

ORGANIC CHEMISTRY

FRANCIS A. CAREY

*Department of Chemistry
University of Virginia*

McGRAW-HILL BOOK COMPANY

*New York St. Louis San Francisco Auckland Bogotá
Hamburg London Madrid Mexico Milan
Montreal New Delhi Panama Paris São Paulo
Singapore Sydney Tokyo Toronto*

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.

ORGANIC CHEMISTRY

Copyright © 1987 by McGraw-Hill, Inc. All rights reserved. Printed in the United States of America. Except as permitted under the United States Copyright Act of 1976, no part of this publication may be reproduced or distributed in any form or by any means, or stored in a data base or retrieval system, without the prior written permission of the publisher.

2 3 4 5 6 7 8 9 0 DOWDOW 8 9 4 3 2 1 0 9 8 7

ISBN 0-07-009831-X

This book was set in Serif by Progressive Typographers, Inc. The editors were Karen S. Mislner, Randi B. Kashan, and David A. Damstra; the production supervisor was Leroy A. Young; the designer was Rafael Hernandez. The drawings were done by J & R Services, Inc. R. R. Donnelley and Sons Company was printer and binder.

Library of Congress Cataloging-in-Publication Data

Carey, Francis A. (date)

Organic chemistry.

Bibliography: p.

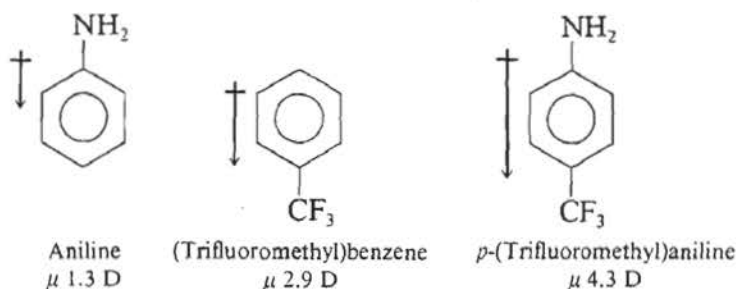
Includes index.

I. Chemistry, Organic. I. Title.

QD251.2.C364 1987 547 86-10374

ISBN 0-07-009831-X

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.



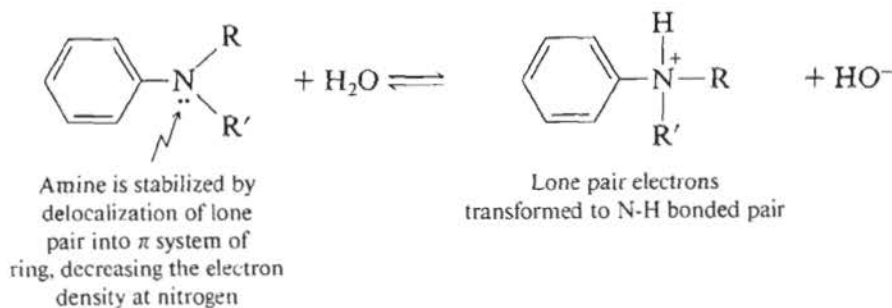
The separate effects of the amino group and the trifluoromethyl group must reinforce, rather than oppose, each other. Since the trifluoromethyl group attracts electrons, the amino group must release them.

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

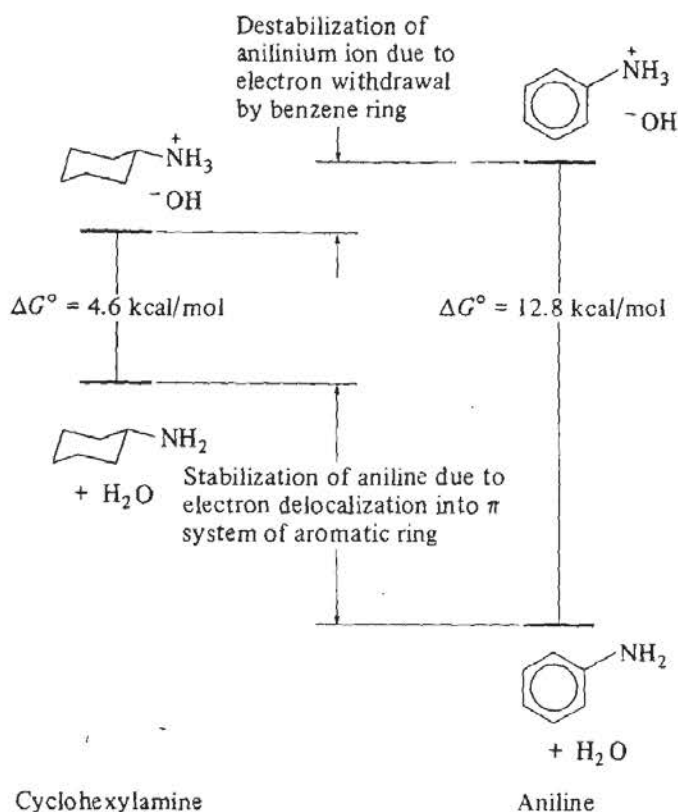
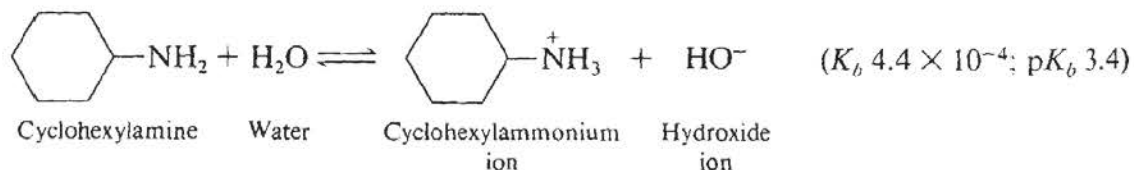
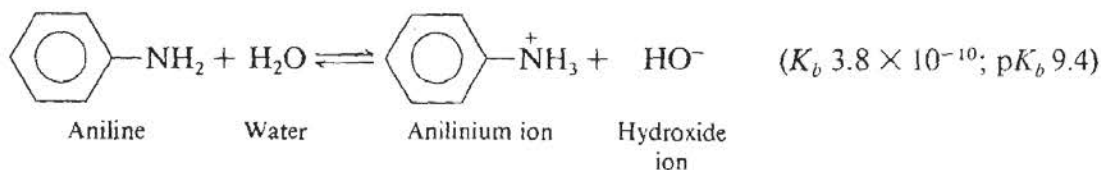


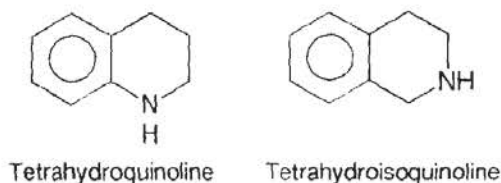
FIGURE 24.3 Free energy changes accompanying protonation of aniline and cyclohexylamine by water.

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
$(K_b, 3.8 \times 10^{-10};$ $pK_b, 9.4)$	$(K_b, 6 \times 10^{-14};$ $pK_b, 13.2)$	$(K_b, \sim 10^{-19};$ $pK_b, \sim 19)$

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.

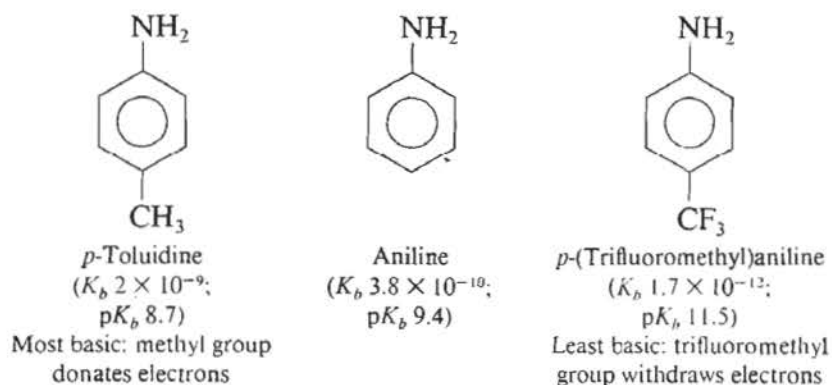


TABLE 24.2
Basicities of Some Arylamines

Substituent in $H_2NC_6H_4X$	Position of substituent X and K_b (pK_b)*		
	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)

* In water at 25°C

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.