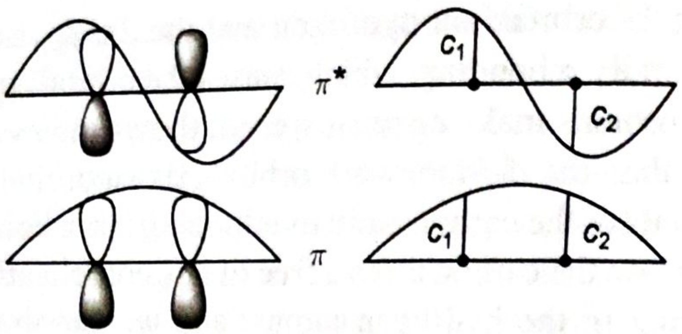


Fig. 1.23 The π orbitals of ethylene and the electron in the box

A better picture, which we keep as a mental reservation when confronted with the conventional drawings, is the contour diagram. A better sense of the π overlap from two p orbitals is given in Fig. 1.24, where we see more clearly from the contours on the left that in the bonding combination there is an enhanced electron population between the nuclei, but that it is no longer directly on a line between the nuclei. The wire-mesh diagrams illustrate the shapes of the π and π* orbitals with some sense of their 3D character.

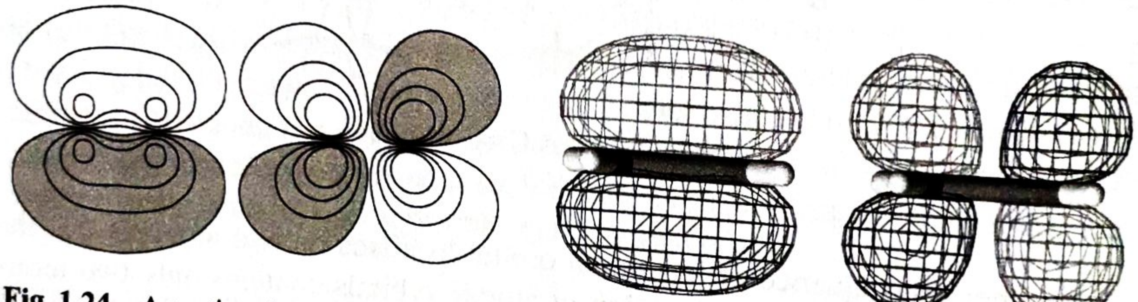


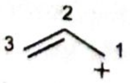
Fig. 1.24 A section through the contours of the π and π* wave functions of ethylene, and wire-mesh outlines of one contour of each

1.4 Conjugation—Hückel Theory

The two p orbitals of ethylene are described as being conjugated with each other in making the π bond. To make longer conjugated systems we add one p orbital at a time to the π bond to make successively the allyl system, butadiene, the pentadienyl system and so on. We continue to separate completely the σ framework (using the 2s, $2p_x$ and $2p_y$ orbitals on carbon with the 1s orbitals on hydrogen) from the π system made up from the $2p_z$ orbitals.

1.4.1 *The Allyl System*

The members of the allyl system are reactive intermediates, and there are three of them: the allyl cation **1.1**, the allyl radical **1.2** and the allyl anion **1.3**. They have the same orbitals, but different numbers of electrons.

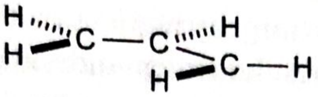


1.1

1.2

1.3

The cation, radical and anion have the same σ framework **1.4**, with fourteen bonding molecular orbitals filled with 28 electrons made by mixing the 1s orbitals of the five hydrogen atoms either with the 2s, $2p_x$ and $2p_y$ orbitals of the three carbon atoms or with the sp^2 hybrids. The allyl systems are bent not linear, but we shall treat the π system as linear to simplify the discussion.



1.4

The π system is made up from the three p_z orbitals on the carbon atoms. The linear combination of these orbitals takes the form of Equation 1.9, with three terms, creating a pattern of three molecular orbitals, ψ_1, ψ_2 and $\psi_3{}^*$. In the allyl cation there are two electrons left to go into the π system after filling the σ framework (and in the radical, three, and in the anion, four).

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 \tag{1.9}$$

We can derive a picture of these orbitals using the electron in the box, and recognising that we now have three orbitals and therefore three energy levels. If the lowest energy orbital is, as usual, to have no nodes (except the inevitable one in the plane of the molecule), and the next one up one node, we now need an orbital with two nodes. We therefore construct a diagram, Fig. 1.25, with one more turn of the sine curve, to include that for 540°, the next one up in energy that fulfils the criterion that there are nodes at the edges of the box, one bond length out, as well as the two inside.

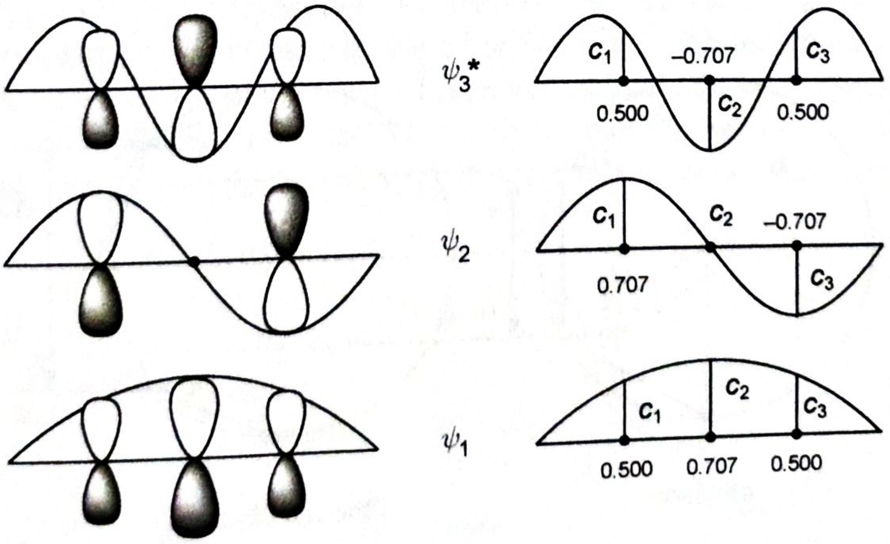


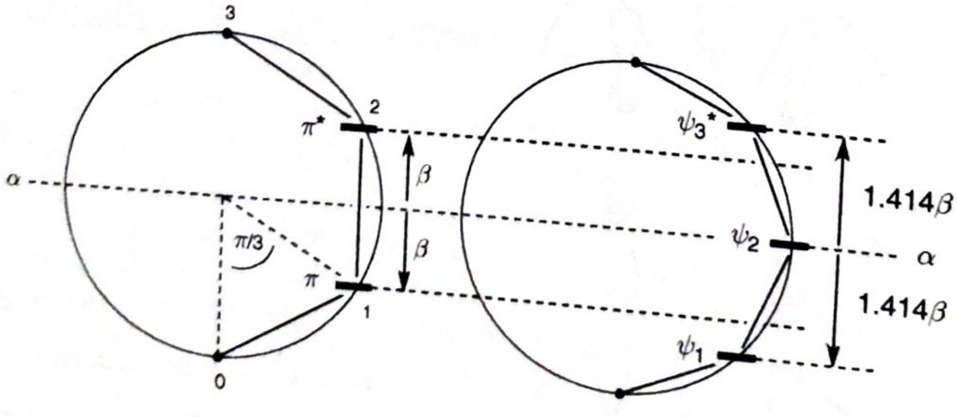
Fig. 1.25 The π orbitals of the allyl system

The lowest-energy orbital, ψ_1, has bonding across the whole conjugated system, with the electrons concentrated in the middle. The next orbital up in energy ψ_2 must have a node in the middle of the conjugated system occupied by an *atom* and not by a *bond*. Having a node in the middle means having a zero coefficient c_2 on C-2, and hence the coefficients on C-l and C-3 in this orbital must be $\pm 1/\sqrt{2}$, if, squared and summed, they are to equal one. The atomic orbitals in ψ_2 are far apart in space and their repulsive interaction does not significantly raise the energy of this molecular orbital relative to that of an isolated p orbital—whether filled or not, it does not contribute significantly to the overall bonding. If the sum of the squares of the three orbitals on C-2 is also to equal one, then the coefficients on C-2 in ψ_1 and ψ_3* must also be $\pm 1/\sqrt{2}$. Finally, since symmetry requires that the coefficients on C-1 and C-3 in ψ_1 and ψ_3* have the same absolute magnitude, and the sum of their squares must equal $1-(1/\sqrt{2})^2$, we can deduce the set of *c*-values in Fig. 1.25.

In this picture of the bonding, we get no immediate appreciation of the energies of these orbitals relative to those of ethylene. The nonbonding orbital ψ_2 is clearly on the α level, that of a p orbital on carbon, and ψ_1 is lowered by the extra π bonding and ψ_3* is raised. To assess the energies, there is a simple geometrical device that works for linear conjugated systems. The conjugated system, *including the dummy atoms at the ends of the sine curves*, is inscribed vertically inside a circle of radius 2β, following the convention that one π bond in ethylene defines β. This is shown for ethylene and the allyl system in Fig. 1.26. The energies *E* of the π orbitals can then be calculated using Equation 1.10:

$$E = 2\beta\cos\frac{k\pi}{n+1} \qquad 1.10$$

where *k* is the number of the atom along the sequence of *n* atoms. This is simply an expression based on the trigonometry of Fig. 1.26. The π orbital of ethylene, the placing of which defines the value of β, is on the first level ($k = 1$) of the sequence of two ($n = 2$) reading anticlockwise from the bottom. Thus the energies of the π orbitals in the allyl system are 1.414β below the α level, and 1.414β above the α level.



ethylene the allyl system

Fig. 1.26 Energies of π molecular orbitals in ethylene and the allyl system

We can gain further insight by building the picture of the π orbitals of the allyl system in another way. Instead of mixing together three p orbitals on carbon, we can combine two of them in a π bond first, and then work out the consequences of having a third p orbital held within bonding distance of the C=C π bond. We have to consider the effect of the p orbital, on the right of Fig. 1.27, on both the π and π^* orbitals of ethylene on the left. If we look *only* at the interaction of the p orbital with the π orbital, we can expect to create two new orbitals in much the same way as we saw when the two $2p_z$ orbitals of carbon were allowed to interact in the formation of the π bond of Fig. 1.22. One orbital ψ_1 will be lowered in energy and the other ψ_x raised. Similarly if we look *only* at its interaction with the π^* orbital, we can expect to create two new orbitals, one lowered in energy ψ_y and one raised $\psi_3{}^*$. We cannot create four orbitals from three, because we cannot use the p orbital separately twice.

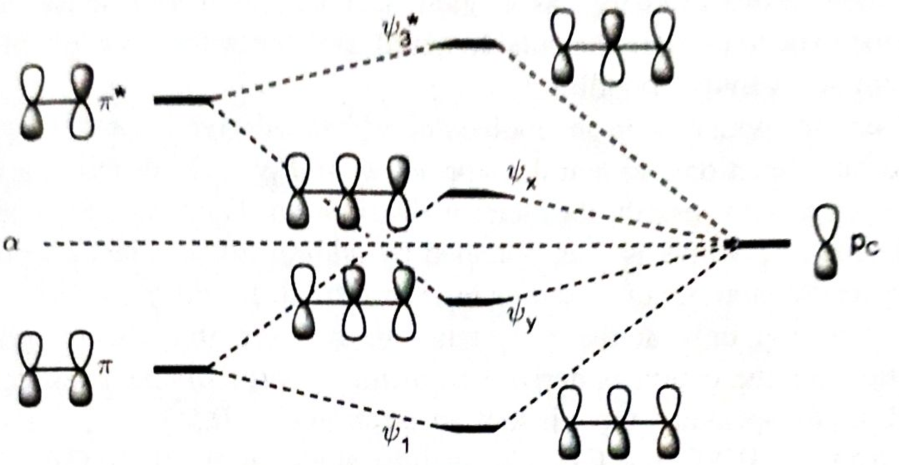


Fig. 1.27 A p orbital interacting independently with π and π^* orbitals. (No attempt is made to represent the relative sizes of the atomic orbitals)

We can see in Fig. 1.27 that the orbital ψ_1 has been created by mixing the p orbital with the π orbital in a *bonding* sense, with the signs of the wave function of the two adjacent atomic orbitals matching. We can also see that the orbital $\psi_3{}^*$ has been created by mixing the p orbital with the π^* orbital in an *antibonding* sense, with the signs of the wave functions unmatched. The third orbital that we are seeking, ψ_2 in Fig. 1.28, is a combination created by mixing the p orbital with the π orbital in an *antibonding* sense *and* with the π^* orbital in a *bonding* sense. We do not get two

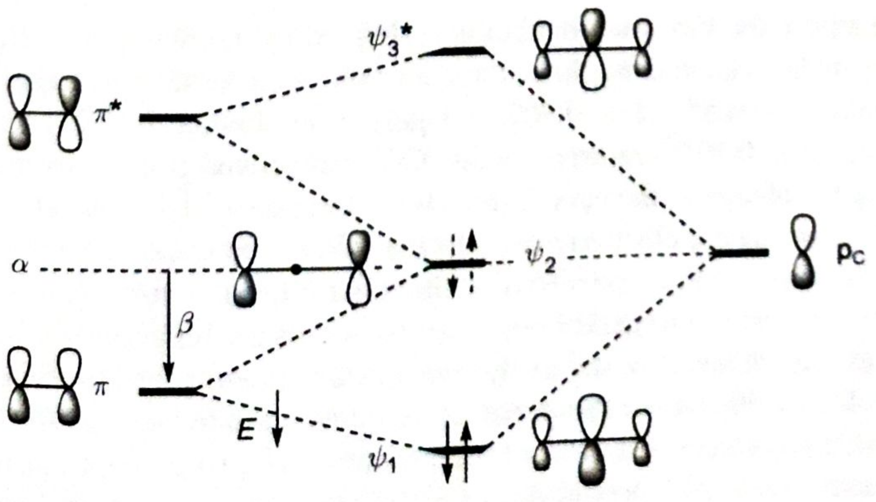
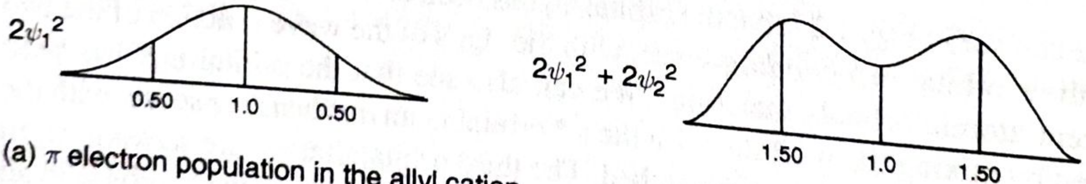


Fig. 1.28 The allyl system by interaction of a p orbital with π and π^* orbitals

orbitals, ψ_x and ψ_y in Fig. 1.27, but something in between, namely ψ_2 in Fig. 1.28. By adding ψ_x and ψ_y in this way, the atomic orbitals, drawn to the left of ψ_x and ψ_y in Fig. 1.27 cancel each other out on C-2 and reinforce each other on C-1 and C-3, thereby creating the molecular orbital ψ_2 in Fig. 1.28.

We have of course arrived at the same picture for the molecular orbitals as that created from mixing the three separate p orbitals in Fig. 1.25. The overall π energy of the allyl cation, radical and anion has dropped relative to the energy of an isolated p orbital and ethylene by $2E$, which we know from Fig. 1.26 is $2 \times 0.414\beta$ or something of the order of 116 kJ mol^{-1}. (It is not uncommon to express these drops in energy as a 'gain' in energy—in this sense, the gain is understood to be to us, or to the outside world, and hence means a loss of energy in the system and stronger bonding.)

The electron population in any molecular orbital is derived from the square of the atomic orbital functions, so that the sine waves in Fig. 1.25 describing the coefficients are squared to describe the electron distribution. The π electron population in the molecule as a whole is then obtained by adding up the electron populations, allowing for the number of electrons in each orbital, for all the *filled* π molecular orbitals. Looking only at the π system, we can see that the overall electron distribution for the cation is derived from the squares of the coefficients in ψ_1 alone. Roughly speaking, there is half an electron (2×0.5^2) on C-1 and C-3, and one electron (2×0.707^2) on C-2. This is illustrated graphically in Fig. 1.29a. Since the nucleus has a charge of +1, the excess charge on C-1 and C-3 is +0.5, in other words the electron deficiency in the cation is concentrated at the two ends.



(a) π electron population in the allyl cation

(b) π electron population in the allyl anion

Fig. 1.29 Total π electron populations in the allyl cation and anion

For the anion, the electron population is derived by adding up the squares of the coefficients in both ψ_1 and ψ_2. Since there are two electrons in both orbitals, there are 1.5 electrons ($2 \times 0.5^2 + 2 \times 0.707^2$) roughly centred on each of C-1 and C-3, and one electron (2×0.707^2) centred on C-2. This is illustrated graphically in Fig. 1.29b. Subtracting the charge of the nucleus then gives the excess charge as −0.5 on C-1 and C-3, in other words the electron excess in the anion is concentrated at the two ends.

One final detail with respect to this, the most important orbital, is that it is not quite perfectly nonbonding. Although the two atoms are separated they do interact slightly, as can be seen in ψ_2 in the wire-mesh drawing of the nonlinear allyl system in Fig. 1.30, where the perspective allows one to see that the right-hand lobes, which are somewhat closer to the viewer, are just perceptibly repelled by the left-hand lobes. This orbital does not therefore have exactly the same energy as an isolated p orbital—it is slightly higher in energy.

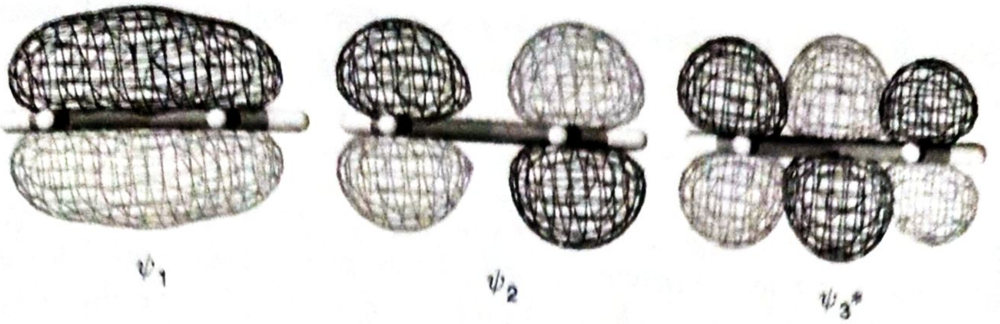
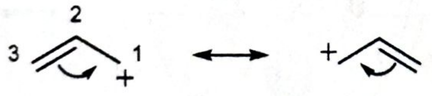


Fig. 1.30 The π molecular orbitals of the allyl system

There is a problem with the conventional representation **1.1** of an allyl cation, which seems to imply that C-1 has the positive charge (an empty p orbital), and that C-2 and C-3 are in a double bond. But we could have drawn the cation **1.1**, redrawn as **1.1a**, equally well the other way round as **1.1b**, and the curly arrow symbolism shows how the two *drawings* are interconvertible. This device is at the heart of valence bond theory. For now we need only to recognise that these two drawings are representations of the *same* species—there is no reaction connecting them, although many people sooner or later fall into the trap of thinking that 'resonance' like **1.1a** → **1.1b** is a step in a reaction sequence. The double-headed arrow interconnecting them is a useful signal; this symbol should only be used to show the equivalence of 'resonance structures' and never to represent an equilibrium. There are corresponding pairs of drawings for the radical and for the anion.



1.1a **1.1b**

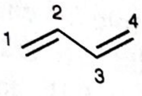
1.1c

One way of avoiding these misleading structures is to draw the allyl cation as in **1.1c**, illustrating the delocalisation of the p orbitals with a dashed line, and placing the positive or negative charge in the middle. The trouble with these drawings is that they are hard to use clearly with curly arrows in mechanistic schemes, and they do not show that the positive charge is largely concentrated on C-1 and C-3. It is probably better in most situations to use one of the localised drawings for the cation, radical or anion, rather than the 'molecular orbital' version like **1.1c**, but always make the necessary mental reservation that each of the localised drawings implies the other, and that the molecular orbitals give a better picture.

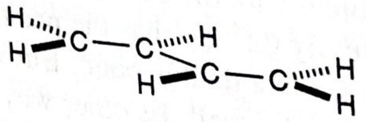
As we shall see later, the most important orbitals with respect to reactivity are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). These are the *frontier orbitals*. For the allyl cation, the LUMO is ψ_2, and the drawings of the allyl cation **1.1a** and **1.1b** emphasise the electron distribution in the LUMO. Similarly, the corresponding drawings of the allyl anion emphasise ψ_2, the HOMO for that species. It is significant that it is the LUMO of the cation and the HOMO of the anion that will prove to be the more important frontier orbital in each case. Similarly in the allyl radical, the localised drawing illustrates the electron distribution in the singly occupied molecular orbital (SOMO), the most important orbital in that species.

1.4.2 *Butadiene*

The next step up in complexity comes with four p orbitals conjugated together, with butadiene **1.5** as the parent member. There is a σ framework **1.6** with 36 electrons and four p orbitals to house the remaining four. Using the electron in the box with four p orbitals, we can construct Fig. 1.31, which shows the four wave functions, inside which the p orbitals are placed at the appropriate regular intervals. We get a new set of orbitals, ψ_1, ψ_2, ψ_3*, and ψ_4*, each described by Equation 1.11 with four terms.



1.5



1.6

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4 \qquad 1.11$$

The lowest-energy orbital ψ_1 has all the c-values positive, and hence bonding is at its best. The next-highest energy level has one node, between C-2 and C-3; in

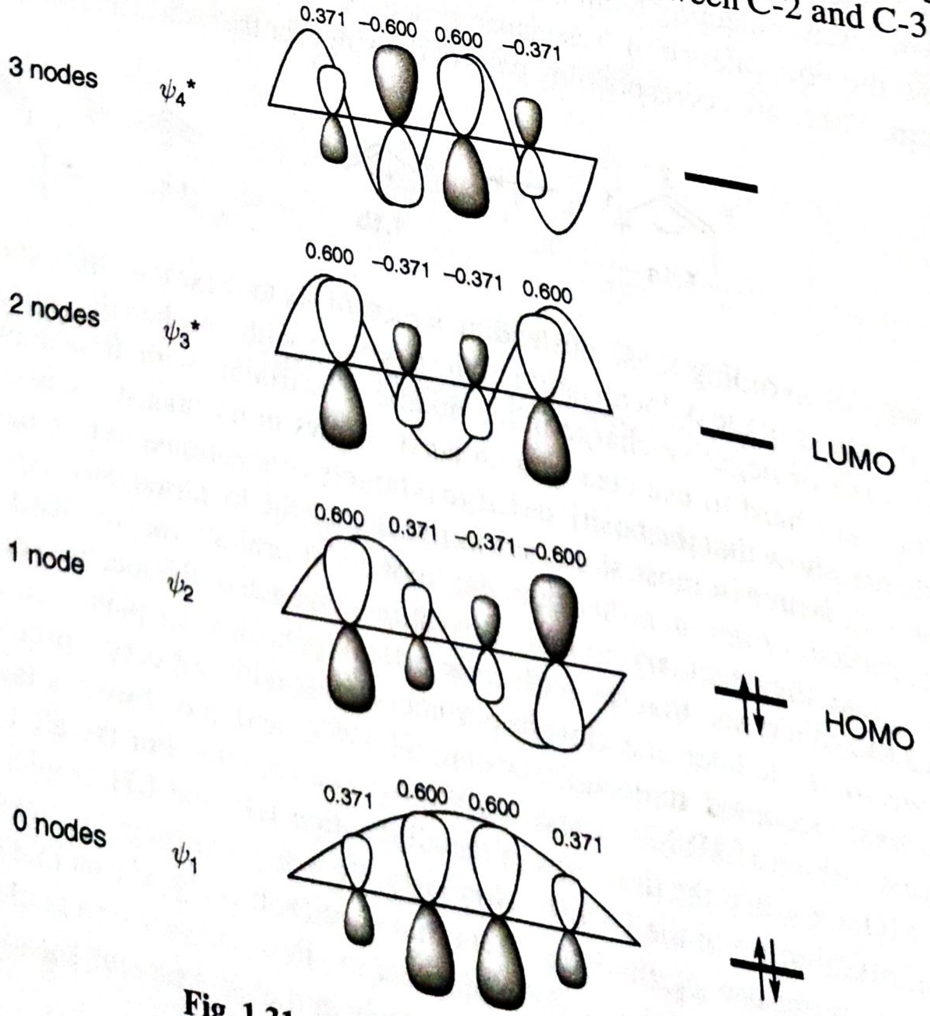


Fig. 1.31 π Molecular orbitals of butadiene

other words, c_1 and c_2 are positive and c_3 and c_4 are negative. There is therefore bonding between C-l and C-2 and between C-3 and C-4, but not between C-2 and C-3. With two bonding and one antibonding interaction this orbital is also overall bonding. Thus the lowest-energy orbital of butadiene, ψ_1, reasonably enough, has a high population of electrons in the middle, but in the next orbital up, ψ_2, because of the repulsion between the wave functions of opposite sign on C-2 and C-3, the electron population is concentrated at the ends of the conjugated system. Overall, summing the squares of the coefficients of the filled orbitals, ψ_1 and ψ_2, the π electrons are evenly spread over all four carbon atoms of the conjugated system.

We can easily give numerical values to these coefficients for the linear conjugated system. The coefficients are proportional to the sine of the angle, as defined by the position of the atom within the sine curve. Equation 1.12 is the algebraic expression for this idea, illustrated in Fig. 1.31 with the atomic orbitals inscribed within the sine curves:

$$c_{jr} = \sqrt{\frac{2}{n+1}} \sin \frac{rj\pi}{n+1} \tag{1.12}$$

giving the coefficient c_{jr} for atom j in molecular orbital r of a conjugated system of n atoms (so that j and $r = 1, 2, 3, \ldots, n$).

In butadiene, as in all alternant conjugated systems (those having no odd-membered rings), the $|c|$ values are reflected across a mirror plane placed horizontally, halfway between ψ_2 and $\psi_3{}^*$, and also across a mirror plane placed vertically, halfway between C-2 and C-3. It is only necessary therefore to calculate four of the 16 numbers in Fig. 1.31, and deduce the rest from the symmetry.

We can set up the conjugated system of butadiene by looking at the consequences of allowing two isolated π bonds to interact, as they will if they are held within bonding distance. Let us first look at the consequence of allowing the orbitals close in energy to interact, which they will do strongly. (For a brief account of how the energy difference between interacting orbitals affects the extent of their interaction, see the discussion on page 47 of Equations 1.13 and 1.14.) We see that ψ_1 is derived by the interaction of π with π in a bonding sense, lowering the energy of ψ_1 below that of the π orbital, and ψ_2 is derived from the interaction of π with π in an antibonding sense, raising the energy above that of the π orbital. Similarly, the interaction of π^* with π^* in a bonding sense creates the orbital $\psi_3{}^*$ and in an antibonding sense the orbital $\psi_4{}^*$. Now we look at the consequence of the weaker interactions of π with π^*. The interaction of π with π^* in a bonding sense lowers the energy of ψ_1 and ψ_2, and the interaction of π with π^* in an antibonding sense raises the energy of $\psi_3{}^*$ and $\psi_4{}^*$. Mixing these two sets together, and allowing for the greater contribution from the stronger interactions, we get the set of orbitals (Fig. 1.32), matching those we saw in Fig. 1.31. The net effect is to lower the energy of ψ_1 below the π level, and to raise the energy of ψ_2 above the π level, but without raising it up to the α level. Likewise $\psi_3{}^*$ is lowered in energy, but remains above the α level. Yet another way of looking at this

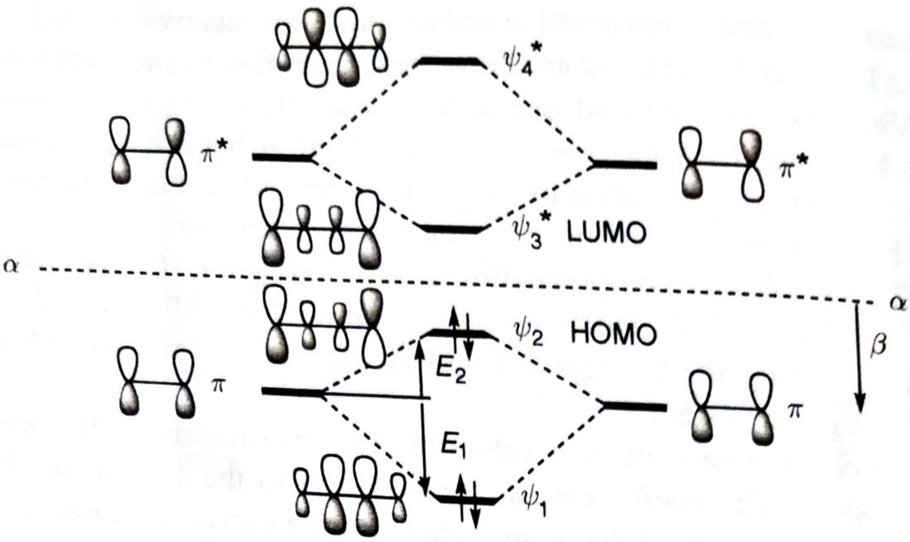


Fig. 1.32 Energies of the π molecular orbitals of ethylene and butadiene by orbital interaction

system, is to say that the orbitals ψ_1 and ψ_2 and the orbitals $\psi_3{}^*$ and $\psi_4{}^*$ mutually repel each other.

We are now in a position to explain the well-known property that conjugated systems are often, but not always, lower in energy than unconjugated systems. It comes about because ψ_1 is lowered in energy more than ψ_2 is raised (E_1 in Fig. 1.32 is larger than E_2). The energy (E_1) given out in forming ψ_1 comes from the overlap between the atomic orbitals on C-2 and C-3; this overlap did not exist in the isolated π bonds. It is particularly effective in lowering the energy of ψ_1, because the coefficients on C-2 and C-3 are large. By contrast, the increase in energy of ψ_2, caused by the repulsion between the orbitals on C-2 and C-3, is not as great, because the coefficients on these atoms are smaller in ψ_2. Thus the energy lost from the system in forming ψ_1 is greater than the energy needed to form ψ_2, and the overall π energy of the ground state of the system ($\psi_1{}^2\psi_2{}^2$) is lower. We can of course see the same pattern, and attach some approximate numbers, using the geometrical analogy.

This is illustrated in Fig. 1.33, which shows that ψ_2 is raised above π by 0.382β and ψ_1 is lowered below π by 0.618β. The overall lowering in energy for the extra

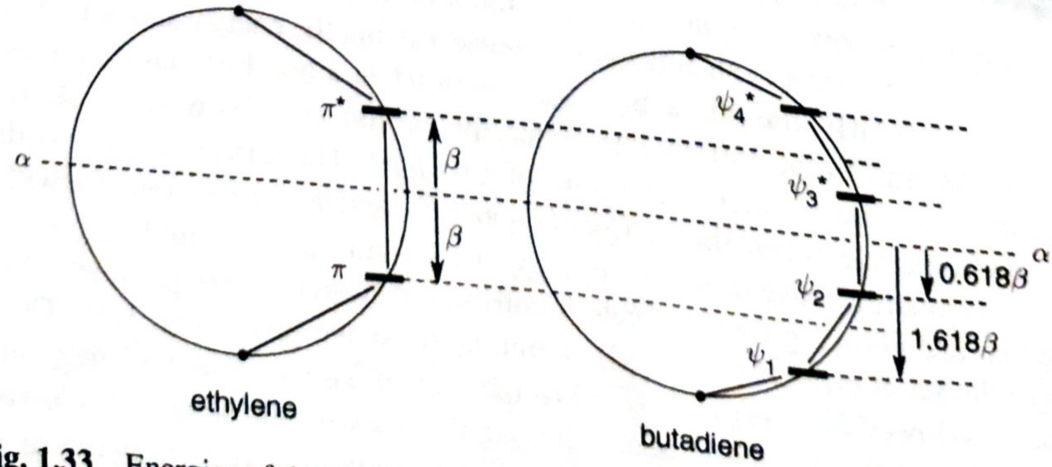


Fig. 1.33 Energies of the π molecular orbitals of ethylene and butadiene by geometry

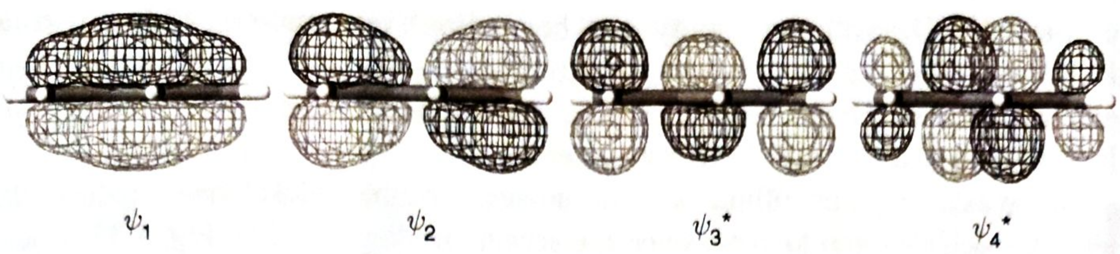


Fig. 1.34 The π molecular orbitals of butadiene

conjugation is therefore $(2 \times 0.618 + 2 \times 1.618) - 4 = 0.472\beta$ or about 66 kJ mol^{-1}. Finally, it is instructive to look at the same π orbitals in wire-mesh diagrams (Fig. 1.34) to reveal more accurately what the electron distribution in the π molecular orbitals looks like.

1.4.3 Longer Conjugated Systems

The π orbitals of longer linear conjugated systems are derived in essentially the same way. The energies and coefficients of the π molecular orbitals for all six systems from an isolated p orbital up to hexatriene are summarised in Fig. 1.35. The viewpoint in this drawing is directly above the p orbitals, which appear therefore to be circular. This is a common simplification, rarely likely to lead to confusion between a p orbital and an s orbital, and we shall use it through much of this book.

The longer the conjugated system, the lower the energy of ψ_1, but each successive drop in energy is less than that of the system with one fewer atoms, with a limit at infinite length of 2β. Among the even-atom species, the longer the conjugated system, the higher the energy of the HOMO, and the lower the energy

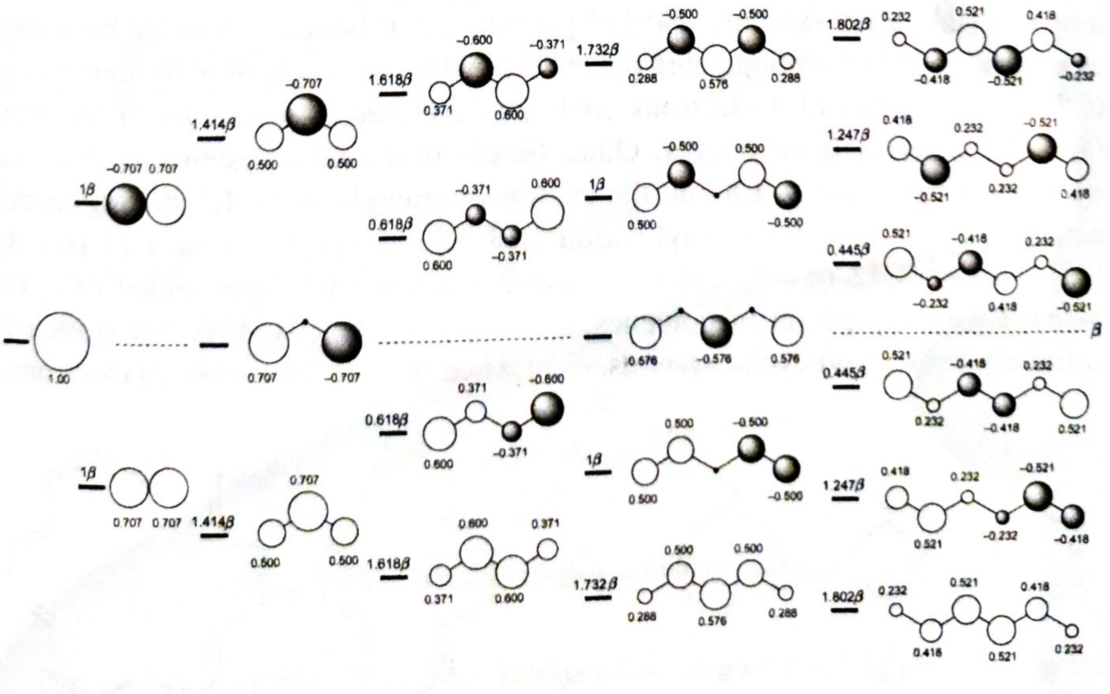


Fig. 1.35 The energies and coefficients of the π molecular orbitals of the smaller conjugated systems

of the LUMO, with the energy gap becoming ever smaller. With a narrow HOMO—LUMO gap, polyenes require less energy in order to promote an electron from the HOMO to the LUMO, leading the absorption of UV and visible light to take place at ever longer wavelength.

At the extreme of an infinite polyene, however, simple Hückel theory reduces the HOMO—LUMO gap to zero, since the secants in diagrams like Fig. 1.33, would become infinitely small. Such a polyene would have equal bond lengths between each pair of carbon atoms, the gap between the HOMO and the LUMO would be zero.

A zero gap between the HOMO and the LUMO is characteristic of a metallic conductor, but long polyenes have alternating double and single bonds, and their interconversion, which is the equivalent of the movement of current along the chain, requires energy. The theoretical description of this modification to simple Hückel theory is known by physicists as a Peierls distortion. It has its counterpart for chemists in the Jahn-Teller distortion seen, for example, in cyclobutadiene, which distorts to have alternating double and single bonds, avoiding the degenerate orbitals and equal bond lengths of square cyclobutadiene. The simple Hückel picture is seriously wrong at the extreme of long conjugated systems. One way of appreciating what is happening is to think of the HOMO and the LUMO repelling each other more strongly when they are close in energy, just as the filled and unfilled orbitals of butadiene repel each other (Fig. 1.32), but more so.

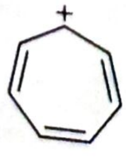
1.5 Aromaticity

1.5.1 *Aromatic Systems*

One of the most striking properties of conjugated organic molecules is the special stability found in the group of molecules called aromatic, with benzene **1.7** as the longest established example. Hückel predicted that benzene was by no means alone, and that cyclic conjugated polyenes would have exceptionally low energy if the total number of π electrons could be described as a number of the form $(4n+2)$, where n is an integer. Other 6π-electron cyclic systems such as the cyclopentadienyl anion **1.8** and the cycloheptatrienyl cation **1.9** belong in this category, and the cyclopropenyl cation **1.10** $(n=0)$, [14]annulene **1.11** $(n=3)$, [18]annulene **1.12** $(n=4)$ and many other systems have been added over the years. Like conjugation in polyenes, however, aromaticity does not stretch to infinitely conjugated cyclic systems, even when they do have $(4n+2)$ electrons.

1.7

1.8



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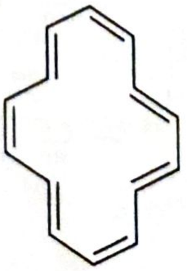

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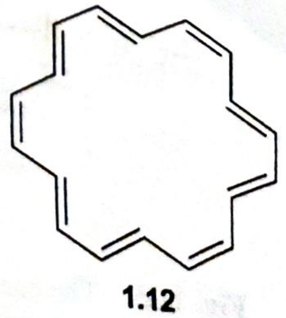


1.12

Where does this special stability come from? We can approach this question in much the same way as we approached the derivation of the molecular orbitals of conjugated systems. We begin with a σ framework containing the C—C and C—H σ bonds. We must then deduce the nodal properties of the molecular orbitals created from six p orbitals in the ring. They are all shown both in elevation and in plan in Fig. 1.36. The lowest-energy orbital ψ_1 has no node as usual, but because the conjugated system goes round the ring instead of spilling out at the ends of the molecule, as it did with the linear conjugated systems, the coefficients on all six atoms are equal. The other special feature is that there are two orbitals having the same energy with one node ψ_2 and ψ_3, because they can be created in two symmetrical ways, one with the node horizontal ψ_2 and one with it vertical ψ_3. Similarly, there are two antibonding orbitals, $\psi_4{}^*$ and $\psi_5{}^*$, with the same energy having two nodes. Finally there is another antibonding orbital, $\psi_6{}^*$, with three nodes.

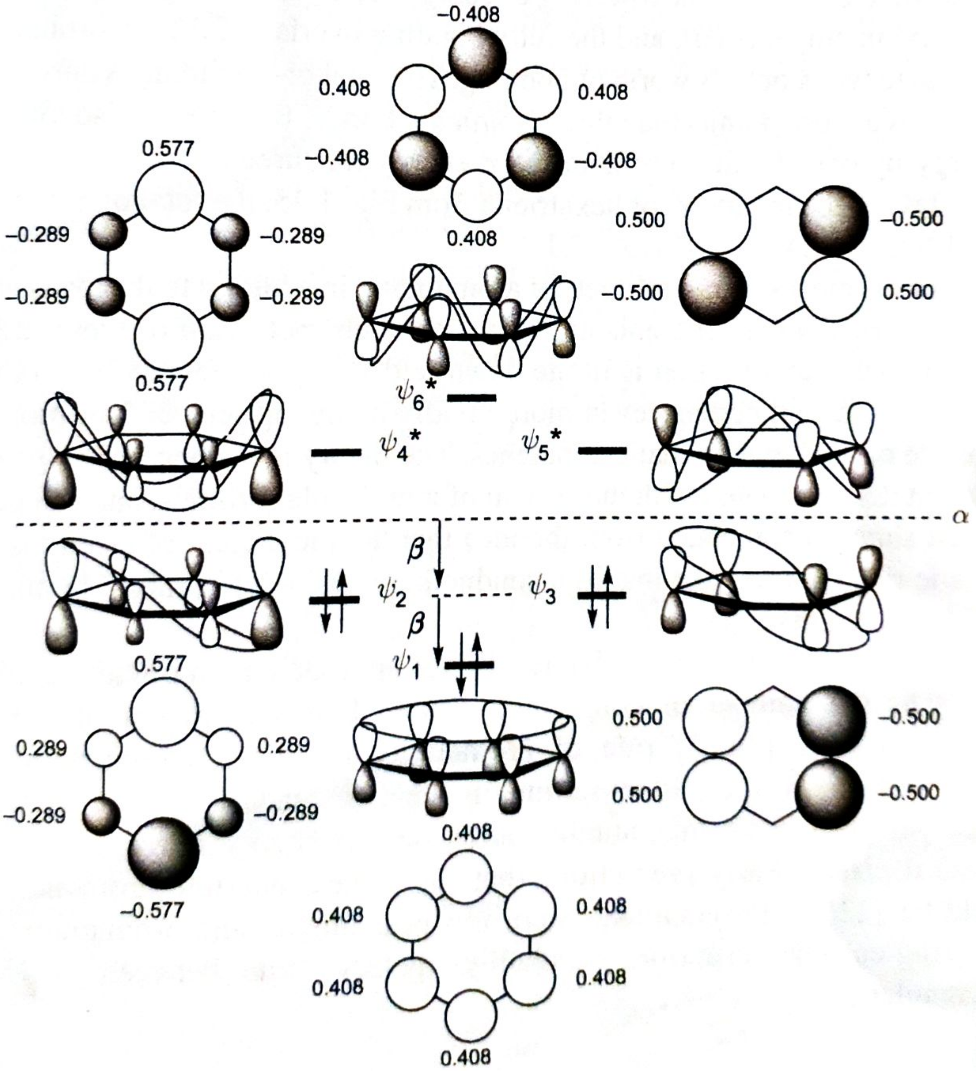


Fig. 1.36 The π molecular orbitals of benzene

The energies of the molecular orbitals can be deduced by inscribing the conjugated system inside a circle of radius 2β. There is no need for dummy atoms, since the sine curves go right round the ring, and the picture is therefore

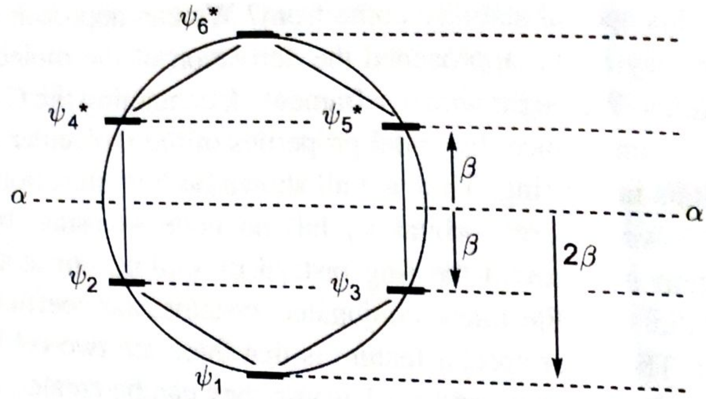


Fig. 1.37 The energies of the π molecular orbitals of benzene

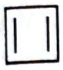
that shown in Fig. 1.37. The lowering of energy for ψ_2 and for ψ_3 is equal to that of the π bond in ethylene (β), and the fully bonding overlap of the six orbitals in ψ_1 gives rise to two π bond's worth of bonding. The total of π bonding is thus $2 \times 4\beta$, which is two more β units than three *isolated* π bonds. Benzene is also lowered in π energy by one β unit more than the π energy for three *linearly conjugated* π bonds: taking the numbers for hexatriene from Fig. 1.35, the total of π bonding is $2 \times (1.802 + 1.247 + 0.445)\beta = 7\beta$.

One of the most striking artifacts of aromaticity, in addition to the lowering in π energy, is the diamagnetic anisotropy, which is characteristic of these rings. Its most obvious manifestation is in the downfield shift experienced by protons on aromatic rings, and perhaps even more vividly by the upfield shift of protons on the inside of the large aromatic annulenes. The theory is beyond the scope of this book, but it is associated with the system of π molecular orbitals, and can perhaps be most simply appreciated from the idea that the movement of electrons round aromatic rings is free, like that in a conducting wire, as epitomised by the equal C—C bond lengths.

We saw earlier that long polyenes do not approach a state with equal bond lengths as the number of conjugated double bonds increases. In the same way, the simple ($4n$+2) rule of aromaticity has been predicted to break down, with bond alternation setting in when n reaches a large number. It is not yet clear what that number is as neither theory nor experiment has proved decisive. Early predictions that the largest possible aromatic system would be [22] or [26]annulene were too pessimistic, and aromaticity, using the ring-current criterion, probably peters out between [34] and [38]annulene.

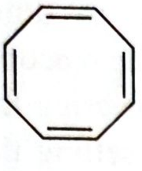
1.5.2 Antiaromatic Systems

A molecule with $4n$ π electrons in the ring, with the molecular orbitals made up from $4n$ p orbitals, does not show this extra stabilisation. Molecules in this class that have been made include cyclobutadiene **1.13** ($n = 1$), the cyclopentadienyl cation **1.14**, cyclooctatetraene **1.15** and pentalene **1.16** ($n = 2$), [12]annulene **1.17** ($n = 3$) and [16]annulene **1.18** ($n = 4$).

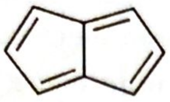


1.13

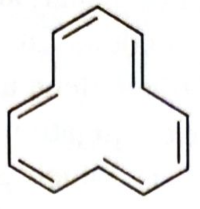
1.14



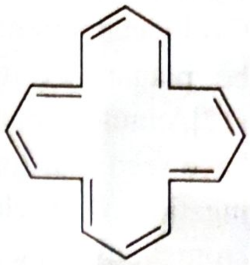
1.15



1.16



1.17



1.18

We can see this most easily by looking at the molecular orbitals of square cyclobutadiene in Fig. 1.38. As usual, the lowest-energy orbital ψ_1 has no nodes, and, as with benzene, and because of the symmetry, there are two exactly equivalent orbitals with one node, ψ_2 and ψ_3. The bonding in ψ_1 gives an energy lowering of 2β (this makes an assumption that the p orbitals are held at the same distance by the σ framework). In contrast, the bonding interactions both in ψ_2 and ψ_3 are exactly matched by the antibonding interactions, and there is no lowering of the energy below the line (α) representing the energy of a p atomic orbital on carbon. The molecular orbitals ψ_2 and ψ_3 are therefore nonbonding orbitals, and the net lowering in energy for the π bonding in cyclobutadiene is only $2 \times 2\beta$. The energies of the four π orbitals are similarly deduced from the model inscribing the conjugated system in a circle, with the point of the square at the bottom. The total π stabilisation of $2 \times 2\beta$ is no better than having two isolated π bonds. There is however less stabilisation than that found in a pair of *conjugated* double bonds—the overall π bonding in butadiene, taking values from Fig. 1.33, is 4.5β and the overall π bonding in cyclobutadiene is only 4β.

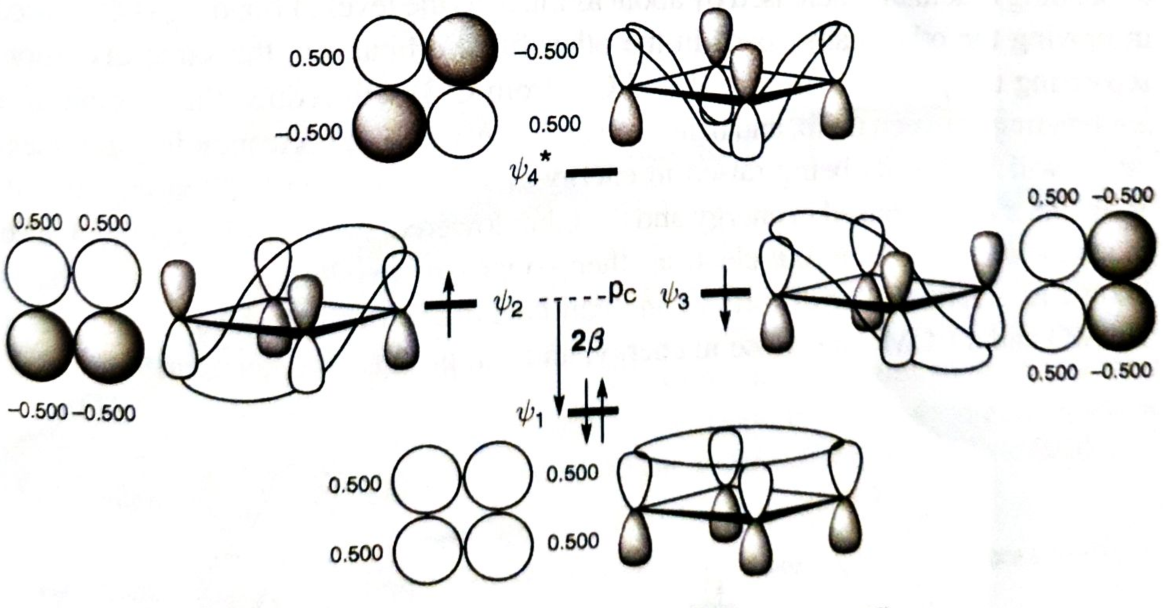


Fig. 1.38 The π molecular orbitals of cyclobutadiene

There is much evidence that cyclic conjugated systems of $4n$ electrons are significantly more reactive than the corresponding open-chain polyenes. There has been much speculation that they not only lack stabilisation but are actually destabilised. They have been called 'anti-aromatic' as distinct from nonaromatic.

Cyclobutadiene dimerises at extraordinarily low temperatures (>35 K). Cyclooctatetraene is not planar, and behaves like an alkene. When it is forced to be planar, as in pentalene, it becomes unstable to dimerisation at 0 °C. [12]Annulene and [16]annulene undergo electrocyclic reactions below 0 °C. We have seen that linear conjugation is more energy lowering than the cyclic conjugation of $4n$ electrons, which goes some way to setting the concept of antiaromaticity on a physical basis. That $4n$ systems are unusually reactive is also explicable with an argument based on the frontier orbitals—the HOMO (at the nonbonding α level for cyclobutadiene) is unusually high in energy for a neutral molecule, significantly above the level of the HOMO of the linear conjugated hydrocarbon, and the LUMO is correspondingly low in energy.

The prediction from the argument in Fig. 1.38 is that square cyclobutadiene ought to be a diradical with one electron in each of ψ_2 and ψ_3, on the grounds that putting a second electron into an occupied orbital is not as energy lowering as putting the first electron into that orbital. This is not borne out by experiment, which has shown that cyclobutadiene is rectangular, with alternating double and single bonds, and shows no electron spin resonance (ESR) signal.

We can easily explain why the rectangular structure is lower in energy than the square. So far, we have made all π bonds contribute equally one β-value to every π bond. The difference in β-values, and hence in the strengths of π bonds, is a function of how closely the p orbitals are held. In the rectangular structure of cyclobutadiene, in which we have moved the upper pair of carbon atoms away from the lower pair but moved the left-hand pair closer to the right-hand pair, the symmetry is lowered, and the molecular orbitals corresponding to ψ_2 and ψ_3 are no longer equal in energy (Fig. 1.39). The overall bonding in ψ_1 is more or less the same as in the square structure—C-1 and C-2 (and C-3 and C-4) move closer together in ψ_1, and the level of bonding is actually increased by about as much as the level of bonding is decreased in moving the other pairs apart. In the other filled orbital, ψ_2, the same distortion, separating the pair (C-1 from C-4 and C-2 from C-3) will reduce the amount of π antibonding between them, and hence lower the energy. The corresponding argument on ψ_3 will lead to its being raised in energy and becoming an antibonding orbital. With one π orbital raised in energy and the other lowered, the overall π energy will be much the same, and the four electrons then go into the two bonding orbitals. This is known as a Jahn-Teller distortion, and can be expected to be a factor whenever a HOMO and a LUMO are close in energy, and can push each other apart.

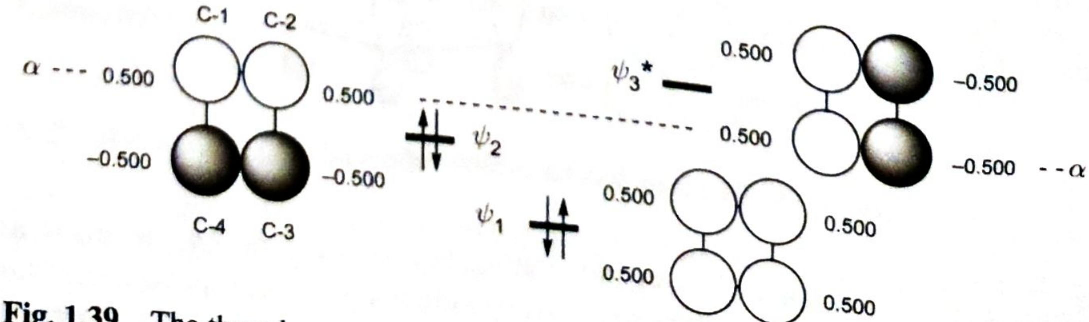


Fig. 1.39 The three lowest-energy π molecular orbitals of rectangular cyclobutadiene

1.5.3 *The Cyclopentadienyl Anion and Cation*

The device of inscribing the pentagon in a circle sets up the molecular orbitals of the cyclopentadienyl anion and cation in Fig. 1.40. The total of π-bonding energy is $2 \times 3.236\beta$ for the anion, in which there are two electrons in ψ_1, two electrons in ψ_2, and two electrons in ψ_3. The anion is clearly aromatic, since the open-chain analogue, the pentadienyl anion has only $2 \times 2.732\beta$ worth of π bonding (Fig. 1.35). The cyclopentadienyl anion **1.8**, a $4n+2$ system, is exceptionally stabilised, with the pK_a of cyclopentadiene at 16 being strikingly low for a hydrocarbon. The cation **1.14**, however, has π-bonding energy of $2 \times 2.618\beta$, whereas its open-chain analogue, the pentadienyl cation, has $2 \times 2.732\beta$ worth of π bonding. The cyclopentadienyl cation is not formed from its iodide by solvolysis under conditions where even the unconjugated cyclopentyl iodide ionises easily.

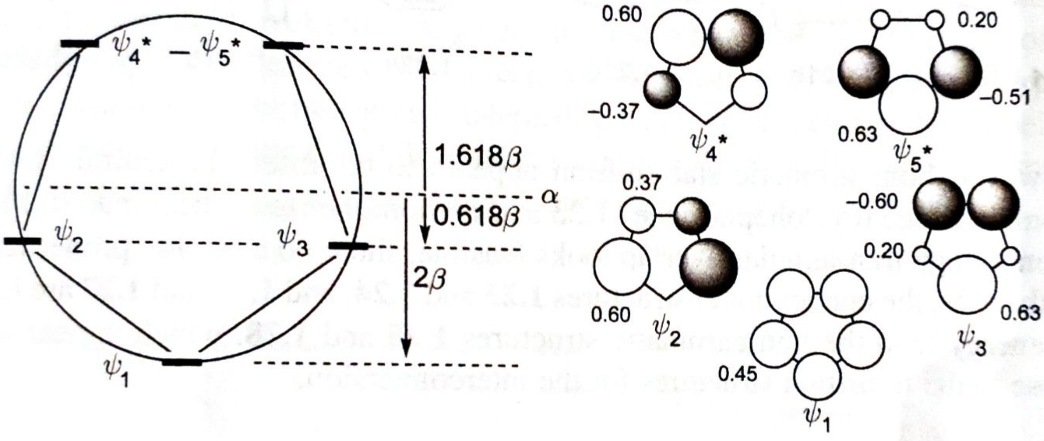


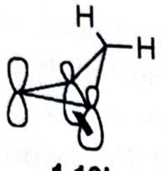
Fig. 1.40 The energies and coefficients of the π molecular orbitals of the cyclopentadienyl system

A striking difference between all the aromatic and all the anti-aromatic systems is the energy *difference* between the HOMO and the LUMO. The aromatic systems have a substantial gap between the frontier orbitals, and the anti-aromatic systems have, after the Jahn-Teller distortion, a small gap. The near degeneracy of the HOMO and the LUMO in the $4n$ annulenes allows a low-energy, one-electron transition between them with a magnetic moment perpendicular to the ring, whereas the aromatic systems do not. As a result, anti-aromatic rings with $4n$ electrons have a paramagnetic ring current—the protons at the perimeter of a $4n$ annulene come into resonance at high field, and protons on the inside of the ring at low field.

1.5.4 *Homoaromaticity*

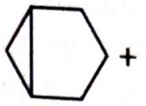
The concept of aromaticity can also be extended to systems in which the conjugated system is interrupted, by a methylene group, or other insulating structural feature, provided that the overlap between the p orbitals of the conjugated systems can still take place through space. When such overlap has energy-lowering consequences, evident in the properties of the molecule, the phenomenon is called homoaromaticity. Examples are the homocyclopropenyl cation **1.19**, the trishomocyclopropenyl cation **1.20**, the bishomocyclopentadienyl anion **1.21** and the homocycloheptatrienyl cation **1.22**, each of which shows evidence of transannular overlap, illustrated, and emphasised with a bold line on the orbitals in the drawings **1.19b**, **1.20b**, **1.21b** and **1.22b**.

1.19a

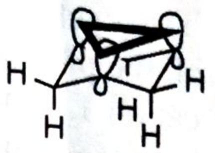


1.19b

1.19c



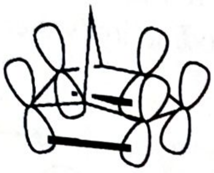
1.20a



1.20b

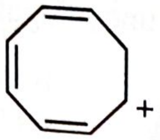
1.20c

1.21a

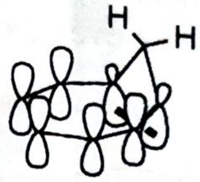


1.21b

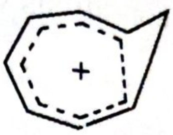
1.21c



1.22a

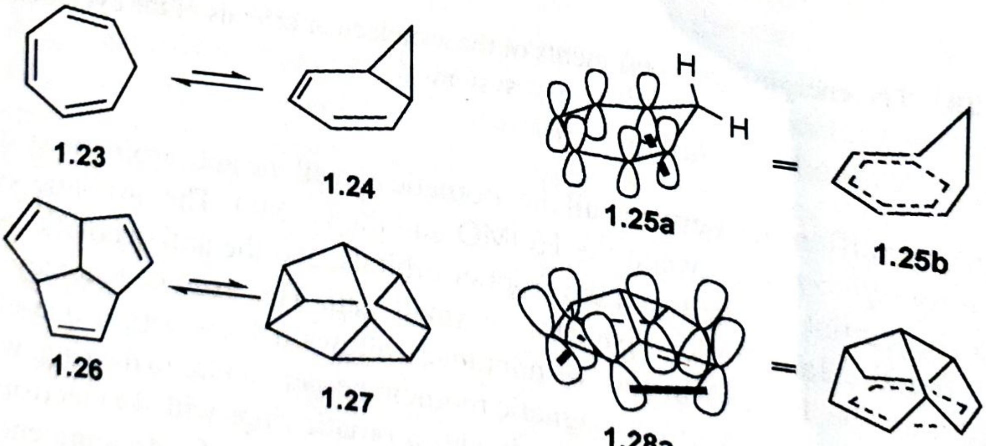


1.22b



1.22c

However, homoaromatic stabilisation appears to be absent in neutral systems. Homobenzene (cycloheptatriene) **1.23** and trishomobenzene (triquinacene) **1.26**, even though transannular overlap looks feasible, show no aromatic properties. In both cases, the conventional structures **1.23** and **1.24**, and **1.26** and **1.27** are lower in energy than the homoaromatic structures **1.25** and **1.28**, which appear to be close to the transition structures for the interconversion.

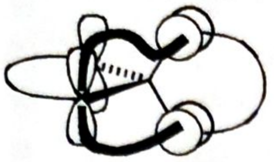


1.23 **1.24** **1.25a** **1.25b**

1.26 **1.27** **1.28a** **1.28b**

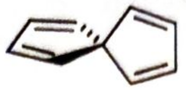
1.5.5 Spiro Conjugation

In addition to σ and π overlap, p orbitals can overlap in another way, even less effective in lowering the energy, but still detectable. If one conjugated system is held at right angles to another in a spiro structure **1.29**, the p orbitals of one can overlap with the p orbitals of the other, as symbolised by the bold lines on the front lobes. The overlap integral will be small, but overlap of molecular orbitals with the right symmetry can raise or lower the orbital energy in the usual way. The hydrocarbons **1.30** and **1.31** are representative examples.



1.29

1.30



1.31

Take spiroheptatriene **1.30**, with the unperturbed orbitals of each component shown on the left and right in Fig. 1.41. The only orbitals that can interact are ψ_2 on the left and π^* on right, all the others having the wrong symmetry. For example, the interaction of the top lobes of ψ_1 on the left and the upper p orbital of the π orbital on the right, one in front and one behind, have one in phase and one out of phase, exactly cancelling each other out; similarly with the front π lobes on the right and the upper and lower lobes of the front-right p orbital of ψ_1 on the left. The two orbitals that do interact create the usual pair of new orbitals, one raised and one lowered. Since there are only two electrons to go into the new orbitals, the overall energy of the conjugated system is lowered. The effect, ΔE_s, is small, both because of the poor overlap, and because the two orbitals interacting are far apart in energy. Nevertheless, it is a general conclusion that if the total number of π electrons is a $(4n+2)$ number, the spiro system is stabilised, leading to the concept of spiro-aromaticity.

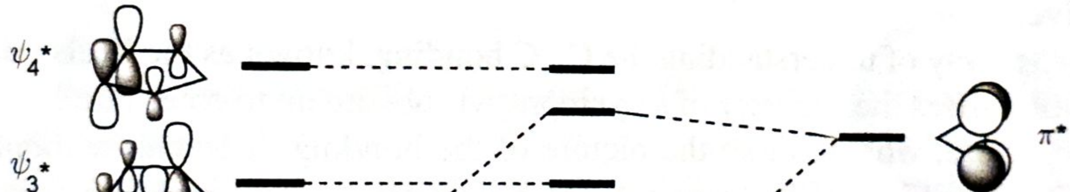


Fig. 1.41 π Molecular orbitals of the 'aromatic' spiroheptatriene **1.30**