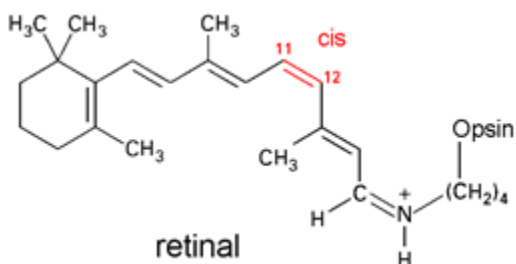


1. Answer the questions about the structure of rhodopsin's chromophore, retinal, shown below.



a) How many molecular orbitals will retinal's conjugate pi system have?

(1) 6 (2) 8 (3) 10 **((4) 12)** (5) 15

Rationalization: 12 AO's, therefore 12 MO's.

b) How many nodes would the HOMO of retinal's conjugate pi system have?

(1) 1 (2) 3 **((3) 5)** (4) 7 (5) 9

12 MO's with 12 e-'s, therefore HOMO is ψ_6 . With nodes increasing by 1 with each new MO, ψ_6 will have 5 nodes.

2. I often get the question, why does the HOMO-LUMO gap decrease with increasing conjugation. Presented in this question is one explanation.

a) Draw the HOMO and LUMO for 1,3-butadiene.

<u>MO</u>	<u># nodes</u>	<u>depiction</u>
LUMO ψ_3	2 nodes	
HOMO ψ_2	1 node	

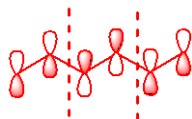
b) Draw the HOMO and LUMO for 1,3,5-hexatriene.

<u>MO</u>	<u># nodes</u>	<u>depiction</u>
LUMO ψ_4	3 nodes	

HOMO

Ψ_3

2 nodes



c) What is the percent increase in the number of nodes for 1,3-butadiene?

With 1 node going to 2, there is a 100% increase or doubling of the nodes.

d) What is the percent increase in the number of nodes for 1,3,5-hexatriene?

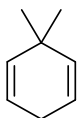
With 2 nodes going to 3, there is a 50% increase in the nodes.

e) Which molecule experiences a greater percentage or relative change in number of nodes and how does this help explain the smaller HOMO-LUMO gap in 1,3,5-hexatriene versus 1,3-butadiene?

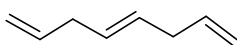
1,3-butadiene has a larger relative change in nodes and, since more nodes means higher energy, you would expect a greater relative increase or difference in the energy of the 1,3-butadiene HOMO and LUMO orbitals.

3. Circle all the structures with chromophores that would be expected to have strong UV-visible absorption.

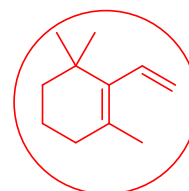
a)



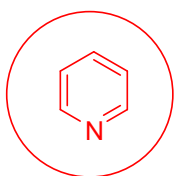
b)



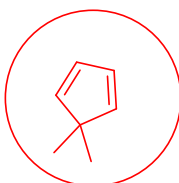
c)



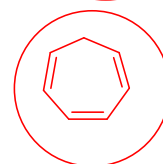
d)



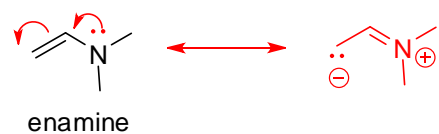
e)



f)



4. The enamine functional group shown below has a UV absorption with a $\lambda_{\max}=230$ nm. You will recall that the λ_{\max} for 1,3-butadiene is 217 nm. How does the enamine functional group mimic the π system of 1,3-butadiene allowing it to absorb UV radiation?



enamine

The N of the enamine has a lone pair of electrons which is in conjugation with the adjacent alkene π electrons as seen in the resonance form. This creates a π system with 4 electrons similar to 1,3-butadiene and therefore capable of absorbing UV radiation.