

* Woodward-Fieser Rules for calculating λ_{max} in conjugated dienes, trienes and polyenes-

CONJUGATED DIENES - alternative double bonds

Types: i) Acyclic conjugated diene-



(Parent value - 215 nm)

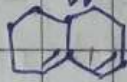
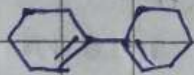
ii) Homoannular diene - cyclic diene having conjugated double bond in the same ring.



(Parent value - 253 nm)

iii) Heteroannular diene -

cyclic diene in which double bonds in conjugation are present in different rings.



(Parent value - 215 nm)

iv) endocyclic double bond -

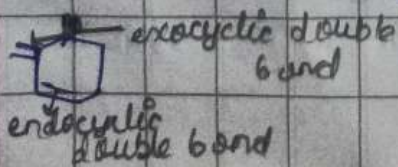
It is a double bond present in a ring.



v) Exocyclic double bond - It is a double bond in which one of the doubly bonded atoms is a part of ring system. eg:



(Parent value - 5 nm)



Ring A → 1 endocyclic + 1 exocyclic

Ring B → 1 endocyclic

According to these rules, each type of diene/triene system is having a certain fixed value at which absorption takes place, known as basic / parent value.

Thus λ_{max} for a particular compound.

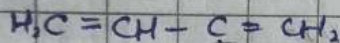
Parent value + alkyl substituents or ring residue's contribution + double bond extending conjugation + polar groups (-Cl, -Br, -OR)

• Double bond extending conjugation -



Value +30 nm

• Alkyl substitute / Ring residue -



alkyl substitute = 1



ring residue = 3

Value for each ring residue / alkyl substitute = +5 nm

Auxochromes	Value
-OR	6 nm
-SR	30 nm
-Cl, -Br	5 nm
-NR ₂	60 nm
-OCOCH ₃	0 nm

• Examples:

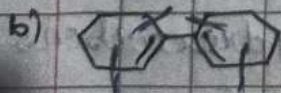


Parent value for homoannular diene = 253 nm

Two alkyl substituents = $2 \times 5 = 10$ nm

Two ring residues = $2 \times 5 = 10$ nm

$\lambda_{max} = 273$ nm



Parent value for heteroannular diene = 215 nm

Four ring residues = 20 nm

(4×5) $\lambda_{max} = 235$ nm