

ORGANIC CHEMISTRY

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ABOUT THE COVER

The cover depicts a new kind of molecular structure, one characterized by a spherical cluster of 60 carbon atoms. This compound, referred to as "buckminsterfullerene," has been described by Professor Richard E. Smalley and his coworkers in the Chemistry Department at Rice University. They suggest that it may be present among the products formed by high-vacuum laser vaporization of graphite. The interior of the molecule is large enough to accommodate other atoms and the + sign represents an atom of lanthanum trapped within the spherical cavity. The colored dots indicate the approximate van der Waals surface of the molecule. Theoretical calculations indicate that buckminsterfullerene and its metal complexes should be quite stable, yet further research is needed to conclusively establish the proposed structure.

In addition to Professor Smalley, I would also like to thank Professor Florante Quiocho and John C. Spurlino of the Biochemistry Department at Rice for permission to reproduce their computer graphics depiction of buckminsterfullerene.

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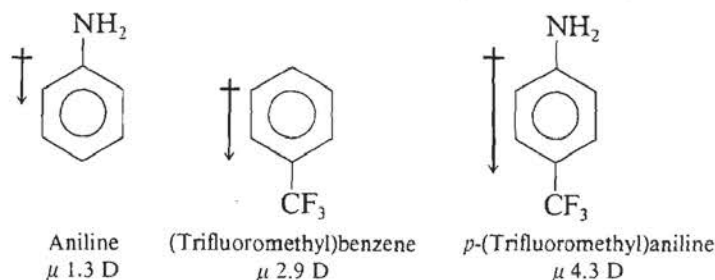
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The direction of polarization is not revealed directly by dipole moment measurements but can be deduced by examining the effects of substituents. The dipole moment of *p*-(trifluoromethyl)aniline, for example, is approximately equal to the sum of the separate dipole moments of aniline and (trifluoromethyl)benzene.



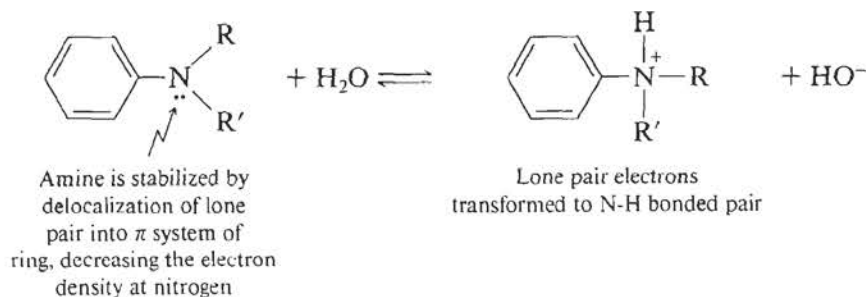
The separate effects of the amino group and the trifluoromethyl group must reinforce, rather than oppose, each other. Since the trifluoromethyl group attracts electrons, the amino group must release them.

PROBLEM 24.4 Which would you expect to have the greater dipole moment, *p*-dinitrobenzene or *p*-nitroaniline? Why?

Because of its electronegativity nitrogen tends to withdraw electrons from carbon by polarization of the electron distribution in σ bonds. Because nitrogen has an unshared pair of electrons, it can donate them to adjacent π systems. Dipole moment data reveal that the π donor effect of an amino substituent on an aromatic ring substantially exceeds its electron-withdrawing effect on σ bonds.

24.4 BASICITY OF ARYLAMINES

Aromatic amines are several orders of magnitude less basic than alkylamines; while K_b for most alkylamines is on the order of 10^{-5} (pK_b 5), arylamines have K_b 's in the 10^{-10} range. The sharply decreased basicity of arylamines arises because the stabilizing effect of lone pair electron delocalization is sacrificed on protonation.



The aromatic ring does very little to disperse the positive charge in the ammonium ion. Indeed, since the ring carbon attached to nitrogen is sp^2 hybridized, it is electron withdrawing and destabilizes the ammonium ion. Stabilization of the amine and destabilization of the ammonium ion combine to make the equilibrium constant for amine protonation smaller for arylamines than for alkylamines. This relationship is depicted in Figure 24.3, where the free energies of protonation of cyclohexylamine

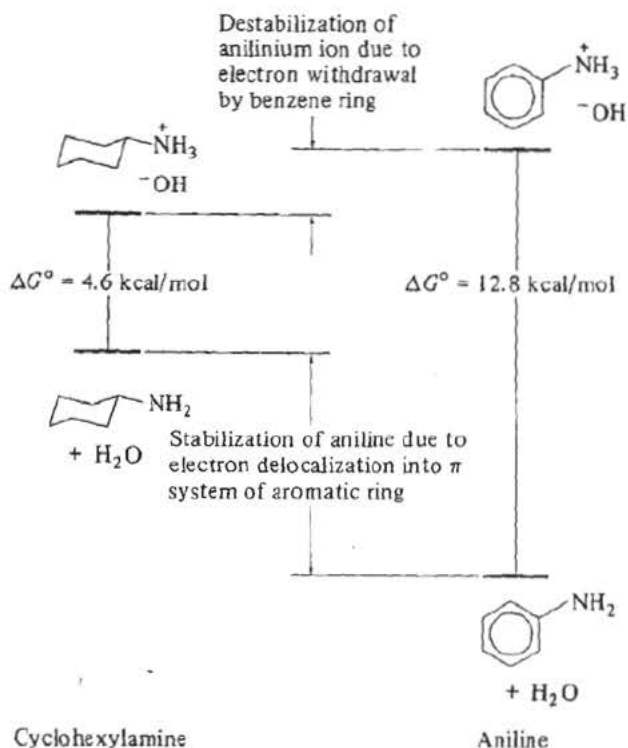
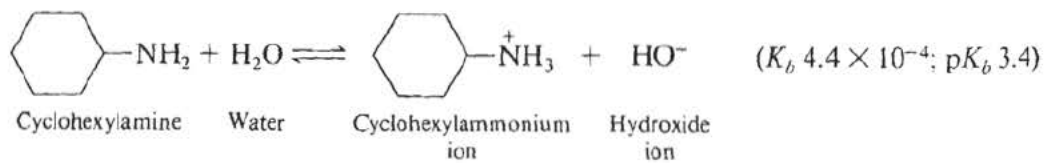
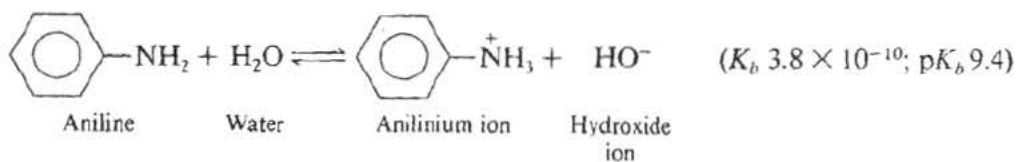


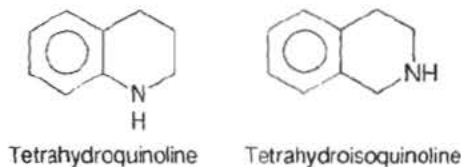
FIGURE 24.3 Free energy changes accompanying protonation of aniline and cyclohexylamine by water.

and aniline are compared. As measured by their respective K_b 's, cyclohexylamine is almost 1 million times more basic than aniline.



When the proton donor is a strong acid, arylamines can be completely protonated. Aniline is extracted from an ether solution into 1 *N* hydrochloric acid because it is converted to a water-soluble anilinium ion salt under these conditions.

PROBLEM 24.5 The two amines shown differ by a factor of 40,000 in their K_b values. Which is the stronger base? Why?



Conjugation of the amino group with a second aromatic ring, then a third, reduces its basicity even further. Diphenylamine is 6300 times less basic than aniline, while triphenylamine is scarcely a base at all, being estimated as 10^8 times less basic than aniline and 10^{14} times less basic than ammonia.

$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
Aniline	Diphenylamine	Triphenylamine
(K_b 3.8×10^{-10} ; pK_b 9.4)	(K_b 6×10^{-14} ; pK_b 13.2)	($K_b \sim 10^{-19}$; $pK_b \sim 19$)

The effects of some representative aryl substituents on the basicity of arylamines are summarized in Table 24.2. In general, electron-donating groups increase the basicity of aniline slightly while electron-withdrawing groups decrease it, in some cases dramatically. Thus, the basicity constant K_b of *p*-toluidine is 5 to 6 times greater than that of aniline, but aniline is 220 times more basic than its *p*-trifluoromethyl derivative.

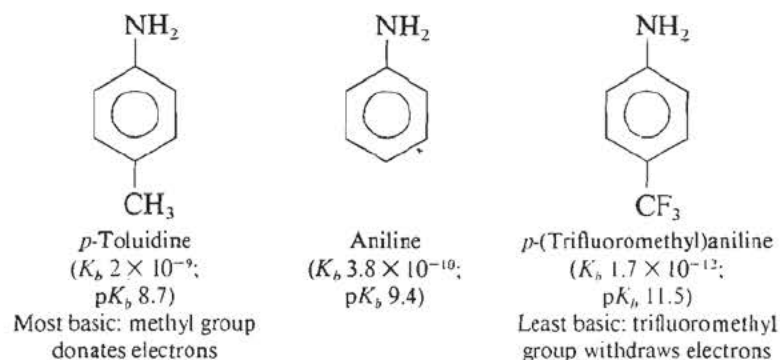


TABLE 24.2
Basicities of Some Arylamines

Substituent in $H_2NC_6H_4X$	Position of substituent X and K_b (pK_b) ^a		
	Ortho	Meta	Para
Standard of comparison is aniline			
H	3.8×10^{-10} (9.4)	3.8×10^{-10} (9.4)	3.8×10^{-10} (9.4)
Electron-releasing substituents increase basicity slightly			
OCH ₃	3.8×10^{-10} (9.4)	1.6×10^{-10} (9.8)	2.2×10^{-9} (8.7)
CH ₃	3.3×10^{-10} (9.5)	5.5×10^{-10} (9.3)	2×10^{-9} (8.7)
Electron-withdrawing substituents decrease basicity			
Cl	4.5×10^{-12} (11.3)	3.8×10^{-11} (10.4)	7.2×10^{-11} (10.2)
$\begin{array}{c} O \\ \\ CCH_3 \end{array}$	2.5×10^{-12} (11.6)	4×10^{-11} (10.4)	5×10^{-12} (11.3)
CN	8.9×10^{-14} (13.1)	5.6×10^{-12} (11.2)	5.5×10^{-13} (12.3)
NO ₂	5.5×10^{-15} (14.3)	2.9×10^{-12} (11.5)	1×10^{-13} (13.0)

^a In water at 25°C.

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