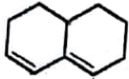
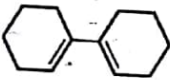
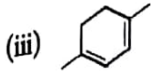
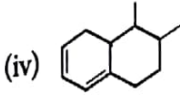


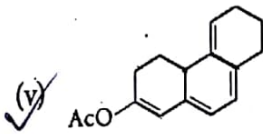
Compound	Answer												
(i) 	<table> <tr> <td>Base value (Heteroannular diene)</td> <td>=</td> <td>217 nm</td> </tr> <tr> <td>Ring residues 3×5</td> <td>=</td> <td>15 nm</td> </tr> <tr> <td>Exocyclic double bonds 1×5</td> <td>=</td> <td>5 nm</td> </tr> <tr> <td colspan="2" style="text-align: right;">Calc. λ_{\max}</td> <td>237 nm</td> </tr> </table>	Base value (Heteroannular diene)	=	217 nm	Ring residues 3×5	=	15 nm	Exocyclic double bonds 1×5	=	5 nm	Calc. λ_{\max}		237 nm
Base value (Heteroannular diene)	=	217 nm											
Ring residues 3×5	=	15 nm											
Exocyclic double bonds 1×5	=	5 nm											
Calc. λ_{\max}		237 nm											
(ii) 	<table> <tr> <td>Base value (Heteroannular diene)</td> <td>=</td> <td>217 nm</td> </tr> <tr> <td>Ring residues 4×5</td> <td>=</td> <td>20 nm</td> </tr> <tr> <td colspan="2" style="text-align: right;">Calc. λ_{\max}</td> <td>237 nm</td> </tr> </table>	Base value (Heteroannular diene)	=	217 nm	Ring residues 4×5	=	20 nm	Calc. λ_{\max}		237 nm			
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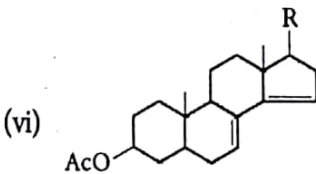
Base value	=	253 nm
(Homoannular diene)		
Substituents 2 × 5	=	10 nm
Ring residues 2 × 5	=	10 nm
<hr/>		
Calc. λ_{max}	=	273 nm



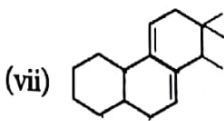
Base value	=	253 nm
(Homoannular diene)		
Ring residues 3 × 5	=	15 nm
Exocyclic double bonds 1 × 5	=	5 nm
<hr/>		
Calc. λ_{max}	=	273 nm



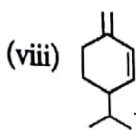
Base value	=	253 nm
(Homoannular diene)		
Double bond extending the conjugation 2 × 30	=	60 nm
Ring residues 5 × 5	=	25 nm
-OAc substituent	=	0 nm
Exocyclic double bonds 3 × 5	=	15 nm
<hr/>		
Calc. λ_{max}	=	353 nm



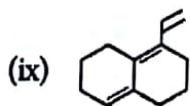
Base value	=	217 nm
(Heteroannular diene)		
Ring residues 4 × 5	=	20 nm
Exocyclic double bonds 2 × 5	=	10 nm
<hr/>		
Calc. λ_{max}	=	247 nm



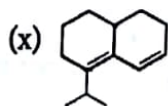
Base value	=	217 nm
(Heteroannular diene)		
Ring residues 4 × 5	=	20 nm
Exocyclic double bonds 2 × 5	=	10 nm
<hr/>		
Calc. λ_{max}	=	247 nm



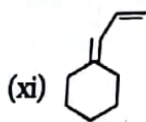
Base value	=	217 nm
(Heteroannular diene)		
Ring residues 2 × 5	=	10 nm
Exocyclic double bonds 1 × 5	=	5 nm
<hr/>		
Calc. λ_{max}	=	232 nm



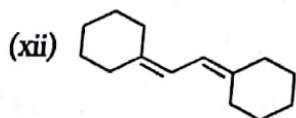
Base value	=	217 nm
(Heteroannular diene)		
Double bond extending the conjugation 1 × 30	=	30 nm
Ring residues 4 × 5	=	20 nm
Exocyclic double bond 2 × 5	=	10 nm
Calc. λ_{max}	=	277 nm



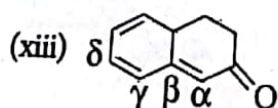
Base value	=	217 nm
(Heteroannular diene)		
Ring residues 3 × 5	=	15 nm
Alkyl substituent 1 × 5	=	5 nm
Exocyclic double bond 1 × 5	=	5 nm
Calc. λ_{max}	=	242 nm



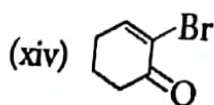
Base value	=	217 nm
(Acyclic diene)		
Ring residues 2 × 5	=	10 nm
Exocyclic double bond 1 × 5	=	5 nm
Calc. λ_{max}	=	232 nm



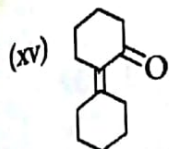
Base value	=	217 nm
(Acyclic diene)		
Ring residues 4 × 5	=	20 nm
Exocyclic double bond 2 × 5	=	10 nm
Calc. λ_{max}	=	247 nm



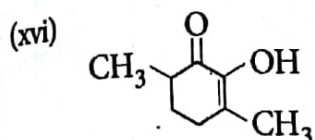
Base value (Enone)	=	215 nm
β substituent 1 × 12	=	12 nm
ω -substituent 1 × 18	=	18 nm
Two double bonds		
Extending conjugation 2 × 30	=	60 nm
Homodiene component 1 × 39	=	39 nm
Exocyclic double bond 1 × 5	=	5 nm
Calc. λ_{max}	=	349 nm



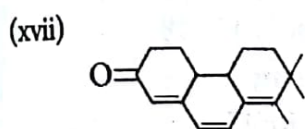
Base value	=	215 nm
(α, β -unsat ketone)	=	25 nm
α -bromo subst. 1 × 25	=	25 nm
β -subst. (ring residue) 1 × 12	=	12 nm
Calc. λ_{max}	=	252 nm



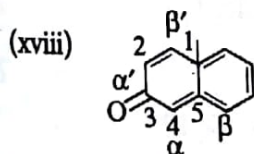
Base value	=	215 nm
(α, β -unsat. ketone)		
α -substituent 1×10	=	10 nm
β -substituents 2×12	=	24 nm
Exocyclic double bond 2×5	=	10 nm
(with respect to both the rings)		
Calc. λ_{max}	=	259 nm



Base value	=	215 nm
OH at α	=	35 nm
β -substituents 2×12	=	24 nm
(one alkyl, one ring residue)		
Calc. λ_{max}	=	274 nm



Base value	=	215 nm
One β -substituent 1×12	=	12 nm
β substituents 1×18	=	18 nm
ω substituents 2×18	=	36 nm
Exocyclic double bond 2×5	=	10 nm
Two double bonds 2×30	=	60 nm
(Extending conjugation)		
Calc. λ_{max}	=	351 nm

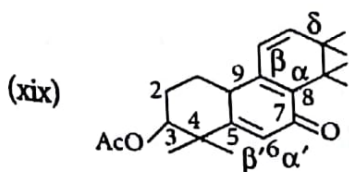


(a)

It is a cross-conjugated system		
Base value ($\Delta^{4,5}$ enone)	=	215 nm
Two β -substituents 2×12	=	24 nm
One exocyclic double bonds	=	5 nm
1×5	=	5 nm
Calc. λ_{max}	=	244 nm

(b)

Base value ($\Delta^{1,2}$ enone)	=	215 nm
One β' -substituent 1×12	=	12 nm
Calc. λ_{max}	=	227 nm
Expected λ_{max}	=	244 nm
(Longest wavelength)		



(a)

Base value ($\Delta^{8,9}$ enone)	=	215 nm
One α -ring residue	=	10 nm
One β -ring residue	=	12 nm
One double bond extending conjugation 1×30	=	30 nm

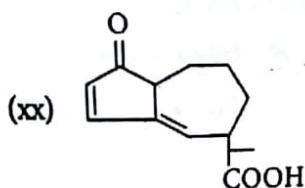
One δ -substituent 1×18	=	18 nm
One homoannular diene 1×39	=	39 nm
(C-ring)		

Calc. λ_{\max}	=	324 nm
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(b) Base ($\Delta^{5,6}$ enone) = 215 nm

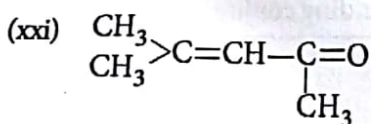
Two β' -substituent 2×12	=	24 nm
One exocyclic		
Double bond 1×5	=	5 nm

Calc. λ_{\max}	=	244 nm
Expected λ_{\max}	=	324 nm



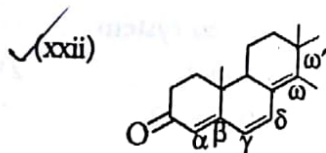
Base value	=	215 nm
One β -substituent 1×12	=	12 nm
One γ -substituent 1×18	=	18 nm
One δ -substituent 1×18	=	18 nm
One exocyclic double		
bond 1×5	=	5 nm

Calc. λ_{\max}	=	268 nm
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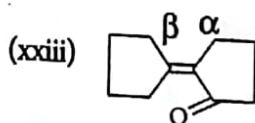
Base value	=	215 nm
Two β -substituents 2×12	=	24 nm

Calc. λ_{\max}	=	239 nm
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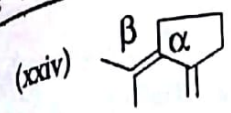
Base value	=	215 nm
One β -substituents 1×12	=	12 nm
One ω -substituents 1×18	=	18 nm
Two ω' -substituents 2×18	=	36 nm
Two double bonds		
extending conjugation 2×30	=	60 nm
Two exocyclic double		
bonds 2×5	=	10 nm

Calc. λ_{\max}	=	351 nm
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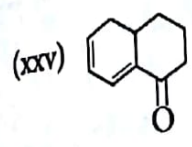


Base value	=	215 nm
one α -ring residue 1×10	=	10 nm
two β -ring residues 2×12	=	24 nm
two exocyclic double bonds		
2×5	=	10 nm

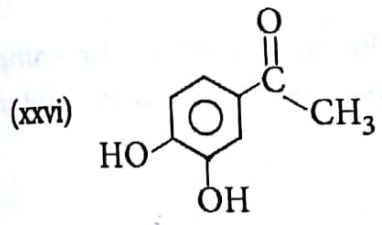
Calc. λ_{\max}	=	259 nm
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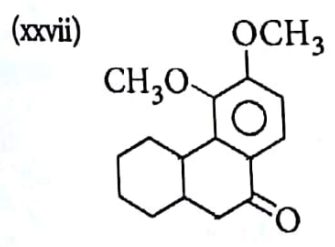
Base value	=	215 nm
One α -substituent (ring residue)		
1×10	=	10 nm
Two β -substituents 2×12	=	24 nm
One exocyclic double bonds 1×5	=	5 nm
<hr/>		
Calc. λ_{max}	=	254 nm



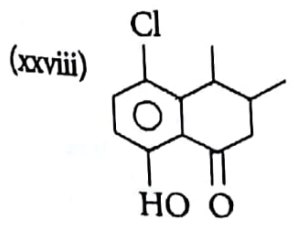
Base value	=	215 nm
One α -substituent 1×10	=	10 nm
One δ -substituent 1×18	=	18 nm
One double bonds extending		
conjugation 1×30	=	30 nm
One exocyclic double bond 1×5	=	5 nm
<hr/>		
Calc. λ_{max}	=	278 nm



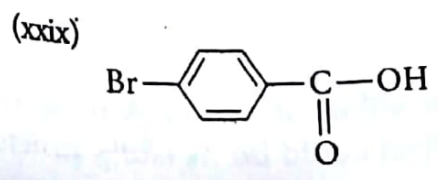
Base value for acyl benzene	=	246 nm
OH at <i>meta</i> position	=	7 nm
OH at <i>para</i> position	=	25 nm
<hr/>		
Calc. λ_{max}	=	278 nm



Base value	=	246 nm
(for acyl benzene)		
OCH ₃ at <i>meta</i>	=	7 nm
OCH ₃ at <i>para</i>	=	25 nm
alkyl group at <i>ortho</i> (ring)	=	3 nm
<hr/>		
Calc. λ_{max}	=	281 nm

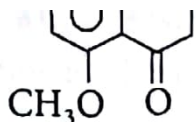


Base value	=	246 nm
OH at <i>ortho</i>	=	7 nm
Cl at <i>meta</i>	=	0 nm
<i>o</i> -ring residues	=	3 nm
<hr/>		
Calc. λ_{max}	=	256 nm



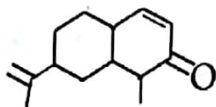
Base value for Ar-C(=O)-OH	=	230 nm
Br at <i>para</i> position	=	15 nm
<hr/>		
Calc. λ_{max}	=	245 nm

(XXXI)



Base value	=	215 nm
<i>o</i> -ring residue	=	3 nm
<i>o</i> -OCH ₃	=	7 nm
<i>p</i> -OCH ₃	=	25 nm
<hr/>		
Calc. λ_{max}	=	281 nm

55. A neutral compound showed λ_{max} at 251 nm. Predict whether the compound has the following structure. If not, propose an alternative one with similar basic skeleton.

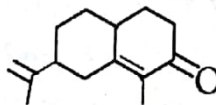


→ The proposed structure will have λ_{max} as below:

Base value	=	215 nm
One β -substituent 1×12	=	12 nm
<hr/>		
Calc. λ_{max}	=	227 nm

So the proposed structure is not the actual structure of the compound.

An alternative structure may be as below:

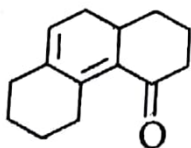


This alternative structure will have λ_{max} as calculated below:

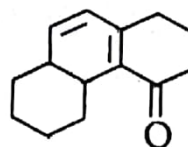
Base value	=	215 nm
One α -substituent 1×10	=	10 nm
Two β -substituents 2×12	=	24 nm
One exocyclic double bonds 1×5	=	5 nm
<hr/>		
Calc. λ_{max}	=	254 nm

This value is within 5 nm of the observed value.

56. An unknown compound is believed to have either structure A or B. Its UV-spectrum shows λ_{max} at 320 nm (Ethanol). What could be its likely structure?



(A)



(B)