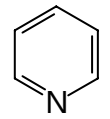
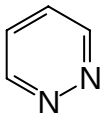
Chapter 2 Aromatic Heterocycles

2.1 Six-atom, six-π-electron heterocycles

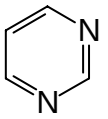
Aza derivatives of benzene



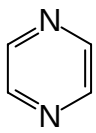
pyridine



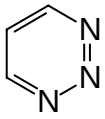
pyridazine



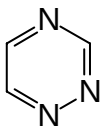
pyrimidine



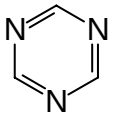
pyrazine



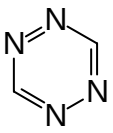
1,2,3-triazine



1,2,4-triazine

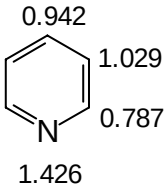


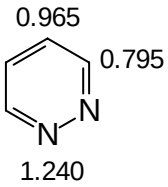
1,3,5-triazine

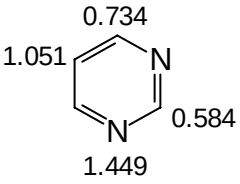


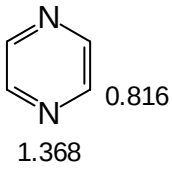
1,2,4,5-tetrazine

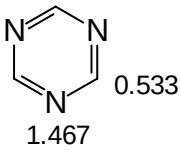
π-Electron populations for azines



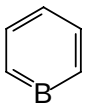




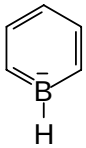




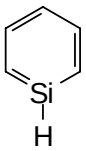
Other heterobenzenes



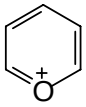
borabenzene



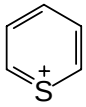
1*H*-borata-benzene



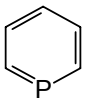
silabenzene



pyrylium cation



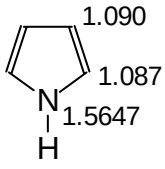
thiopyrylium cation

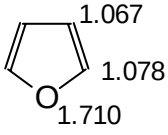


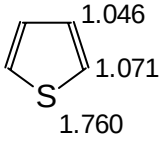
phospha-benzene

2.2 Five-atom, six-π-electron heterocycles

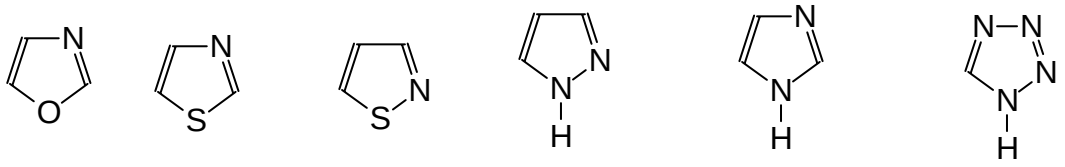
2π-Electron populations for pyrrole, furan and thiophene







Aromatic five-membered heterocycles with two or more heteroatoms



oxazole thiazole isothiazole 1*H*-pyrazole 1*H*-imidazole 1*H*-tetrazole

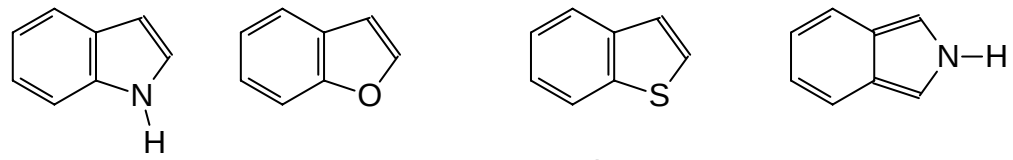
2.3 Benzo-fused ring systems

Benzo-fused six-membered nitrogen heteroaromatics

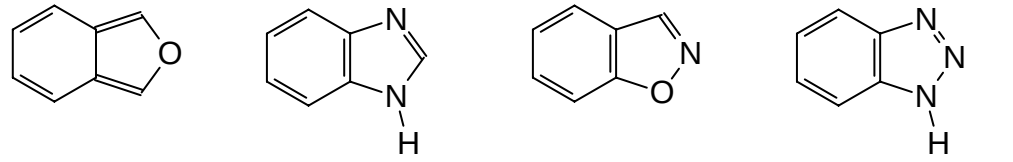
quinoline isoquinoline cinnoline quinazoline

quinoxaline phthalazine 1,2,3-benzotriazine 1,2,4-benzotriazine

Five-membered benzo-fused heterocycles

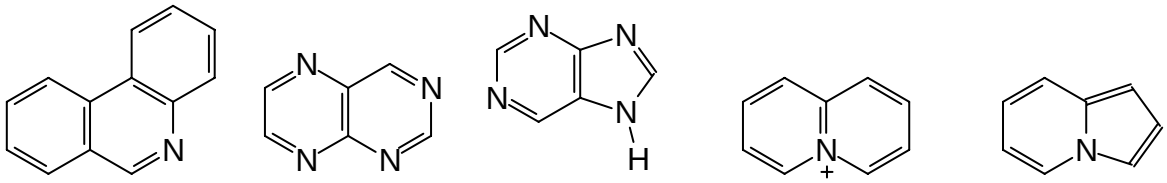


indole benzofuran benzo[*b*]thiophene isoindole



isobenzofuran benzimidazole 1,2-benzisoxazole 1*H*-benzotriazole

Other fused heterocycles



phenanthridine pteridine purine quinolizinium cation indolizine

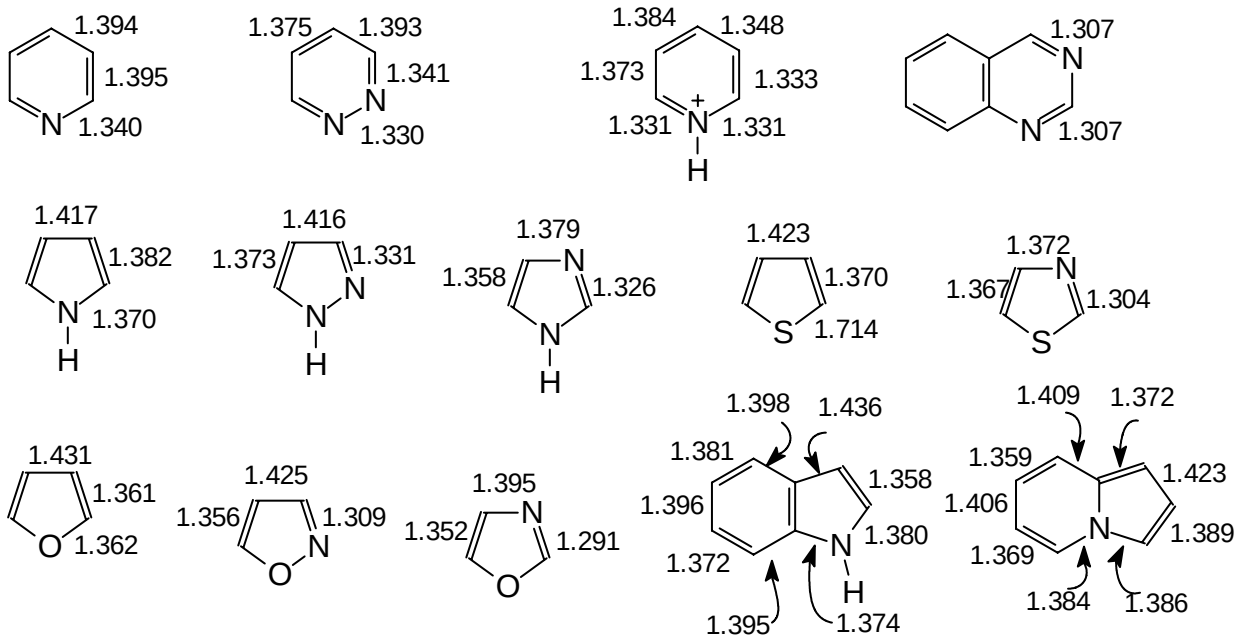
2.4 Some criteria of aromaticity in heterocycles

Bond lengths

Typical lengths (Å) of single and double bonds linking sp^2-hybridized atoms

C−C	1.48	C=C	1.34
C−N	1.45	C=N	1.27
C−O	1.36	C=O	1.22
C−S	1.75	C=S	1.64
N−N	1.41	N=N	1.23

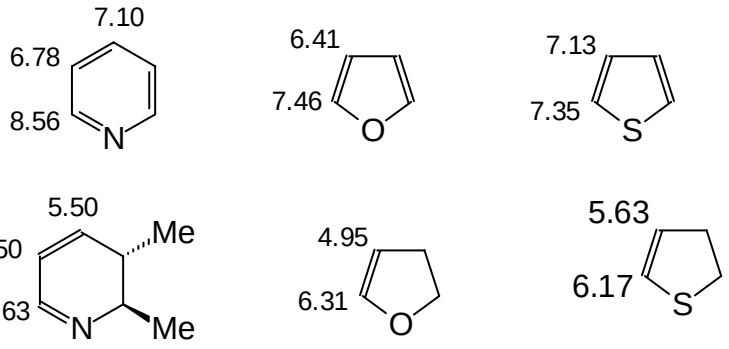
Bond distances (Å) in some heteroaromatic compounds



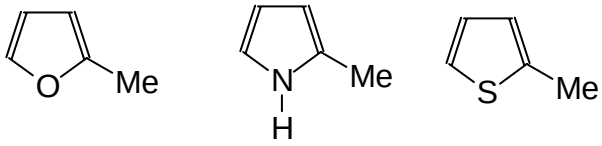
Aromaticity indices of heterocycles based on structure (%)

Benzene	100	Pyridine	82
Pyridazine	65	Pyrimidine	67
Pyrazine	75	Pyrrole	37
Thiophene	45	Furan	12
Pyrazole	61	Imidazole	43
1,2,4-Triazole	71	Tetrazole	80

Chemical shifts of aromatic and nonaromatic heterocycles



Ring current effects on methyl substituents

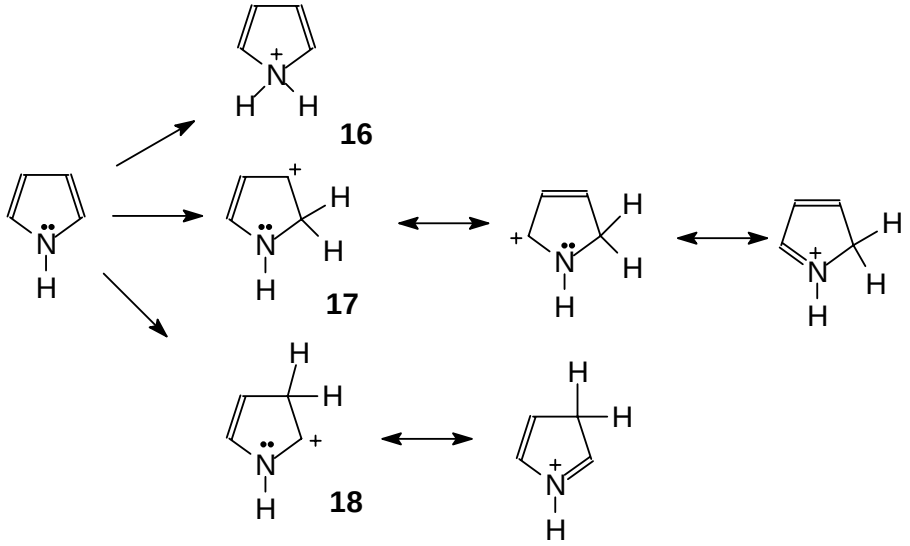


δ (Me) observed	2.30	2.18	2.48
calculated	2.14	1.97	2.19
downfield shift	0.16	0.21	0.29

General conclusions

1. The degree of aromatic character of the monocyclic azabenzenes is slightly less than that of benzene and tends to decrease with increasing numbers of ring nitrogen atoms.
2. Other six-membered ‘heterobenzenes’ have substantial aromatic character.
3. The aromatic character of five-membered monocyclic heterocycles is lower than that of benzene.
4. Five-membered heterocycles containing oxygen tend to show less aromatic character than those containing nitrogen and sulfur.
5. In the five-membered heterocycles aromatic character tends to increase as the number of nitrogen atoms in the ring increases.
6. Benzo-fused heterocyclic ring systems have lower aromatic character than the corresponding monocyclic heterocycles.

2.5 Reactivity of heteroaromatic compounds



16 **17** **18**

17>**18**>**16**

2.6 Tautomerism of heteroaromatic compounds