



Organic Chemistry

SECOND EDITION

G. Marc Loudon

Purdue University



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Library of Congress Cataloging-in-Publication Data

Loudon, G. Marc.
Organic chemistry.

Includes index.

1. Chemistry, Organic. I. Title.

QD251.Z.L68 1988 547 87-29996

ISBN 0-8053-6643-1

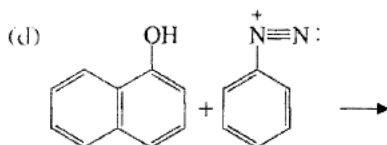
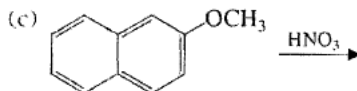
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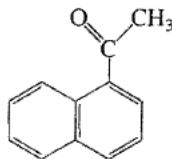
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ABCDEFGHIJ-VH-8987

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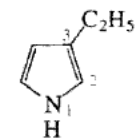
- 4 Propose a synthesis of the following compound from naphthalene. (The Friedel-Crafts reaction cannot be used because it gives a mixture of 1- and 2-acetylnaphthalene that is difficult to separate.)



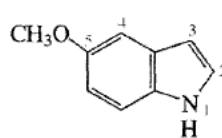
24.2 INTRODUCTION TO THE AROMATIC HETEROCYCLES

A. Nomenclature

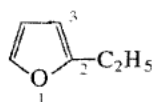
The names and structures of some common aromatic heterocyclic compounds are given in Fig. 24.1. This figure also shows how the rings are numbered in systematic nomenclature. In all but a few cases, a heteroatom is given the number 1. (Isoquinoline is an exception.) As we see in thiazole and oxazole, oxygen and sulfur are given a lower number than nitrogen when a choice exists. Substituent groups are given the lowest number consistent with this scheme.



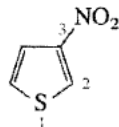
3-ethylpyrrole



5-methoxyindole



2-ethylfuran



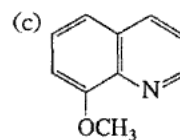
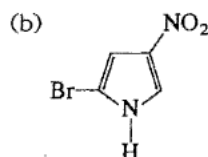
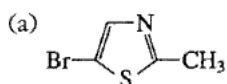
3-nitrothiophene

(These are the same rules used in numbering and naming saturated heterocyclic compounds; see Secs. 8.1C and 23.1B.)

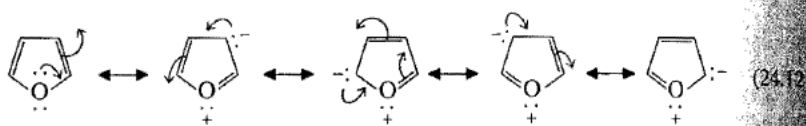
Problems

5 Draw the structure of (a) 4-(dimethylamino)pyridine; (b) 4-ethyl-2-nitroimidazole.

6 Name the following compounds:

**B. Structure and Aromaticity**

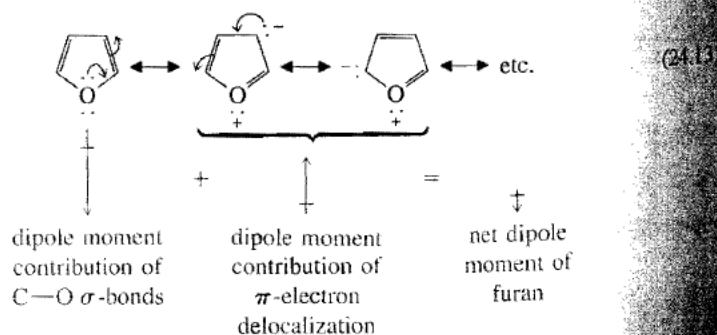
The aromatic heterocyclic compounds furan, thiophene, and pyrrole can be written as resonance hybrids, illustrated here for furan.



Since separation of charge is present in all but the first structure, the first structure is considerably more important than the others. Nevertheless, the importance of the other structures is evident if we compare the dipole moments of furan and tetrahydrofuran, a saturated heterocyclic ether.

	tetrahydrofuran	furan
dipole moment	1.7 D	0.7 D
boiling point	67°	31.4°

The dipole moment of tetrahydrofuran is attributable mostly to the bond dipoles of its polar C—O single bonds. That is, electrons in the σ -bonds are pulled toward the oxygen because of its electronegativity. This same effect is present in furan, but in addition there is a second effect: the resonance delocalization of the oxygen unshared electrons into the ring shown in Eq. 24.12. This tends to push electrons away from oxygen into the π -electron system of the ring.



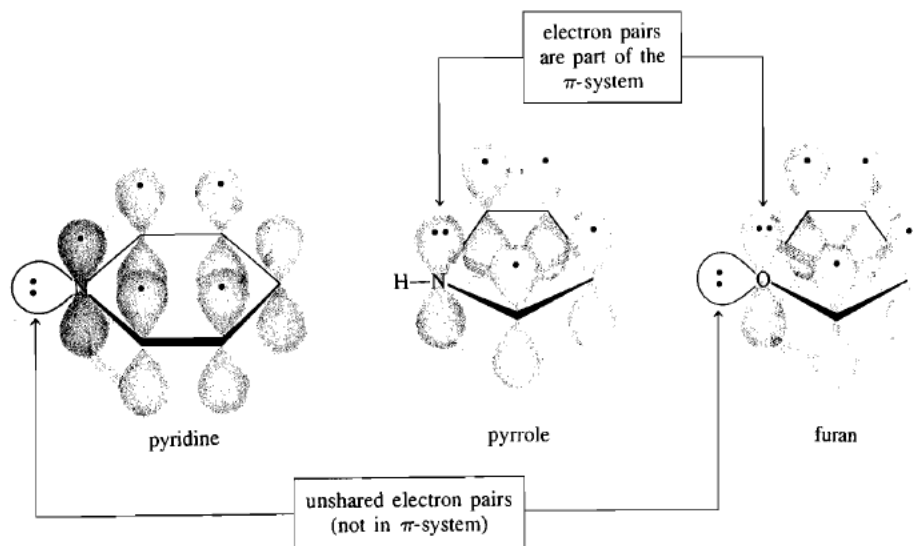
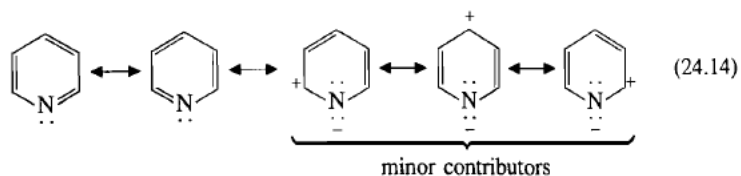


Figure 24.5 The configurations of the unshared electron pairs and π -electrons in pyridine, pyrrole, and furan. The orbitals in each $4n + 2$ -electron π -system are shown in grey; π -interactions are shown in color. Unshared electron pairs not in the π -system are shown in white.

Because these two effects in furan nearly cancel, furan has a very small dipole moment. We can see the effect of dipole moment on the relative boiling points of tetrahydrofuran and furan.

Pyridine, like benzene, can be represented by two equivalent neutral resonance structures. Three additional structures, although involving separation of charge, have some importance because they reflect the relative electronegativity of nitrogen.



The aromaticity of some heterocyclic compounds was considered in our discussion of the Hückel $4n + 2$ rule (Sec. 15.6D). It is important to understand which unshared electron pairs in a heterocyclic compound are part of the $4n + 2$ aromatic π -system, and which are not. Heteroatoms involved in formal double bonds—such as the nitrogen of pyridine—contribute one π -electron to the six π -electron aromatic system, just like each of the carbon atoms in the π -system. The orbital containing the unshared electron pair of the pyridine nitrogen is perpendicular to the p orbitals of the ring and is therefore not involved in π -bonding (Fig. 24.5a). An unshared electron pair on a heteroatom in a formally allylic position—such as the un-

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