
F	0.06			8.40	8.33
H	0	8.47	8.40	8.43	8.35
Me	-0.17	8.45	8.39		8.35
OEt	-0.24		8.45	8.43	8.37
OMe	-0.27	8.48	8.45		8.42
	(-0.5)[f]			8.48	8.41
NMe_2	-0.83		8.49		

[a] In ppm downfield from internal TMS. [b] A.J. Gordon and R.A. Ford, 'The Chemist's Companion', Wiley-Interscience, New York, 1972. [c] Ref. 2; concentrations ca. 30% (w/v) in $CDCl_3$, and values extrapolated to infinite dilution. [d] Ref. 1; concentrations 0.2-0.5M (ca. 4-10%) in $CDCl_3$. [e] Present work; concentrations < 10% in CCl_4. [f] Not listed in standard compilations; approximate value estimated by comparison with those for NMe_2, NHMe (-0.84), NHEt (-0.61), NHBu (-0.51).

Tabei and Saitou[1] did not claim any correlation, but $\delta_{\alpha-H}$ for the dimethylamino-compound was significantly higher than for the other compounds, as expected for a positive value of ρ. We found $\delta_{\alpha-H}$ for the compound (II) with the structurally similar (though less electron-donating) piperidino-group to be higher than for the other compounds, but the corresponding compound (III) did not behave analogously.

In summary, any electronic interaction between 4-substituents and the α-position of N-benzylideneanilines is so weak that a convincing correlation of substituent constants with proton chemical shifts would require very precise measurements on a large number of compounds.

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