

Aromaticity In Benzenoid and non-Benzenoid compounds

Aromaticity or aromatic character exhibits properties which are very much different from those of the analogous aliphatic and alicyclic compounds. Valence Bond theory of aromaticity along with experimental results shows benzene as a regular flat hexagon. All the six hydrogen atoms lying in the same plane of the ring and each C-C-H valency angle is 120° . X-ray analysis shows all the C-C bond lengths are the same i.e. 1.397 \AA . This lies between that of a single bond (1.54 \AA) and that of a double bond (1.33 \AA). Meaning that all the bonds in Benzene have double bond character. The regular hexagonal structure accounts for all the bonding electrons in C_6H_6 to be Six.



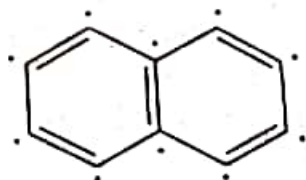
Molecular orbital theory shows each carbon atom in benzene is in a state of trigonal hybridisation. Hence in C_6H_6 , there are six C-H bonds, six C-C bonds and six $2p_z$ electrons, one on each C-atom, which are all parallel and perpendicular to the ring plane.

Monocyclic aromatic hydrocar

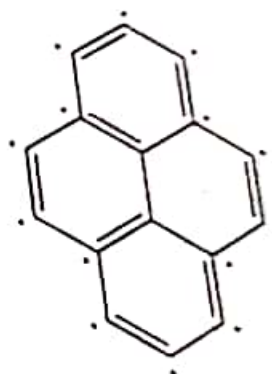
The smallest annulene of the $(4n + 2)$ type is [10]annulene. van Tamelen *et al.* (1971) prepared it by the photolysis of *trans*-9,10-dihydronaphthalene.

[Dehydro] [14]annulene, $C_{14}H_{12}$, is a $(4n)$ molecule, but shows the magnetic properties required for aromaticity. In this molecule, the two inner hydrogen atoms are too far apart to experience annular interaction, and consequently the molecule is *planar*. 1,8-Bisdehydro[14]annulene, $C_{14}H_{10}$ ($4n + 2$) molecule; it has aromatic magnetic property (note that it is not possible to represent this molecule with conjugated double bonds).

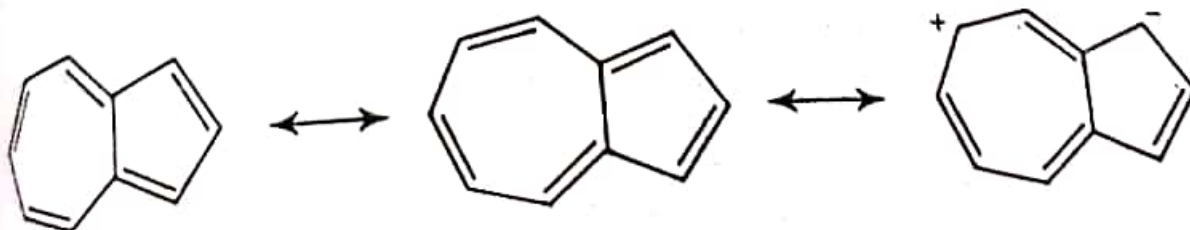
Polycyclic systems. As we have seen, Hückel's $(4n + 2)$ rule applies to *monocyclic* systems. The rule, however, is not necessarily successful for *polycyclic* conjugated systems; it is successful, e.g., naphthalene (10 π -electrons), but not in others, e.g., pyrene (16 π -electrons). These are aromatic *chemically* (both are *benzenoid* compounds). It has been suggested



naphthalene



pyrene



azulene

The $(4n + 2)$ rule should be applied to the *peripheral* (conjugated) π -electron systems: naphthalene, 10 ($n = 2$) peripheral π -electrons; pyrene, 14 π -electrons.

Azulene (intensely blue solid, m.p. 99°C). There are two Kekulé resonance structures containing 10 π -electrons ($n = 2$); and 10 peripheral π -electrons. The five-membered ring contains two π -electrons and the seven-membered ring contains eight π -electrons.

Fig. 20.1

(c)

(d)

...all six carbon atoms, and so are completely delocalised (Fig. 20.1d. of p 129) Since
 2p electrons are involved, six M.O.s are possible, three bonding and three antibonding
 These are shown in Fig. 20.2 (I), (II), (III) are bonding, and (IV), (V), (VI) are anti-
 bonding, all have a node in the plane of the ring; but (II) and (III) have one node, (IV) and (V)
 and (VI) three nodes perpendicular to the plane of the ring. Now, as we have seen, no more

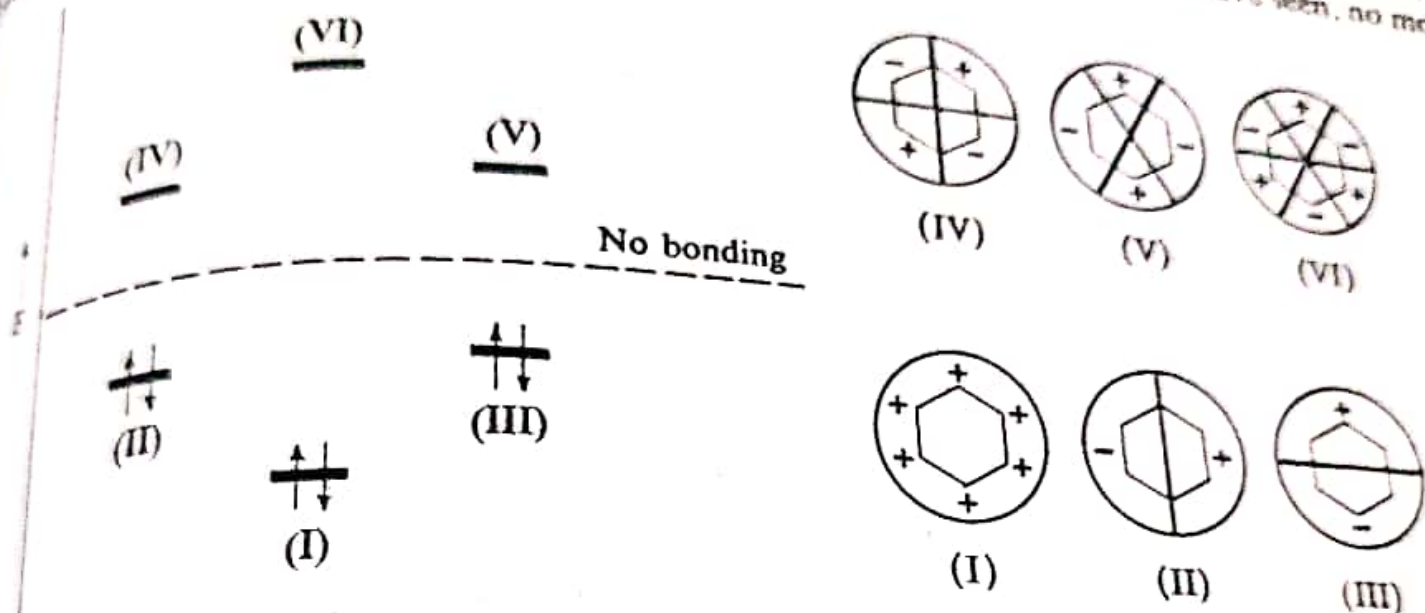


Fig. 20.2

two electrons can occupy any particular M.O. Furthermore, in the ground state, the
 electrons of benzene will occupy, in pairs, the M.O.s of lowest energy. These three are
 (I), (II) and (III); these are the M.O.s in which the number of nodes are fewer than in (IV), (V)
 and (VI). When benzene is in an excited state, one or more of the π -electrons will occupy the h
 igher level M.O.s.

In the ground state, the total energy of the three pairs of *delocalised* π -electrons (Fig. 20.2) is
 lower than that of three pairs of *localised* π -electrons ((b) or (c)), and hence the benzene m
 olecule is stabilised by delocalisation (resonance).

Hückel (4n + 2) rule for aromaticity. Hückel (1937) carried out M.O. calculations on
 cyclic systems C_nH_n containing n π -electrons and each carbon atom providing one π -
 electron. He found a result connected *aromatic stability* (high delocalisation energy or high r
 esonance energy) with the presence of $(4n + 2)$ π -electrons in a closed shell, where

Monocyclic aromatic hydrocarbons

integer. Thus, to be *aromatic*, a molecule must have 2 ($n = 0$), 6 ($n = 1$), 10 ($n = 2$), ... π -electrons. In this description of aromaticity, no mention is made of the *number* of carbon atoms in the ring; the essential requirement is the presence of $(4n+2)$ π -electrons. Another requirement, however, for aromaticity is (reasonable) planarity of the ring. If the ring is not planar, overlap of the p -orbitals is diminished or absent. Thus, if a molecule is a monocyclic (reasonably) planar system and contains $(4n+2)$ π -electrons, that molecule will exhibit aromatic character, *i.e.*, will have unusual stability. For benzene, $n = 1$, and the molecule has a closed shell of six π -electrons, *i.e.*, all occupied bonding molecular orbitals are doubly filled (see Figs. 20.2 and 3).

Non-benzenoid aromatics. Now let us examine the $(4n+2)$ rule in more detail. Figure 20.3 shows the energy levels and configurations of π -electrons for monocyclic systems, C_nH_n (where n is 3-8; note that the number of energy levels is equal to the number of carbon atoms and that M.O. energy levels which are the *same* for a given molecule are said to be *degenerate*). Inspection of Fig. 20.3 (the molecules are in the ground state) shows that only benzene is a $(4n+2)$ π -electron molecule ($n = 1$) and consequently is the only molecule which has a closed shell electron configuration. Thus, for the 3-8 rings, only benzene is aromatic.

	3	4	5	6	7	8
n	0	1	1	1	1	2
Number of π -electrons	$4n+3$	$4n$	$4n+1$	$4n+2$	$4n+3$	$4n$
$E \uparrow$						
non-bonding						

Fig. 20.3