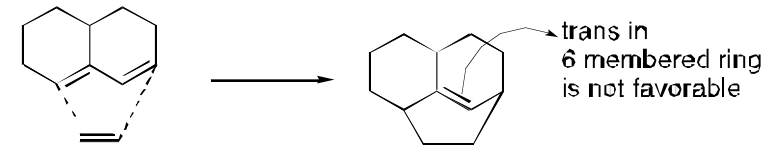
Example of Predicting Stereochemistry

The following example uses 2Z, 4E-hexadiene (diene) and cyclopentene (dienophile) to produce an endo product. As shown before with the furan and maleic anhydride reaction, the stereochemistry of the endo product can be predicted. The methyl group at C6 is similar to that of the H in furan and therefore will be pointing down. The position of the C1 methyl group is similar to that of the oxygen in furan and therefore will point up in the endo product (by convention drawn away from (outside of) the cyclohexene ring).

Note: Diene must be able to attain a cisoid or s-cis conformation

Example below does NOT undergo Diels Alder reaction

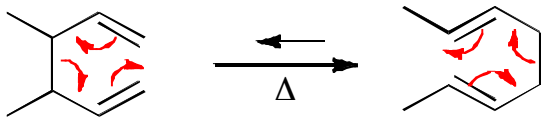


trans diene
no Diels Alder reaction

Other Electrocyclic Reactions

Cope Rearrangement

This is another pericyclic reaction that, like the Diels-Alder reaction, involves 6 electrons.

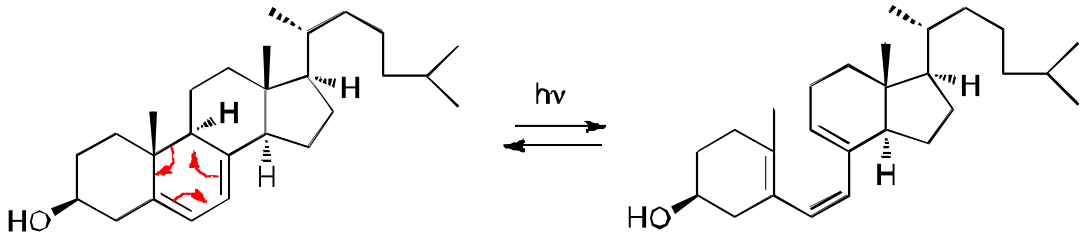


3,4-dimethyl-1,5-hexadiene 2,6-octadiene

This example favours the less sterically crowded isomer, which can be redrawn as:

Note the steric interference between the two methyl groups in the first isomer.

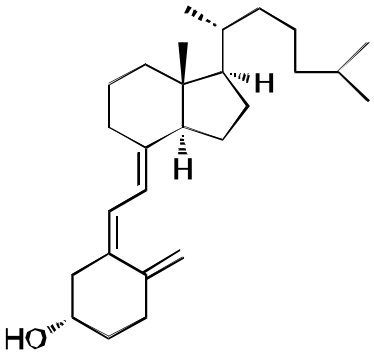
This reaction occurs in nature, as shown below:



dehydrocholesterol
(aka provitamin D_3)

previtamin D_3

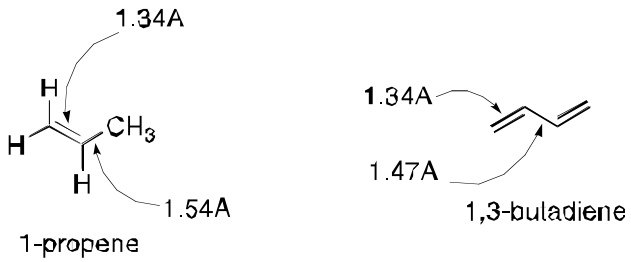
This goes on to form Vitamin D_3, whose structure you should be able to recognize.



Vitamin D_3

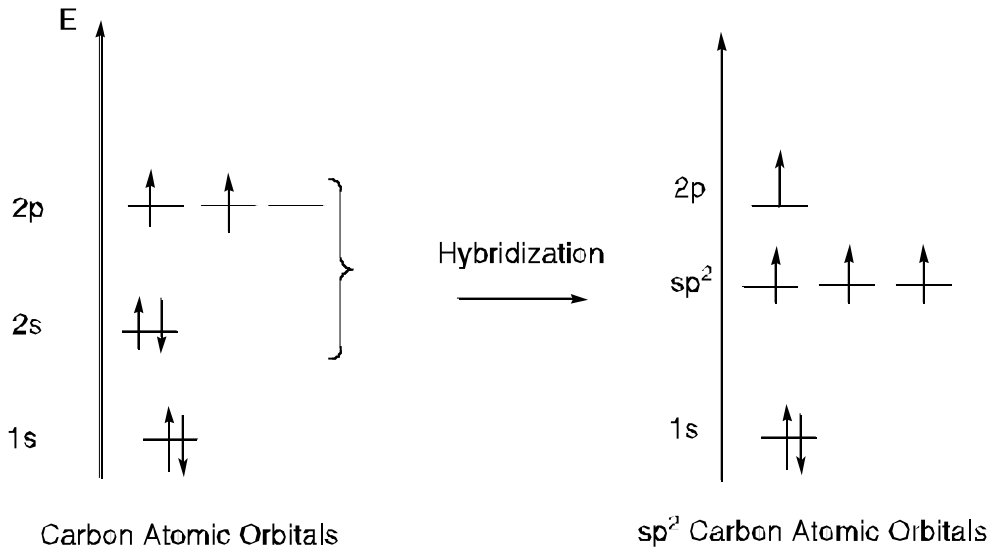
Deficiency of this is known to cause rickets. This was identified around the year 1650.

Bond and Energy Characteristics of Conjugated System

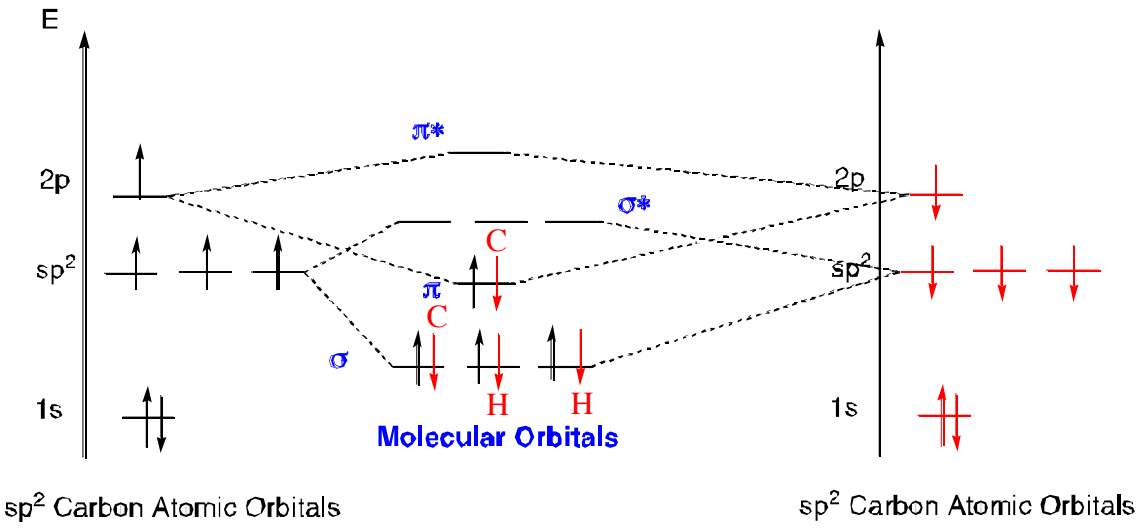


The bond length between the double bond carbons in propene is ca. 1.34 Å (remembering that 1 Å is equal to 10^{-8} cm). In 1,3-butadiene, the bond length of the double bond is 1.34 Å, and the bond length between the two singly bonded carbons is 1.47 Å. Compared to a normal C-C bond length of 1.54 Å, the central single bond in 1,3-butadiene is shorter (has some small amount of double bond character) and is therefore stronger than a normal single bond.

Recall how we can show the energy levels of the atomic orbitals of C. If the C is sp^2 hybridized, two of the 2p orbitals "combine" with the 2s orbital to form two sp^2 hybrid orbitals.

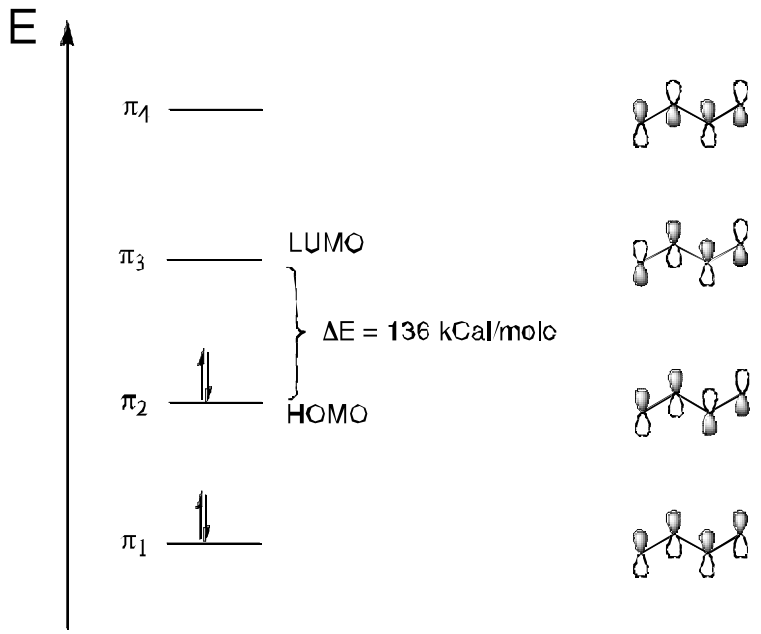


The following molecular orbital (MO) diagram shows the construction of molecular orbitals from the hybrid orbitals of two sp^2 hybridized carbons doubly bonded together (i.e., ethane). One electron pair in the σ MO represents the single bond between the two carbons (and the other two represent C-H bonds), while the electron pair in the π MO represents the double bond (i.e., the π bond) between the two carbons.



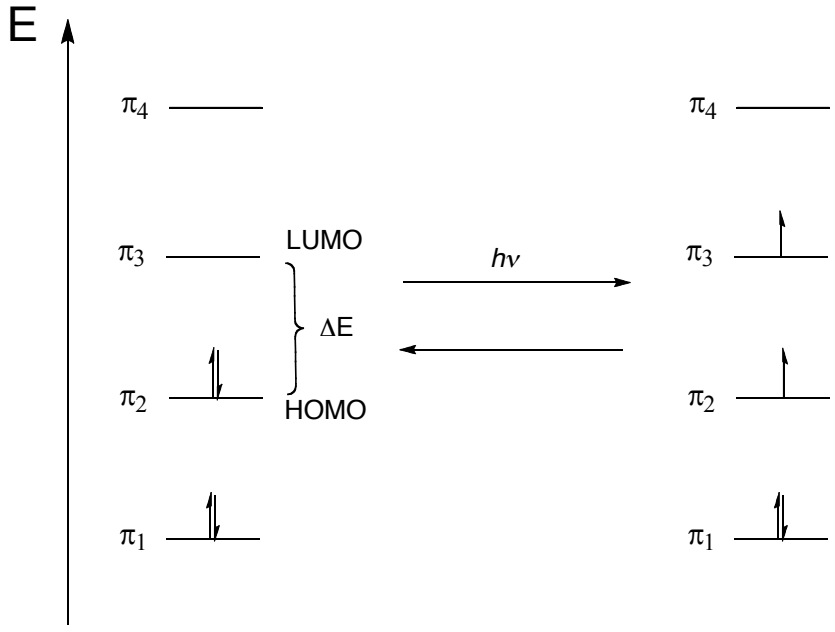
In butadiene, all four carbon atoms have a *2p* orbital. These **atomic** *2p* orbitals will combine to produce 4 π **molecular** orbitals (the number of atomic orbitals combined equals the number of molecular orbitals formed). Since there are two double bonds, there are two bonding and two antibonding π molecular orbitals (recall each π bond system is made by combining two *2p* atomic orbitals). A bonding and an anti-bonding molecular orbital result. In the diagram above, a sigma bond **molecular orbital** also forms by combination of sp^2 from the carbon on the right and sp^2 from the carbon on the left (one antibonding sigma is also formed by this combination). Two other two sigma molecular orbitals with electrons and two more vacant antibonding sigma star orbitals that are shown come from combination of two hydrogen 1s atomic orbitals and the remaining two sp^2 carbon orbitals from the carbon on the left.

As well, two double bonds means that there are 4 π electrons in the conjugated system (1 double bond has 2 π electrons), we can fill the 4 **molecular** orbitals with these electrons starting from the lowest energy level.



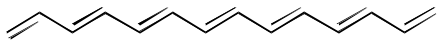
HOMO stands for Highest Occupied Molecular Orbital
LUMO stands for Lowest Unoccupied Molecular Orbital

Molecules absorb energy at the specific wavelength corresponding to the ΔE between the HOMO and LUMO. This is the basis for colour (absorption of light with a wavelength corresponding to visible light) and photosynthesis.

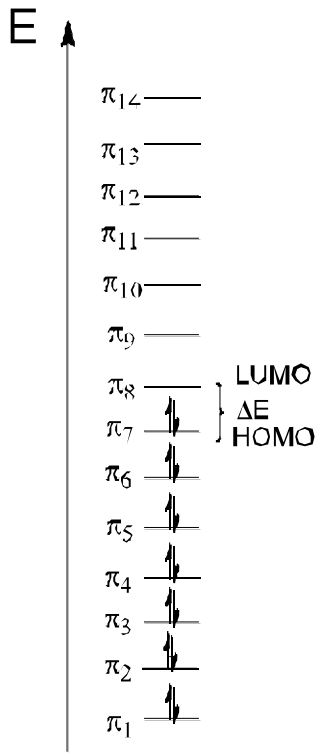


As the molecule becomes more conjugated, the energy gap (ΔE) between the HOMO and LUMO become smaller.

A molecule with ≥ 7 conjugated double bonds absorbs light between 4000 – 8000 Å in the visible region such as the compound shown below.



In this molecule, there are 7 bonding and 7 anti-bonding π molecular orbitals. The energy gap between the LUMO and HOMO is very small. Since E = hc/λ, the wavelength at which this molecule absorbs would be long. It absorbs blue-violet and we see it as yellow.

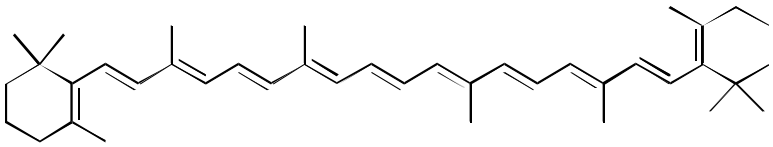


Absorption and Reflection of Visual Light

Absorbed Wavelength (Å)	Colour Absorbed	Visual Colour
4000-4350	violet – blue	yellow – green
4900-5000	blue – green	red
5800-5950	yellow	blue
5950-6050	orange – red	green
6050-7500	red	blue – green

Conjugated Dienes and Colour Continued

Beta-carotene (depicted below) is responsible for the orange-red colour in carrots. Plants produce 10^9 metric tons beta-carotene per year.



β-carotene

Xanthophylls

Xanthophylls are oxygenated carotene molecules. Zeaxanthin, shown below is purple.