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Eu(DPM)$_3$-INDUCED SHIFTS IN SUBSTITUTED ANILINES. THE IMPORTANCE OF BASICITY AND STERIC EFFECTS

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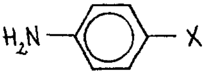
Beauté, Wolkowski, and Thoai[3)] have shown recently that Yb(DPM)$_3$-induced ^{1}H n.m.r. shifts in amines are qualitatively determined by the steric accessibility of the nitrogen lone pair as well as by the basicity of the amine. Their paper prompts us to report our results on several substituted anilines.

In the series of para-substituted anilines (1a through 1g) we found an almost linear correlation between basicity (given in terms of pK$_a$-values[4)]) and n.m.r. shifts (Δδ) of ortho- and meta-protons caused by addition of 0.2 moles of Eu(DPM)$_3$ per mole of 1. Fig. 1 gives the results of these measurements.



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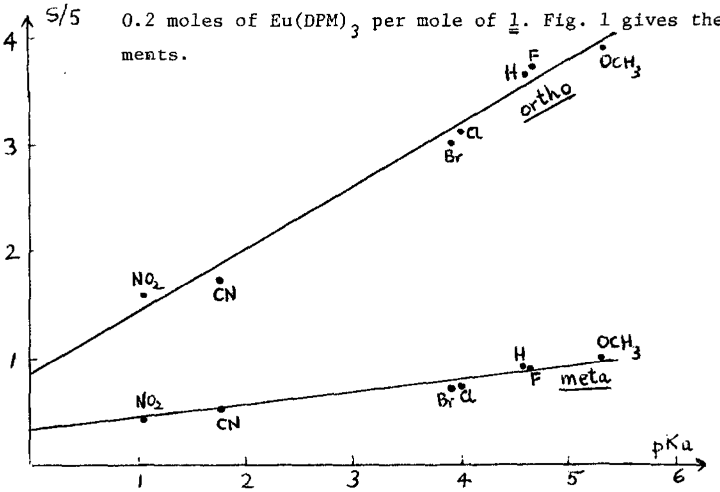
a: X = NO$_2$
b: X = CN
c: X = Br
d: X = Cl
e: X = H
f: X = F
g: X = OCH$_3$



X	pK$_a$	S/5 ortho	S/5 meta
NO$_2$	1.02	1.60	0.44
CN	1.74	1.74	0.57
Br	3.91	3.02	0.72
Cl	3.98	3.15	0.74
H	4.58	3.68	0.92
F	4.65	3.72	0.91
OCH$_3$	5.29	3.91	0.99

Fig.1: Correlation between pK$_a$-values of p-substituted anilines 1 and shifts S/5 of o- and m-protons induced by addition of o.2 molar equivalents of Eu(DPM)$_3$. Solvent: CDCl$_3$

An illustrative example of spectral change by addition of Eu(DPM)$_3$ is given in Fig. 2 for the case of 4-fluoroaniline (**1f**). The normal 60-MHz spectrum (CDCl$_3$ as solvent) shows a complex multiplet structure whereas addition of 0.13 molar equivalents of the shift reagent results in a high-field triplet for protons H^3 and H^5, thus revealing the same magnitude of J_{H^3,F^4} and J_{H^2,H^3}, and a low-field doublet of doublets for H^2 and H^6 giving the values of J_{H^2,H^3} and of J_{H^2,F^4}.

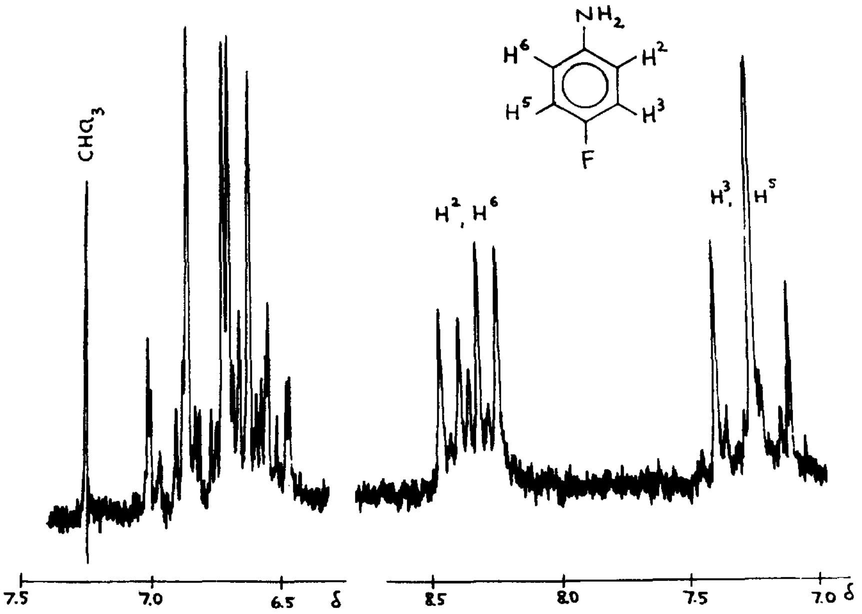
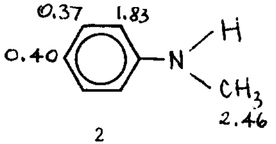


Fig.2: 60-MHz ^{1}H n.m.r. spectrum of 4-fluoroaniline (**1f**) in CDCl$_3$ (left); same after addition of 0.13 molar equivalents of Eu(DPM)$_3$ (right)

The linear correlation between pK$_a$ and induced shifts no longer stands if molecules of different steric requirements are compared. *N*-Methylaniline (**2**) and *N*,*N*-dimethylaniline (**3**), *e.g.*, although of greater basicity (pK$_a$ = 4.85 and 5.06, resp.) than aniline (pK$_a$ = 4.58) show a remarkable decrease of induced shifts due to steric inhibition of coordination to Eu(DPM)$_3$ by substitution of the nitrogen atom.



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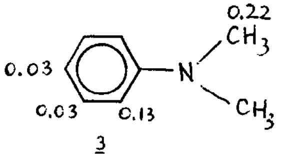

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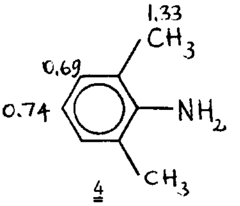
(Figures given with the formulae represent S/5-values as defined above.)

This steric effect is less severe with substitution in the ortho-positions as shown by 2,6-dimethylaniline (4) and 2,4,6-tri-tert.-butylaniline (5).



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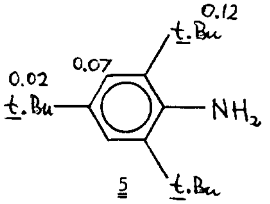

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N,N-Dimethyl-o-toluidine gives no shifts of the ring protons and very small ones for the N- and C-methyl groups (0.03 and 0.02, resp.).

We wish to emphasize that only relative but not absolute values of our Eu(DPM)$_3$-induced shifts are meaningful as their magnitude depends on the molar ratio [reagent]:[amine], thus on the purity of the shift reagent[5]. With one commercially available sample we observed shifts which were about 30% less in magnitude than those reported here.

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3) C.Beauté, Z.W.Wolkowski, and N.Thoai, Tetrahedron Letters 817 (1971).

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5) H.Hart and G.M.Love, Tetrahedron Letters 625 (1971).