Substituent Effects and Benzene-induced Shifts in the Proton Magnetic Resonance Spectra of *N*-(4-Methoxybenzylidene)anilines

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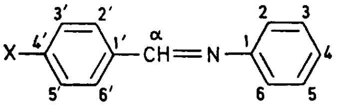
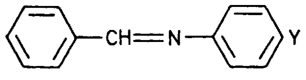
The ^{1}H n.m.r. spectra of 4-substituted *N*-(4-methoxybenzylidine)anilines confirm that transmission of electronic effects from the 4- to the α- or 2′-positions is weak. Correlations of chemical shifts and benzene-induced shifts with Hammett substituent constants and with substituent dipole moments have been used as a probe for through-space field effects.

SEVERAL studies have been reported on the effects of substituents on the n.m.r. spectra of *N*-benzylideneanilines, which throw some light on the transmission of electronic effects within these molecules. In the ^{1}H n.m.r. spectra of 4′-substituted compounds (1) and related series, the chemical shifts for the α-protons correlate with the Hammett constants for the substituents.[1-4] On the other hand, although studies on more sensitive nuclei [^{19}F (ref. 5) and ^{13}C (ref. 2)] have revealed transmission of electronic effects from the 4-position to the α-position, and even to the 4′-position, the effects of 4-substituents on the chemical shifts for the α-protons are very small. Nevertheless, a correlation for the 4-substituted series (2) has been claimed,[2] disputed,[6] and reasserted.[4] In view of the unusual nature of the correlation, for which ρ is *positive*, we have sought a similar effect in another series, the 4′-methoxy-compounds (3).



(1)



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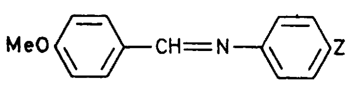

(3)

EXPERIMENTAL

The *N*-benzylideneanilines were prepared by standard methods; the known compounds had m.p.s in agreement with literature values.

N-(4-*Methoxybenzylidene*)-4-*piperidinoaniline* had m.p. 130—131° (from toluene–light petroleum) (Found: C, 77.9; H, 7.3; N, 9.4. $C_{19}H_{22}N_2O$ requires C, 77.5; H, 7.5; N, 9.5%).

The n.m.r. spectra were in most cases measured with a Perkin-Elmer R32 instrument operating at 90 MHz at a series of concentrations in cyclohexane or [$^2H_6$]benzene, with tetramethylsilane as internal reference, at normal probe temperature, and the chemical shifts were extrapolated to infinite dilution. For compounds possessing very low solubility ($\ll$1% w/v), saturated solutions were used, as indicated in Table 1. In two cases the solubility was so low that the spectra were only detectable by means of the Fourier transform technique (Varian CFT20 instrument, operating at 80 MHz; [$^2H_{12}$]cyclohexane as solvent).

Hammett substituent constants were those used previously[6] or were taken from ref. 7. Dipole moment data were taken from refs. 7 and 8. Sign conventions are those adopted in the references cited.

TABLE 1

^{1}H Chemical shifts for
N-(4-methoxybenzylidene)anilines (3) in cyclohexane

Z	σ	$\delta_{\alpha\text{-H}}$	$\delta_{2'\text{-H}}$
NO_2 [a,b]	0.78	8.18	7.74
COMe [a]	0.50	8.21	7.77
CO_2Et	0.45	8.20	7.74
Cl	0.23	8.19	7.73
F	0.06	8.22	7.74
H	0	8.23	7.74
Me [a]	−0.17	8.22	7.72
OEt [a]	−0.24	8.25	7.71
NC_5H_{10} [a,b]	−0.5	8.24	7.69
ρ		+0.049	−0.044
γ [c]		0.86	0.79

[a] Spectra recorded for saturated solutions. [b] Spectra recorded by Fourier transform technique. [c] Correlation coefficient.

RESULTS AND DISCUSSION

It was clear that any correlation of the type sought would only be detectable in the absence of perturbations caused by solvent and concentration effects (*cf.* ref. 4). The chemical shifts were therefore determined for very dilute solutions in cyclohexane, as recorded in Table 1. For the α-protons, the results were remarkably similar to those obtained by the Japanese workers for the series (2). Although the correlation coefficient was not very

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high, we consider that our results reinforce those obtained previously sufficiently to warrant the discussion of the anomalous *positive* value of ρ, for which a through-space field effect has been proposed.[9] Since such an effect might also be apparent at the 2′-positions, the chemical shifts for these protons were also determined (Table 1), but the variations were very small and the correlation could not be regarded as significant.

TABLE 2

^{1}H Chemical shifts (δ) in benzene and solvent-induced shifts [$\Delta = \delta$(cyclohexane) − δ(benzene)] for *N*-(4-methoxybenzylidene)anilines (3)

Z	σ	μ [a]/D	μ cos θ [b]/D	$\delta_{\alpha\text{-H}}$	$\Delta_{\alpha\text{-H}}$	$\delta_{2'\text{-H}}$	$\Delta_{2'\text{-H}}$
NO_2	0.78	3.93	3.93	7.82	0.36	(7.70)	(0.04)
COMe	0.50	2.95	1.97	8.05	0.16	7.78	−0.01
CO_2Et	0.45	1.90	0.89	8.02	0.18	7.74	0.00
Cl	0.23	1.58	1.58	8.01	0.18	7.78	−0.05
F	0.06	1.35	1.35	8.06	0.16	7.78	−0.04
H	0	0	0	8.18	0.05	7.81	−0.07
Me	−0.17	−0.37	−0.37	8.26	−0.04	7.83	−0.11
OEt	−0.24	−0.14	−0.31 [c]	8.28	−0.03	7.85	−0.14
NC_5H_{10}	−0.5	−1.74	−1.51 [d]	8.35	−0.11	7.84	−0.15
ρ				+0.390	−0.341	+0.112	−0.156
r_σ				0.950	0.948	0.928	0.973
r_μ					0.958		0.970
$r_{\mu \cos \theta}$					0.969		0.909

[a] Dipole moment of corresponding monosubstituted benzene. [b] Component of group dipole moment along bond to ring. [c] Obtained by using value of θ for OMe. [d] Obtained by using value of θ for NMe_2.

If through-bond effects of 4-substituents are indeed small,* and the observed variations are due to through-space effects, it might be anticipated that such effects would be reflected in aromatic solvent-induced shifts, since these are believed to arise from dipole–induced dipole [11] (or dipole–quadrupole [12]) interactions within the solvation sphere of the solute. Our results are recorded in Table 2. Marked benzene-induced shifts were indeed observed, and showed significant correlations with both the Hammett substituent constants and the substituent group dipole moments. (The correlations with the component of the group dipole moments along the bond to the ring were only marginally better in the case of the α-protons, and significantly worse in the case of the 2′-protons.)

Although benzene-induced n.m.r. shifts have been extensively studied, few attempts to correlate them with substituent constants have been reported (*cf.* refs. 13—15). Our results suggest that a search for similar correlations in other systems might be profitable and might give further information on field effects in the neighbourhood of organic molecules.

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* Studies on the u.v. spectra of substituted *N*-benzylideneanilines also reinforce this hypothesis, except for cases where a very strong push–pull effect is apparent.[10]

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