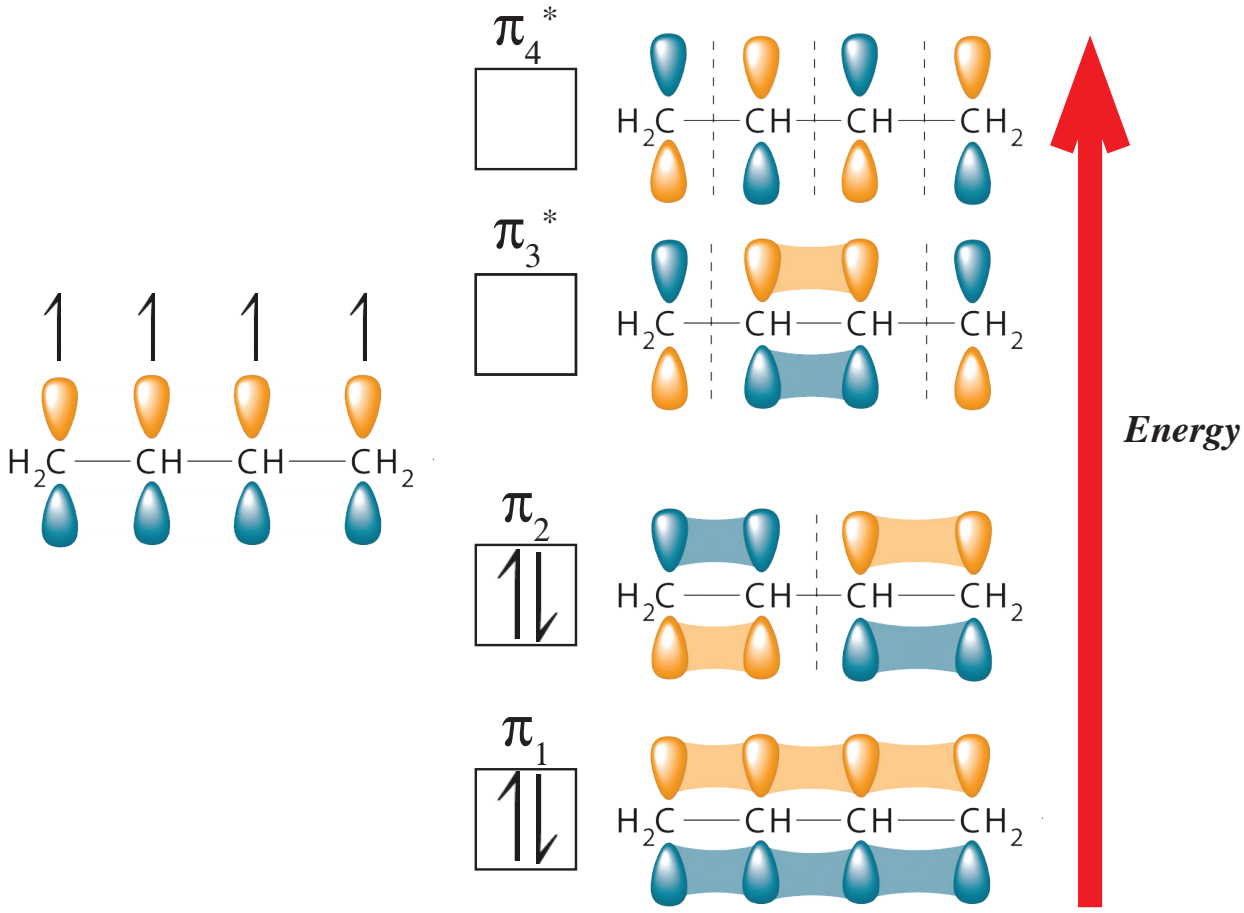
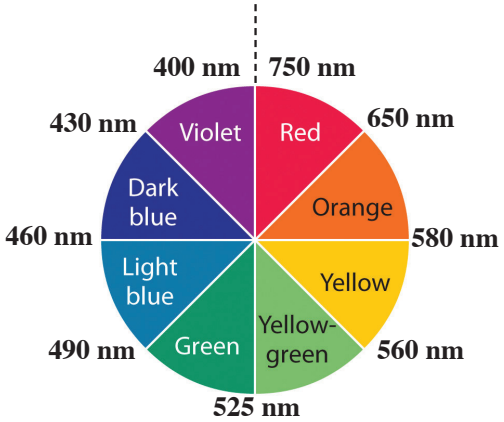


3.4 Molecules & Colour

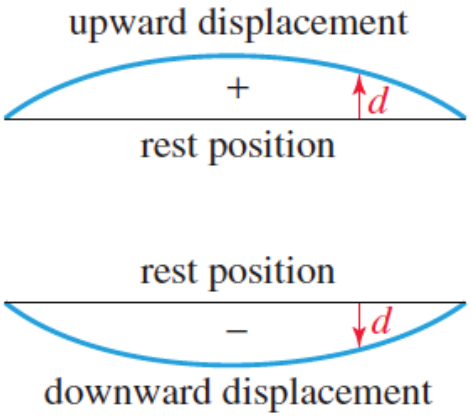


Pupil Notes
Questions

3.4 Colour in Organic Molecules

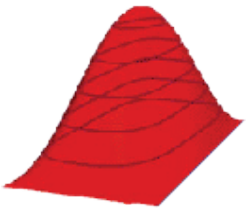
3.4.1 Atomic Orbitals and Molecular Orbitals Revisited

As early 1923, Louis de Broglie suggested that the properties of electrons in atoms are better explained by treating the ***electrons as waves*** rather than as particles. An electron in an ***atomic orbital*** is like a stationary, bound vibration: a ***standing wave***, similar to the wave pattern of a guitar string when it is plucked.



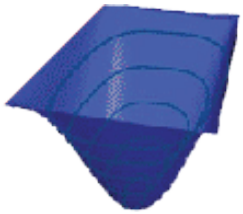
For a split-second the guitar string is displaced upward.

For an instant the wave function, ψ, is positive



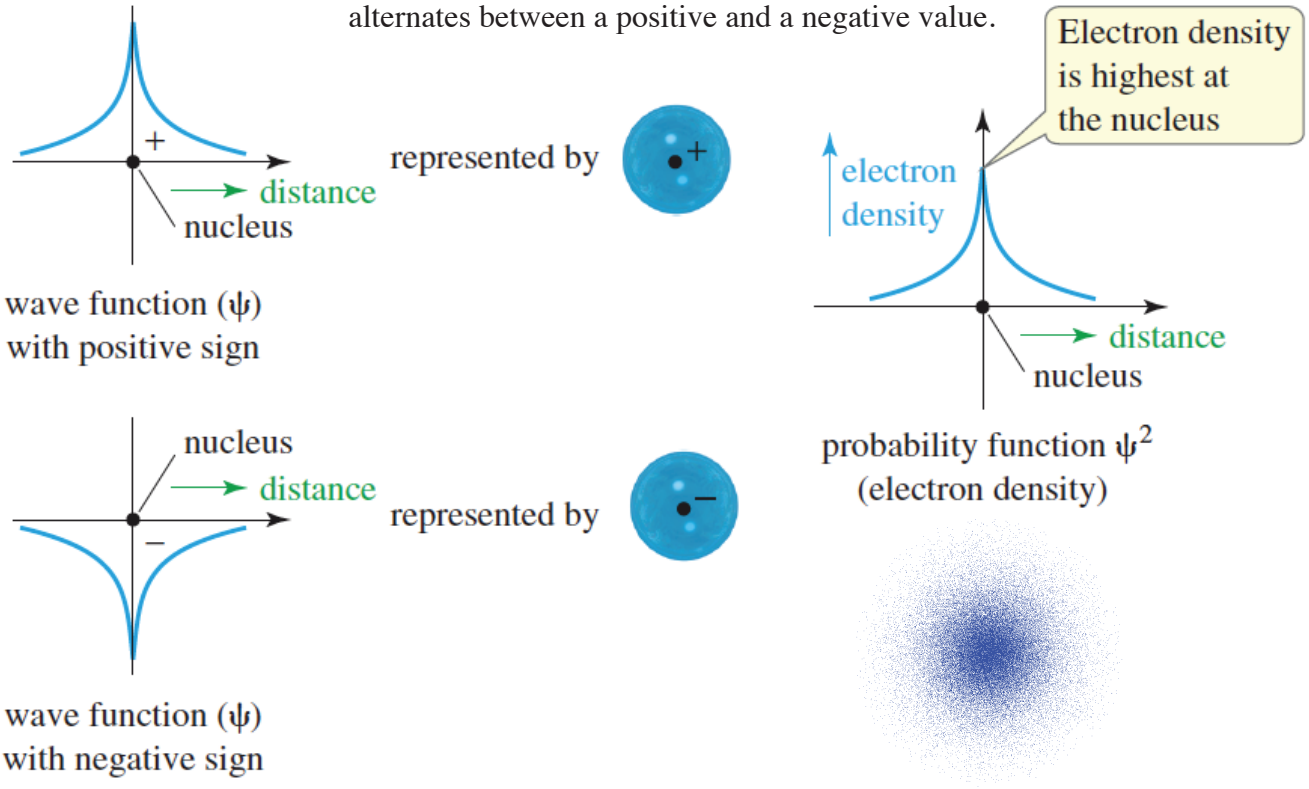
A split-second later the string is displaced downwards.

An instant later the wave function, ψ, is negative

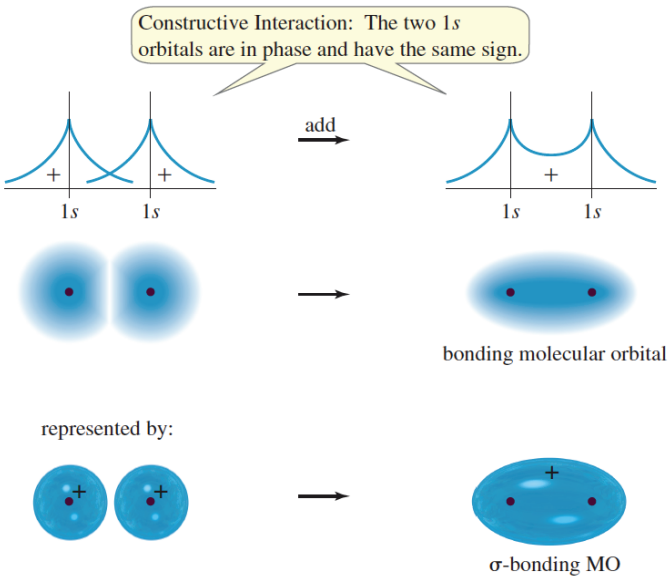


The wave function, ψ, is the mathematical description of the shape of the wave as it vibrates. We are normally more interested in the ***electron density*** which is determined by ψ^2 and, therefore, regardless of the sign of the wave function, an identical ***orbital shape*** will be produced.

As we've seen before, a plot of ***electron density*** for an ***s-orbital*** results in a ***spherical shape*** and most of the time it has been 'irrelevant' that the original wave function alternates between a positive and a negative value.

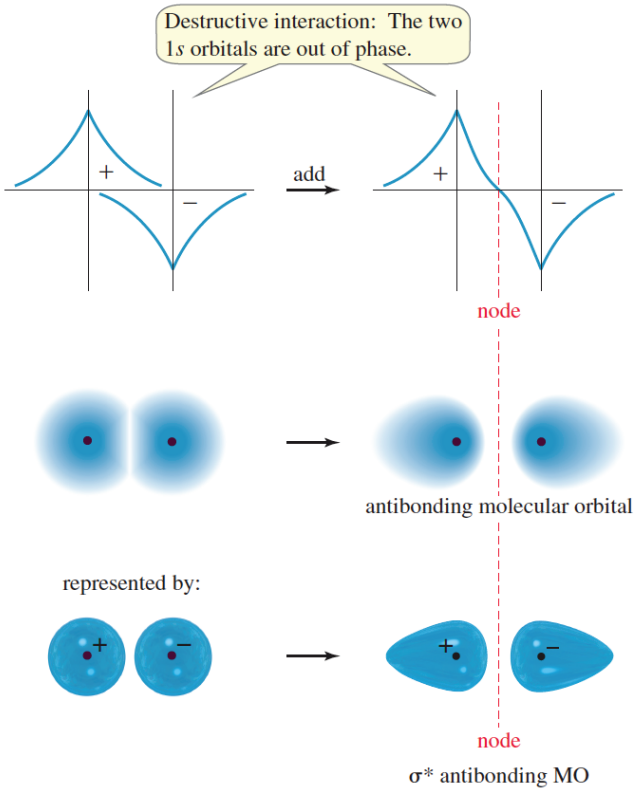


However, when ***atomic orbitals*** overlap to form ***molecular orbitals***, the different possible signs on the wave function become more significant and explain why ***multiple molecular orbitals*** will be formed.



For example, when two s orbitals with the ***same sign*** overlap ***in phase***, the wave functions ***reinforce*** each other and ***increase the electron density*** in this ***bonding region***.

The result is a ***bonding molecular orbital*** (***bonding MO***) which, in this case, is a cylindrically symmetrical bond, or ***sigma bond***, designated σ.

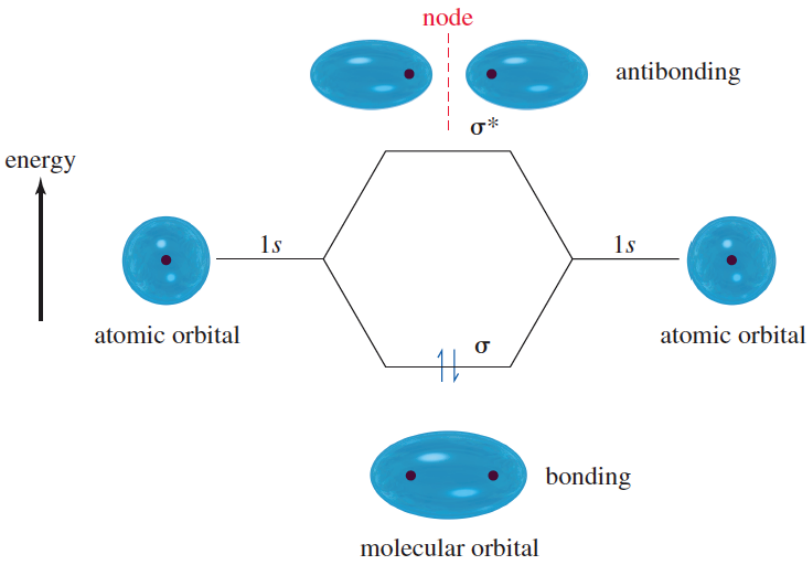


When two s orbitals overlap ***out of phase*** with each other, an ***antibonding molecular orbital*** forms. The two wave functions have ***opposite signs***, so they tend to cancel out where they overlap producing a nodal plane in between.

Not surprisingly, the *more stable* (***lower energy***) *arrangement* is the ***bonding MO*** and it is this orbital that the two ***shared electrons*** will occupy.

We have, so far, ignored the existence of the ***antibonding MO*** which is ***normally empty*** anyway.

However, the existence of these ***empty antibonding orbitals*** can be used to explain how ***organic molecules can absorb energy from the visible spectrum and produce a colour.***



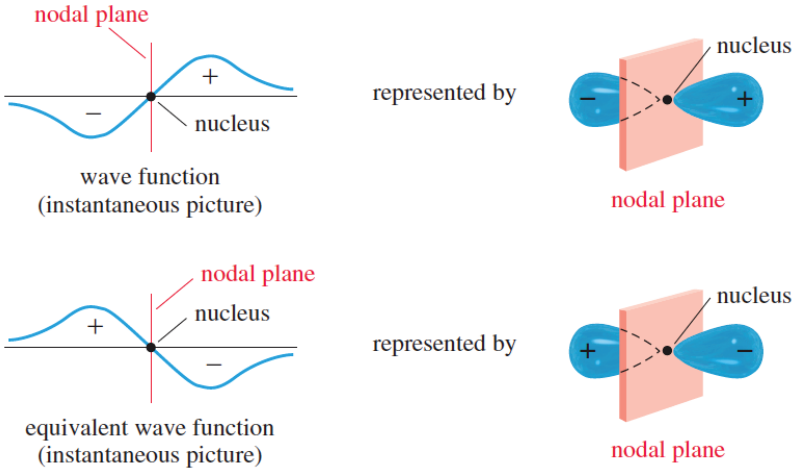
Having said that, ***molecules with only sigma (σ) bonds, such as alkanes, tend to be colourless*** as the ***energy gap*** between the bonding and antibonding orbitals is ***higher than the range of the visible spectrum***, though many of these molecules can ***absorb ultraviolet radiation***.

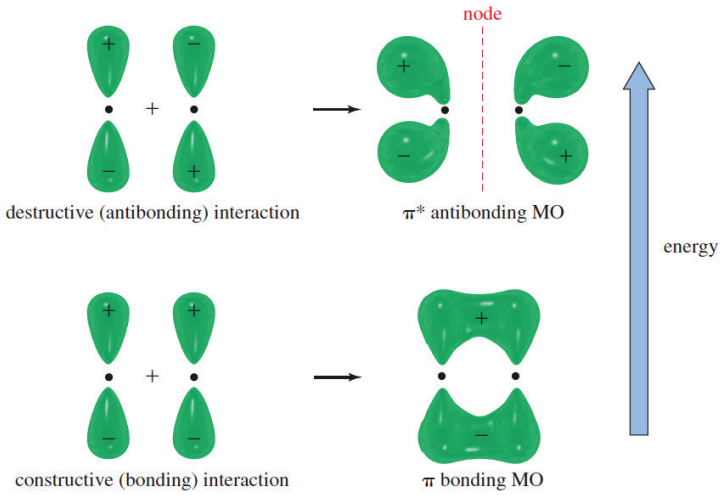
3.4.2 Double Bonds (π orbitals)

The ***p orbitals*** involved in ***multiple*** bonds have ***2 lobes*** separated by a nodal plane.

The two lobes are ***out of phase*** with each other. When one has a ***plus sign***, the other has a ***minus sign***.

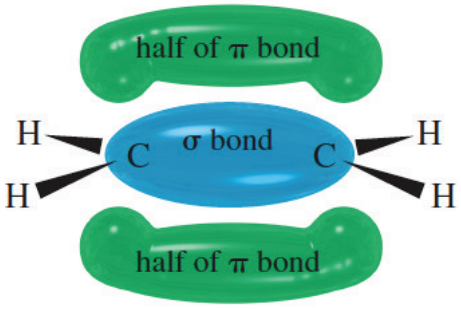
The lobes will be ***constantly changing*** sign resulting in ***two possible*** (*but identical looking*) ***orbitals***.





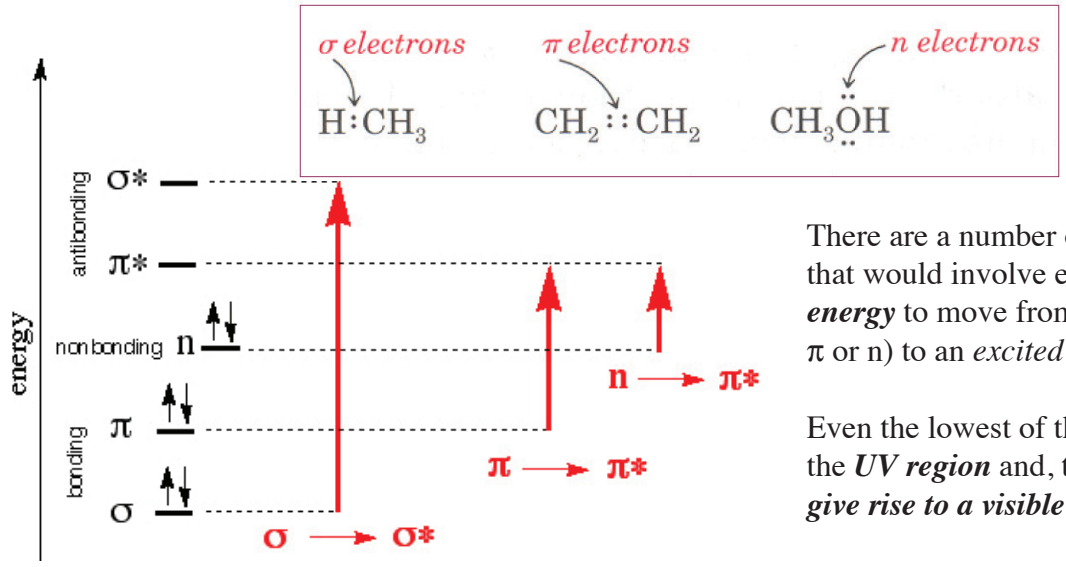
Sideways overlapping of two p-orbitals that are ***in phase*** will result in a ***stable*** (*lower energy*) π ***bonding MO***.

Sideways overlapping of two p-orbitals that are ***out of phase*** will result in a ***less stable*** (*higher energy*) π ***antibonding MO***.



Again, we have simply ignored the existence of the ***antibonding orbital*** as it is ***usually empty of electrons***.

Organic molecules contain ***bonding orbitals*** (σ and π) and ***non-bonding*** (*lone pair*) ***orbitals*** (usually designated with the letter **n**). In addition they also have ***anti-bonding orbitals*** (σ^* and π^*).

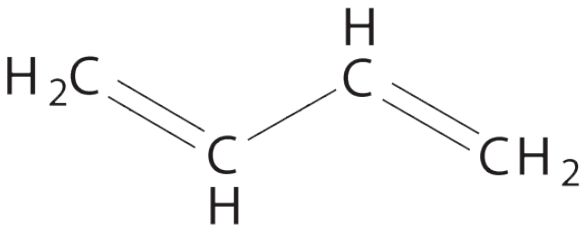


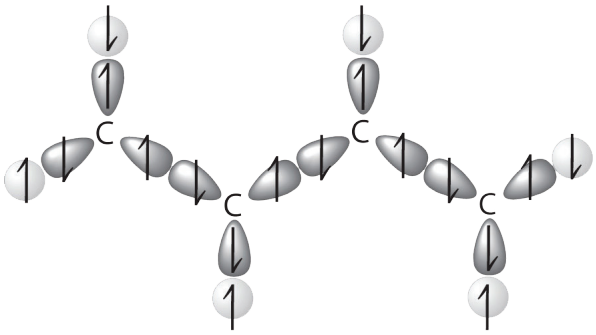
There are a number of ***possible transitions*** that would involve electrons ***absorbing energy*** to move from the *ground state* (σ, π or n) to an *excited state* (σ^* or π^*).

Even the lowest of these (π to π^*) is within the ***UV region*** and, therefore, ***unlikely to give rise to a visible colour***.

3.4.3 Conjugated Systems

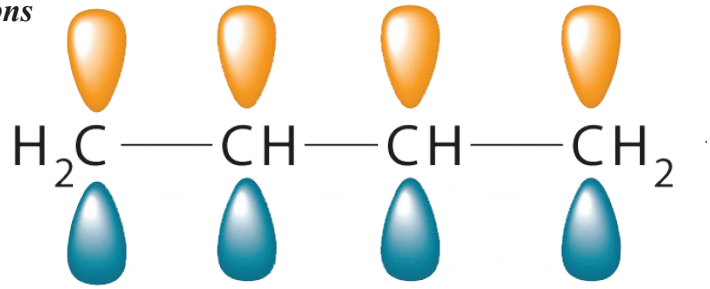
A conjugated system exists when a molecule has alternating single and double bonds. For example, ***buta-1,3-diene*** has the following structure.





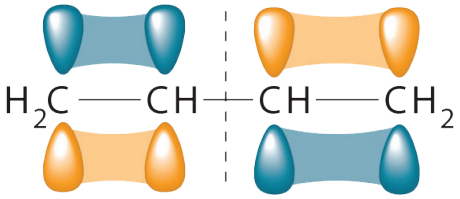
Each carbon will have undergone ***sp^2 hybridisation*** and will be forming ***3 sigma bonds*** each.

This leaves 4 x $2p_z$ orbitals to overlap and ***4 electrons*** left to form two pi bonds.



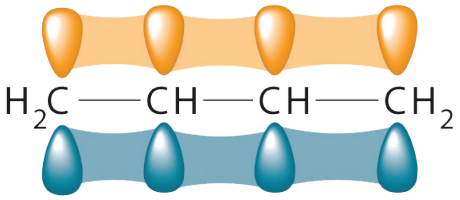
However, the number of possible '*in phase / out of phase*' overlaps mean that there 4 possible sets of molecular orbitals.

Option 1:



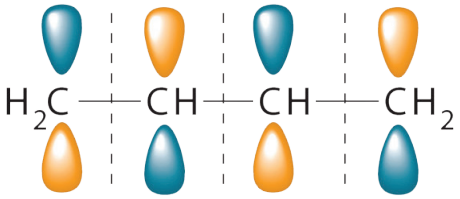
This produces a ***more stable*** (*lower energy*) option and would be a π ***bonding MO*** that matches the 'expected' structure of ***alternating double and single bonds***.

Option 2:



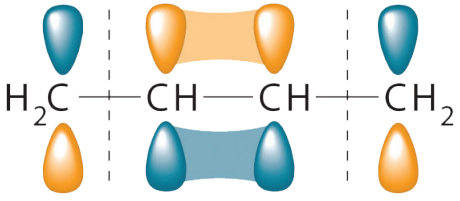
This, however, produces an ***even more stable*** (*lower energy*) option and would also be a π ***bonding MO*** that would have ***3 identical bonds*** in the chain - *more than a single, less than a double bond.*

Option 3:



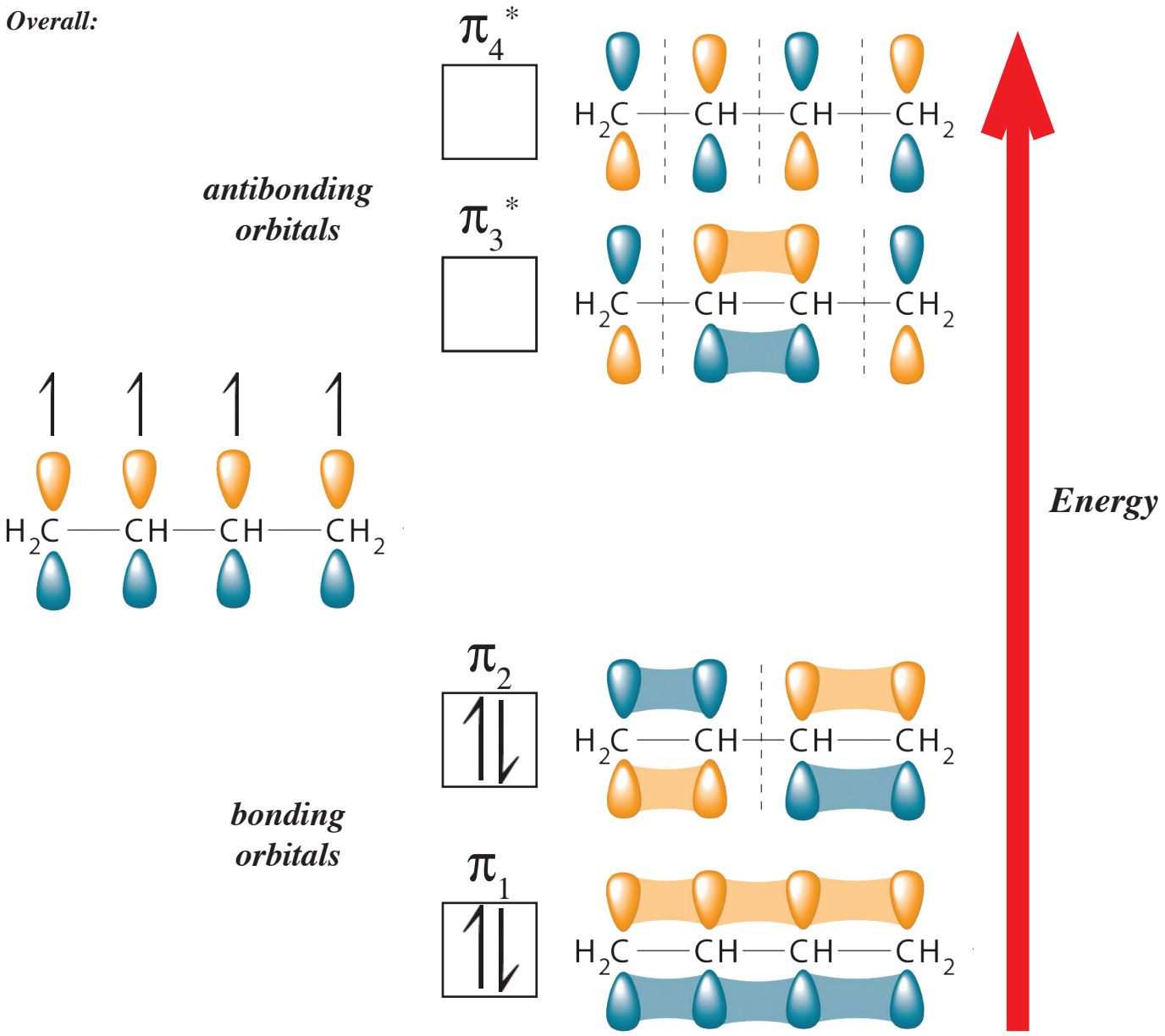
This produces the least stable (highest energy) option and would be a π^* ***antibonding MO*** that would be unlikely to have any of the p_z electrons.

Option 4:



This is also a less stable (higher energy) option and would be a π^* ***antibonding MO***. However, it will be more favourable than ***option 3*** and easier to reach.

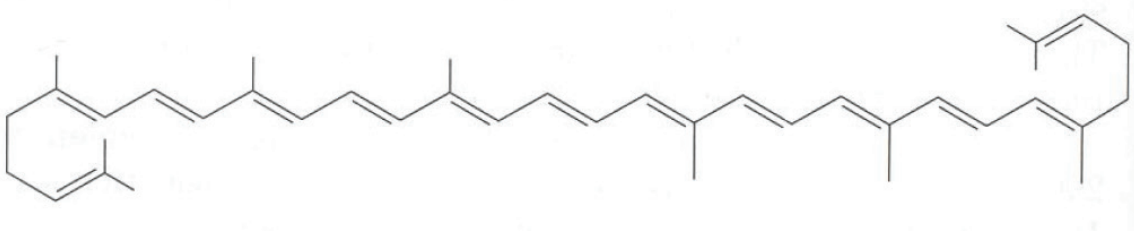
Overall:



The significance of this diagram is that, with increased possibilities for both bonding and antibonding orbitals, the gap between the ***highest occupied*** (*bonding*) ***molecular orbital*** (***HOMO***) and the ***lowest unoccupied*** (*antibonding*) ***molecular orbital*** (***LUMO***) is ***decreasing***.

Buta-1,3-diene, again, only absorbs in the *UV region* of the electromagnetic spectrum but molecules with ***larger conjugated systems*** will absorb from the *Visible spectrum* and ***produce colours***.

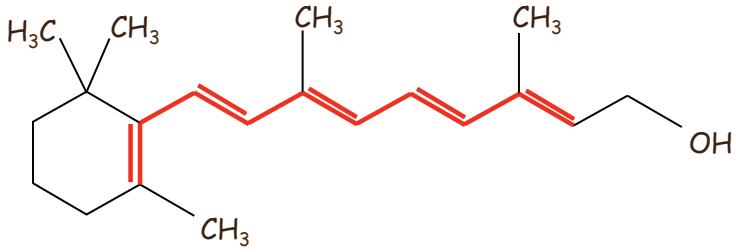
For example, ***lycopene*** which is responsible for the ***red colour*** in *tomatoes*.



lycopene
λ_{max} = 505 nm

3.4.4 Chromophores

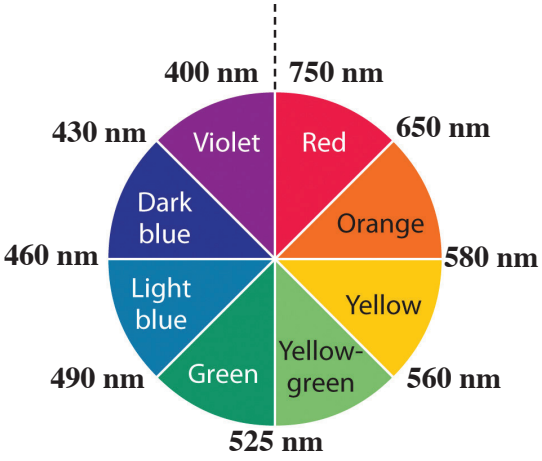
A ***chromophore*** is the ***part of a molecule*** responsible for its ***colour***. This is usually a reasonably large part of the molecule - usually involving a ***conjugated sytem***.



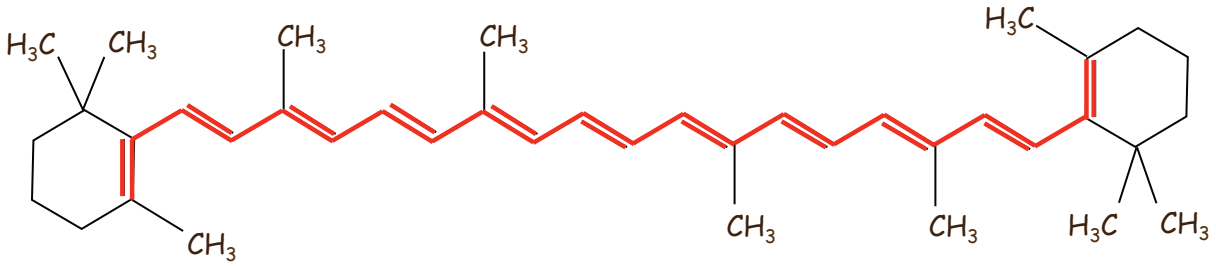
Vitamin A has a conjugated system that spreads over ***five carbon-to-carbon double bonds***.

It appears ***yellow***.

The ***colour observed*** will be the ***complementary colour*** to the one being absorbed.



In the case of ***Vitamin A***, the gap between the ***highest occupied*** (*bonding*) ***molecular orbital*** (***HOMO***) and the ***lowest unoccupied*** (*antibonding*) ***molecular orbital*** (***LUMO***) has ***decreased*** to the point where the absorbance has moved from the UV to the Visible part of the spectrum - ***dark blue*** to be precise.



In the case of ***β-carotene*** (found in *carrots*, *sweet potatoes* and *apricot*), the conjugated system spreads over ***eleven carbon-to-carbon double bonds***. This reduces the gap between ***HOMO*** and ***LUMO*** even further - so the light absorbed decreases from ***dark blue*** (445 nm approx) to ***light blue*** (475 nm).

The colour observed will be correspondingly higher so ***β-carotene*** is ***orange*** in colour.

In general,	as ***gap decreases***	*colour absorbed*	*colour observed*
	UV ⇒ Visible	***Violet ⇒ Green***	***Yellow ⇒ Red***

Lycopene has a conjugated system that also spreads over ***eleven carbon-to-carbon double bonds***.
It appears ***red*** and is responsible for the colour in *tomatoes*, *pink grapefruit* and *watermelons*.

λ_{max} = 505nm

Other examples of coloured molecules include:

Greens - *absorbs red - very small gap*

Blues - *absorbs yellow - small gap*

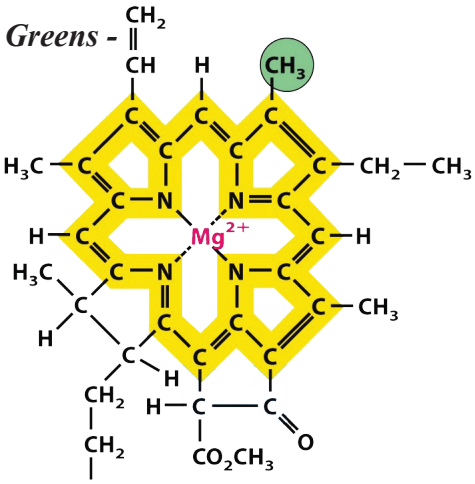
Violets - *absorb greeny-yellow*

Reds - *absorbs green - medium gap*

Oranges - *absorbs light-blue - large gap*

Yellows - *absorbs dark-blue - very large gap*

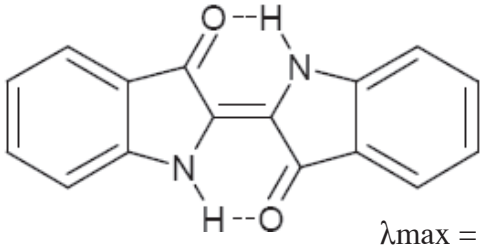
Greens -



Chlorophyll a - Perhaps one of the most important chemicals on Earth, there are two types of chlorophyll, and both are modified porphyrins responsible for most of the light capture into the biosphere.

Both types absorb mostly in the red and blue wavelength regimes (several absorption peaks), leaving a reflected green responsible for the color of green plants, algae, and many photosynthetic bacteria.

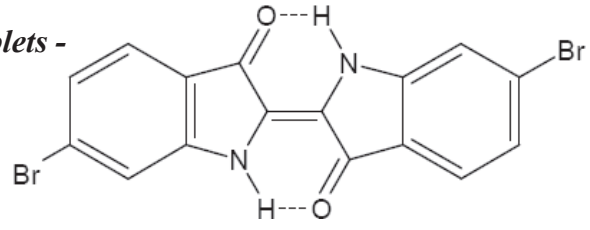
Blues -



λmax = 602 nm

Indigo - Derived from the tropical plants of the genus Indigofera, as well as ***woad*** (Isatis tinctoria) in more temperate climates, this ***dark blue dye*** is now commonly synthesized to color blue jeans and work clothes in the U.S., though is still used as a native colorant by many people around the world.

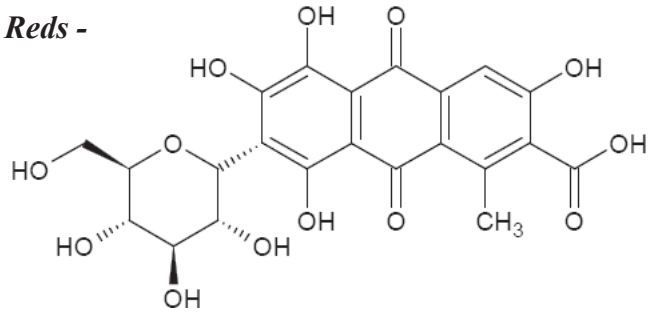
Violets -



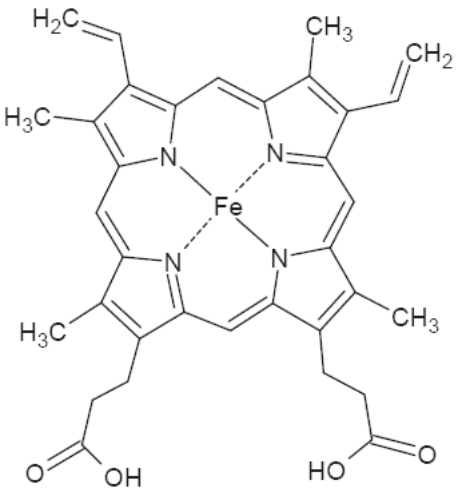
Punicin - Commonly called "***Tyrian (Imperial) Purple***", this compound is derived from the shells of predatory tropical sea snails of the genus Murex.

It was used to create the royal purple dyes used by emperors of Rome and Byzantium, as well as being used for centuries beforehand by other peoples of Asia Minor.

Reds -



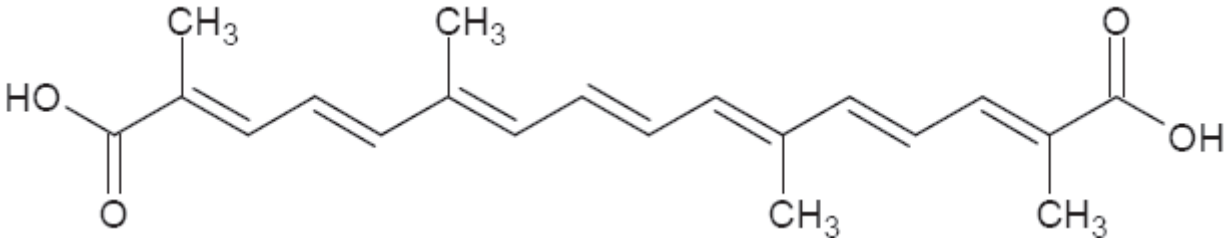
Carminic Acid - An anthraquinone linked to a unit of glucose, this chemical is produced by some scale insects, such as Dactylopius coccus, and is used to dye fabrics a ***deep red***.



Heme B - Important for its role in the transfer of gases for organisms with blood, heme is an iron-containing porphyrin of a ***deep red*** color, giving blood and meat its distinctive color.

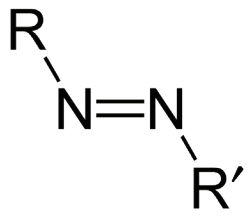
Oranges - β-carotene *(see previously).*

Yellows -

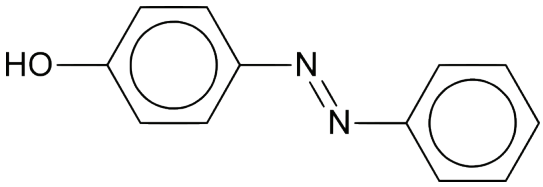


Crocetin - This dicarboxylic acid carotenoid is found in the flowers of Crocus sativus, or ***saffron***, giving them and the spice derived from them a ***golden yellow*** color.

Azo-Dyes - are molecules based on:

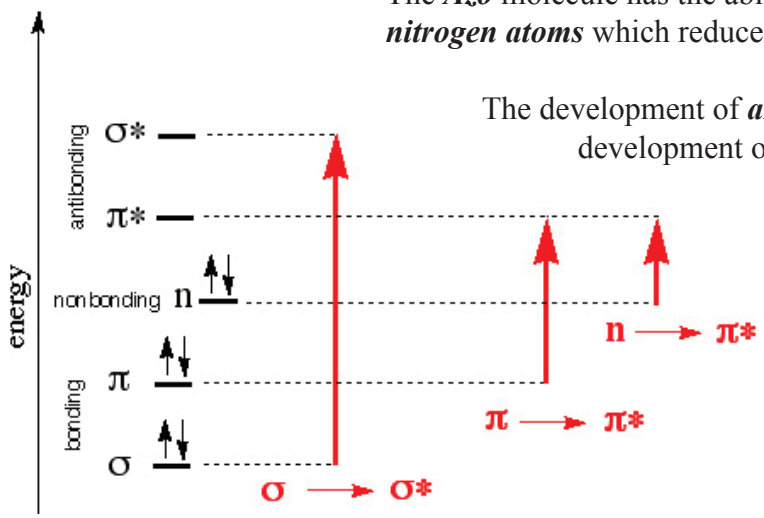


where R and R' can be ***aryl*** or ***alkyl***, which can produce ***very vivid*** coloured molecules.



a typical azo compound: *4-hydroxyphenylazobenzene* aka ***yellow azo dye***

The ***Azo*** molecule has the ability to incorporate the ***lone pairs*** on the ***nitrogen atoms*** which reduces further the gap between *HOMO* and *LUMO*



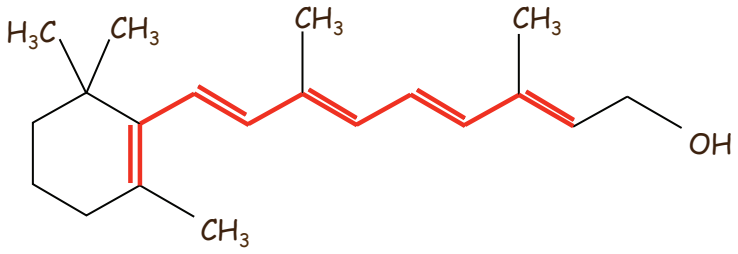
The development of ***azo dyes*** was an important step in the development of the ***chemical industry***.

Delocalisation of these ***electrons*** in ***aryl azo*** compounds produces vivid colors, especially ***reds***, ***orange***s, and ***yellows***.

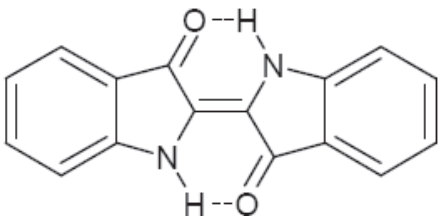
Some azo compounds, e.g., ***methyl orange***, are used as ***acid-base indicators*** due to the different colors of their acid and salt forms.

Questions

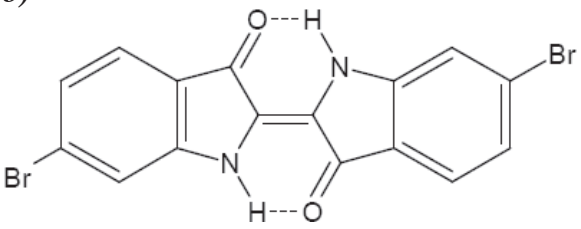
Q1. For each of the molecules below, identify the ***chromophore***, as shown in the example.



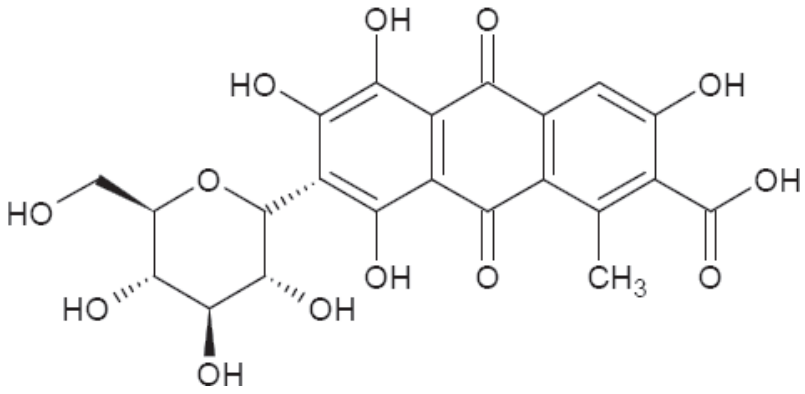
a)



b)



c)



Q2. The presence of different substituents in an azo-dye effect the wavelength of light absorbed and hence the colour observed.

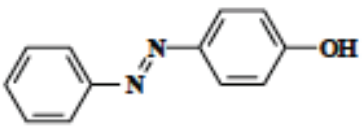
The table below shows the relationship between wavelength absorbed and colour observed.

Wavelength Absorbed (nm)	Colour Absorbed	Colour Observed
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

Q2 contd.

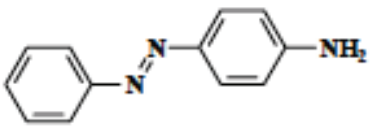
a) Shown below are 5 azo-compounds labelled **A** to **E**.

A



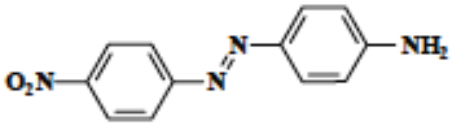
347 nm

B

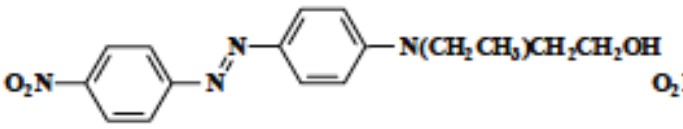


386 nm

C

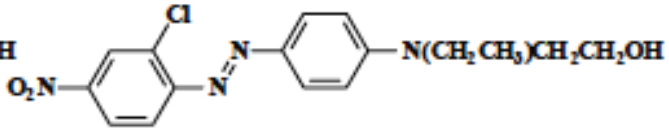


443 nm



502 nm

D



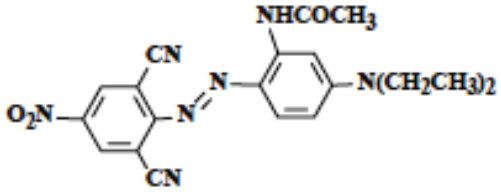
517 nm

E

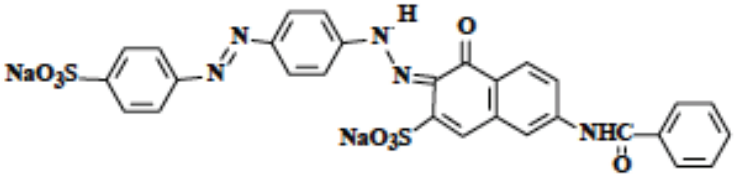
Complete the table below.

Compound	*Wavelength Absorbed (nm)*	*Colour Absorbed*	*Colour Observed*
A			
B			
C			
D			
E			

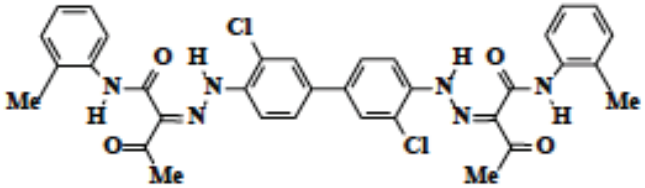
b)



Disperse Blue 165



Direct Red 81



Pigment Yellow 14

State which of these molecules has the largest gap between *HOMO* and *LUMO* ***and*** explain how you arrived at your answer.

Exam Practice

3. The electronic spectra of molecules can be described in terms of the wavelength of maximum absorbance, λ_{max}.

The table below shows a number of compounds with their corresponding λ_{max} values.

Compound	λ_{max}/nm
1.	217
2.	227
3.	263
4.	352

(*a*) Compound 1 is buta-1,3-diene.

Name compound 2. **1**

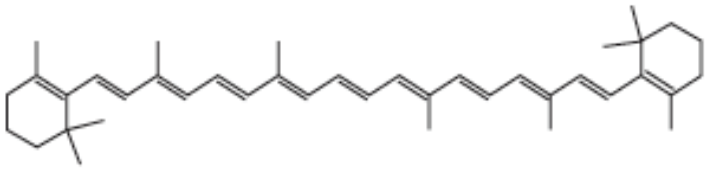
(*b*) Draw the most likely structure for the compound with λ_{max} = 291 nm. **1**

(*c*) The compounds shown have a system of alternating single and double bonds.

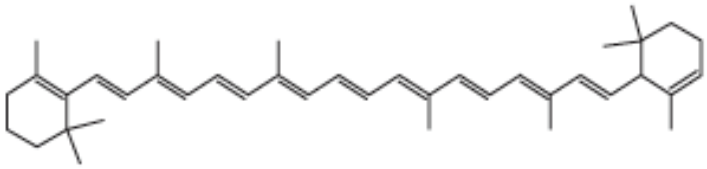
What word is used to describe this type of system? **1**

(*d*) From the information shown in the table draw a conclusion relating the energy difference between the HOMO and the LUMO as the number of alternating single and double bonds increases. **1**

(*e*) β-carotene, λ_{max} = 452 nm gives the orange colour to carrots and has the structure

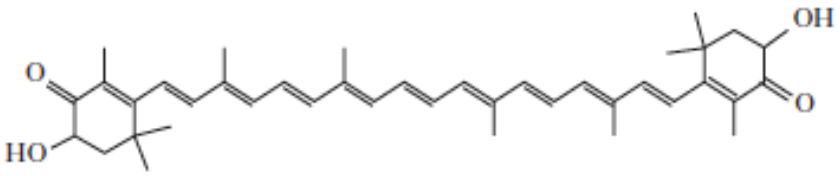


whereas α-carotene, λ_{max} = 434 nm is found in oranges and has the structure:



Explain why there is a difference in the λ_{max} values for these two structures. **1**

(*f*) The pink colour of cooked salmon and lobster is due to astaxanthin which has the structure:



This molecule is optically active.

Draw part of the molecule and circle one of the asymmetric carbon atoms responsible for this optical activity. **1**

(6)