

EQUILIBRIUM NH-ACIDITY OF POLYFLUORINATED ARYLAMINES AND
BENZANILIDES

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Equilibrium NH-acidity of the range of polyfluoroaromatic amines and benzanilides containing Ar_F -group (C_6F_5 , $4-C_5F_4N$) on the nitrogen atom has been established in relation to 9-phenylfluorene (pK 18.5) by overmetallation method in dimethyl sulfoxide (cation K^+). Acidity of para-substituted NH-acids of the type $p-XC_6F_4NHC_6F_5$ and $p-XC_6F_4NHC(O)Ph$ ($X = Me_2N, MeO, Me, H, F, Cl, Br, CF_3$) has been determined in DMSO. From these data Hammet correlations for these series have been found. Examination of pK values for investigated compounds and respective non-fluorinated NH-acids shows that acidifying effect (ΔpK) of C_6F_5 -group to neighboring N-H-bond are more that of Ph-group from 6,5 to 7,5 pK units. The same difference of acidifying effects of C_6F_5 - and Ph-groups have been found in CH-acids (from 5 to 6 pK units from the results of pK s in dimethoxyethane). This is attributed to the increase of inductive influence of C_6F_5 -group on the acidity both CH- and NH-acids.

The ρ_K - σ correlations

Series	Equation
$p\text{-XC}_6\text{F}_4\text{NHC}_6\text{F}_5$	$\rho_K = -3.45\sigma_p^- + 12.6$ $r -0.972, s 0.33, n 8$
$p\text{-XC}_6\text{F}_4\text{NHC(O)C}_6\text{H}_5$	$\rho_K = -2.92\sigma_p^- + 13.6$ $r -0.966, s 0.25, n 6$

The ρ_K values of polyfluorinated arylamines and benzamides in DMSO (cation K^+) relative to 9-phenylfluorene (ρ_K 18.5)

Compound	ρ_K
$\text{C}_6\text{F}_5\text{NH}_2$	23.1
$4\text{-NH}_2\text{C}_5\text{F}_4\text{N}$	19.2
$\text{C}_6\text{F}_5\text{NHPH}$	19.2
$4\text{-Me}_2\text{NC}_6\text{F}_6\text{F}_4\text{NHC}_6\text{F}_5$	13.6
$4\text{-MeC}_6\text{F}_4\text{NHC}_6\text{F}_5$	13.3
$4\text{-HC}_6\text{F}_4\text{NHC}_6\text{F}_5$	12.8
$\text{C}_6\text{F}_5\text{NHC}_6\text{F}_5$	12.6
$4\text{-BrC}_6\text{F}_4\text{NHC}_6\text{F}_5$	12.2
$4\text{-ClC}_6\text{F}_4\text{NHC}_6\text{F}_5$	12.0
$\text{C}_6\text{F}_5\text{NHC}_{10}\text{F}_7^-$	11.8
$4\text{-CF}_3\text{C}_6\text{F}_4\text{NHC}_6\text{F}_5$	10.6
$4\text{-NCC}_6\text{F}_4\text{NHC}_6\text{F}_5$	9.1
$4\text{-MeOC}_6\text{F}_4\text{NHC(O)Ph}$	14.1
$4\text{-MeC}_6\text{F}_4\text{NHC(O)Ph}$	14.2
$4\text{-HC}_6\text{F}_4\text{NHC(O)Ph}$	13.6
$\text{C}_6\text{F}_5\text{NHC(O)Ph}$	13.0
$4\text{-CF}_3\text{C}_6\text{F}_4\text{NHC(O)Ph}$	11.8
$\text{C}_6\text{F}_5\text{NHC(O)C}_6\text{F}_5$	10.8