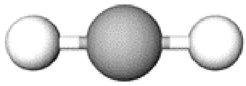
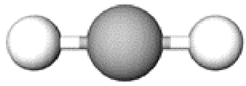
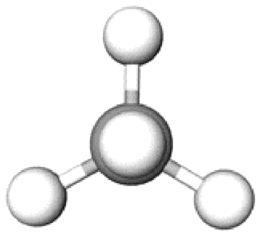
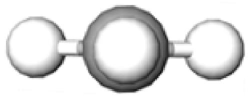
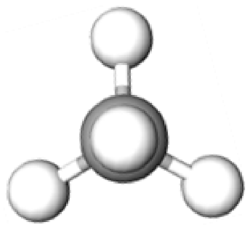
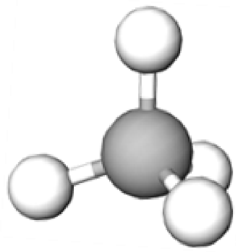
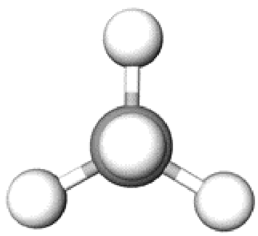
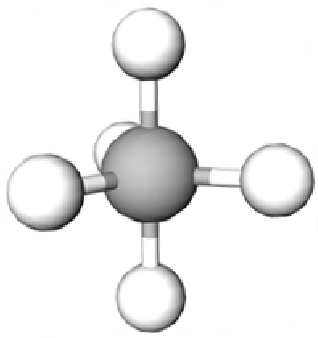
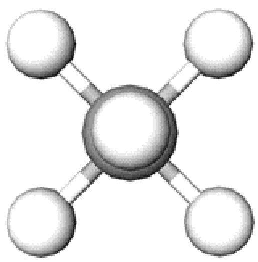
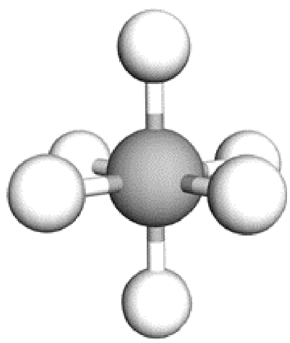
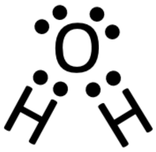
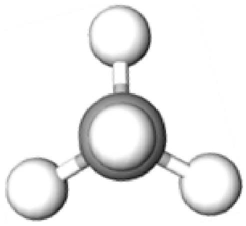
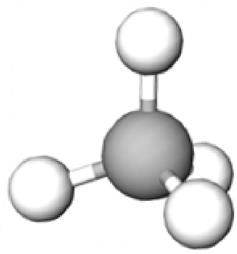
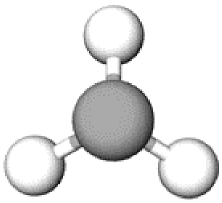
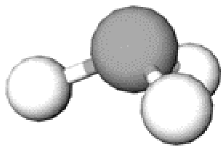
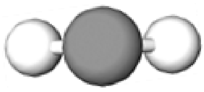
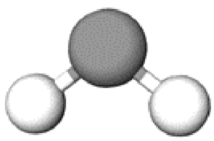
Recall that the electron geometry of a molecule is determined by the number of *domains* (i.e. lone pairs or atoms) around the central atom, as given in the table below.

Number of domains	**Electron Geometry**	**Top View**	**Side View**
2	Linear		
3	Trigonal Planar		
4	Tetrahedral		
5	Trigonal Bipyramidal		
6	Octahedral		

For example, the central oxygen in water (drawn below) is bonded to two hydrogen atoms and contains two electron lone pairs. As such, there are four domains around the central oxygen and its electron geometry is tetrahedral.



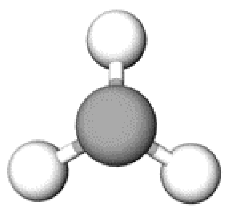
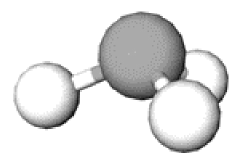
To determine the molecular geometry of a molecule, we only look at the geometry of the atoms surrounding a particular molecule (not including lone pairs). As an example, the possible configurations for 4 domains are shown in the table below.

Number of Domains	**Number of Lone Pairs**	**Molecular Geometry**	**Top View**	**Side View**
4	0	Tetrahedral		
4	1	Trigonal Pyramidal		
4	2	Bent		

For example, since water has two lone pairs and four domains around the central oxygen, it has a bent molecular geometry.

(e) Identify the number of domains and lone pairs bonded to the central atom in each of the following molecular geometries.

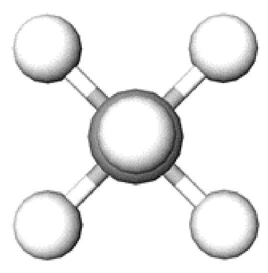
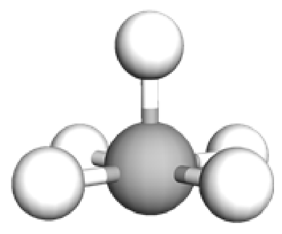
(i)

Top View	Side View
	

Domains:

Lone pairs:

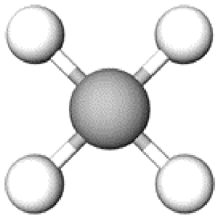
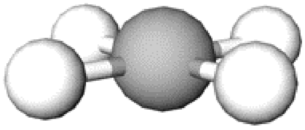
(ii)

Top View	Side View
	

Domains:

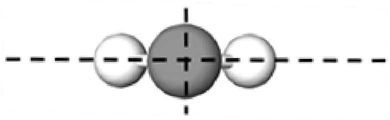
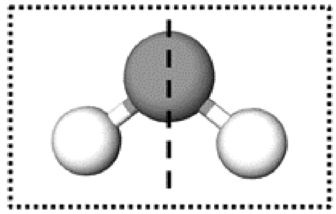
Lone pairs:

(iii)

Top View	Side View
	

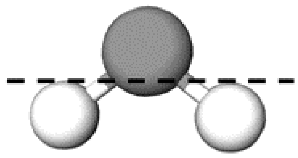
Domains: Lone pairs:

Now that we have revised molecular geometries, we can consider the symmetries that molecules may have. The first type of symmetry we will consider is reflectional symmetry. To be precise, a molecule has a mirror plane of symmetry if reflecting the molecule through that plane leaves the molecule exactly the same. For example, water has two planes of symmetry, shown below.

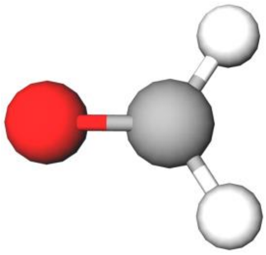
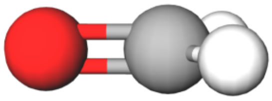
Top View	**Side View**
	

The dotted rectangle indicates a plane of symmetry in the plane of the page.

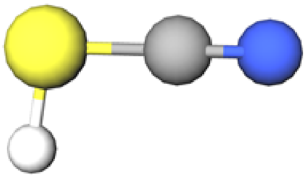
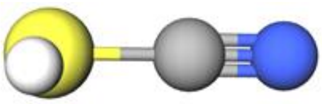
However, the following is **not** a plane of symmetry of water, since it does not leave the configuration of the atoms the same:



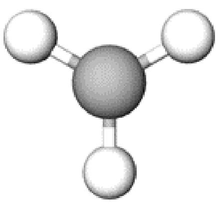
(f) How many planes of symmetry does a CH_2O molecule have?

Top View	Side View
	

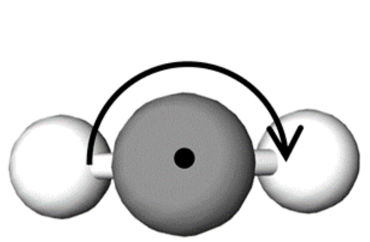
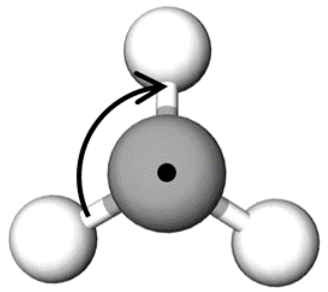
(g) How many planes of symmetry does a HSCN molecule have?

Top View	Side View
	

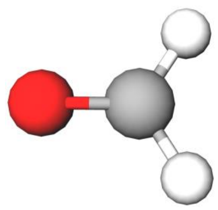
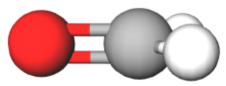
(h) How many planes of symmetry does a BF_3 molecule have?

Top View	Side View
	

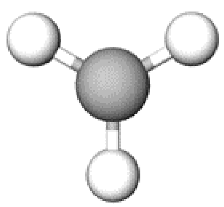
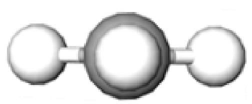
The second type of symmetry we consider is **rotational symmetry**. A molecule has an *n*-fold rotational symmetry about an axis (where $n \geq 2$), if rotating around that axis by an angle $\frac{360°}{n}$ leaves the molecule the same. For example, water has a 2-fold (180°) rotational symmetry about the vertical axis while ammonia (NH_3) has a 3-fold (120°) rotational symmetry about the vertical axis:

Water (top view)	**Ammonia (top view)**
	

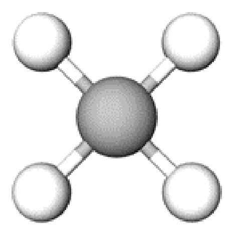
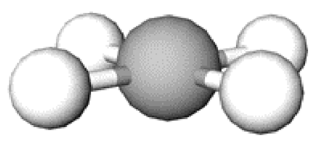
(i) How many axes of symmetry does a CH_2O molecule have?

Top View	**Side View**
	

(j) How many axes of symmetry does a $AlCl_3$ molecule have?

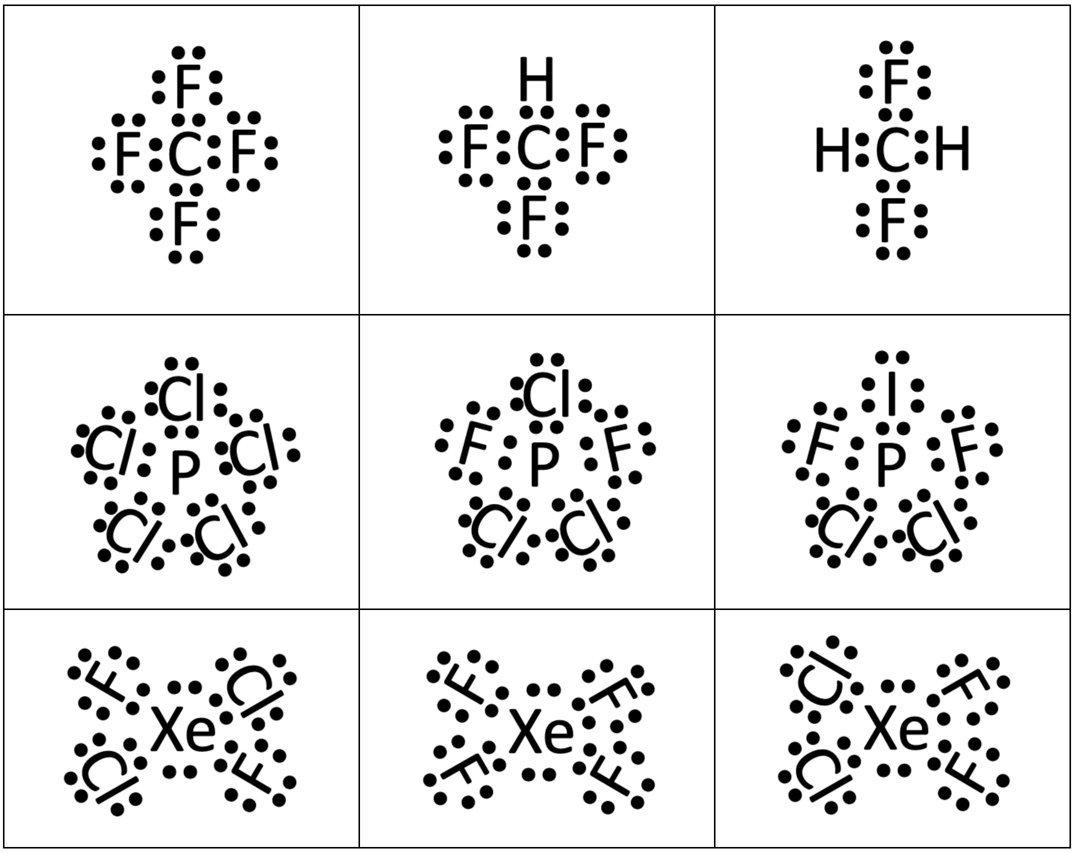
Top View	**Side View**
	

The following XeF_4 molecule has five axes of symmetry.

Top View	**Side View**
	

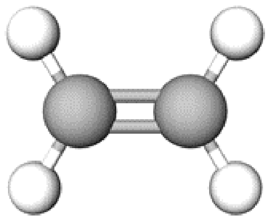
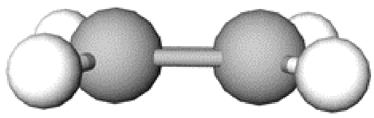
(k) How many axes of symmetry of each degree, *n*, does XeF_4 have?

(l) Which of the following molecules has four 3-fold axes of symmetry and three 2-fold axes of symmetry?



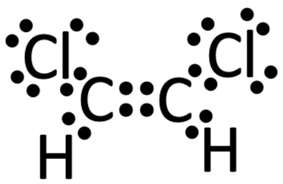
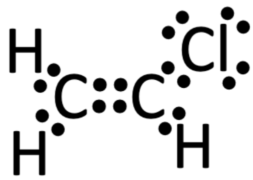
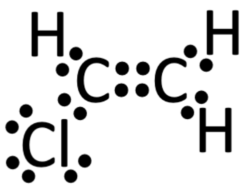
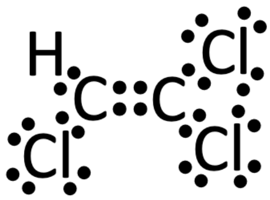
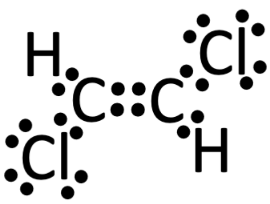
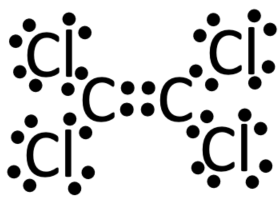
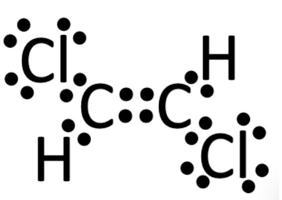
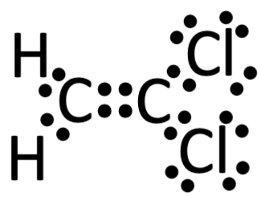
We can now discuss the first application of symmetry to the properties of molecules - dipole moments. A molecule is *non-polar* if it contains two or more different rotational axes of symmetry, *or* if it contains a mirror plane of symmetry perpendicular to a rotation axis. Otherwise, the molecule is *polar*.

First consider ethene, whose molecular geometry is given below. Note that the hydrogen atoms on each side of the double bond cannot rotate relative to each other.

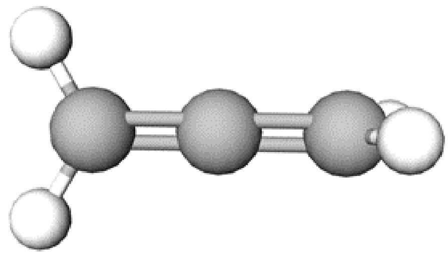
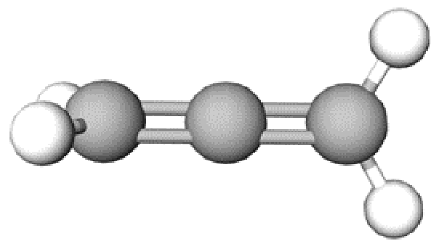
Top View	**Side View**
	

Now consider the following molecules, which have been formed by replacing some of the hydrogen atoms in ethene with chlorine atoms.

Select all of the molecules that are **non**-polar.

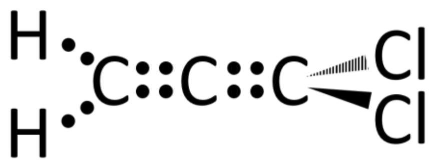
	
	
	
	

Next, consider allene, whose molecular geometry is given below. Note that the hydrogen atoms on each side of the double bond cannot rotate relative to each other.

Top View	**Side View**
	

Now consider the following molecules, which have been formed by replacing some of the hydrogen atoms in allene with chlorine atoms. *Note that in the diagrams below, the wedged line refers to the atoms coming out of the page in the side view, while the dashed line refers to the atoms going into the page.*

Select all of the molecules that are non-polar.

(m) Consider a water molecule. Which of the following factors would turn water into a more polar species?

A. Replacing both H atoms with Cl atoms.

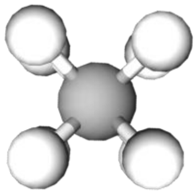
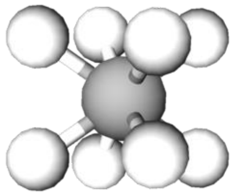
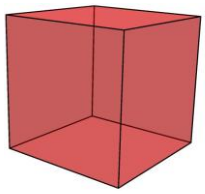
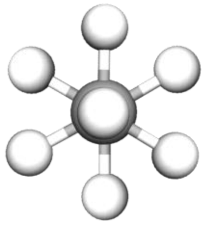
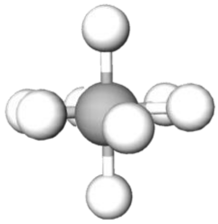
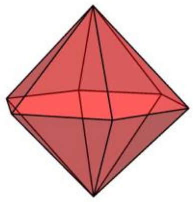
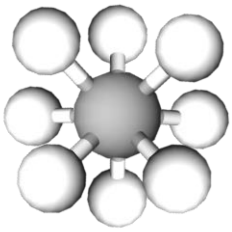
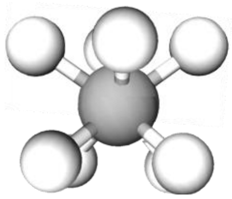
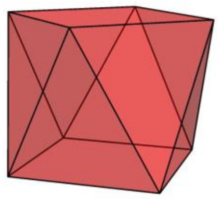
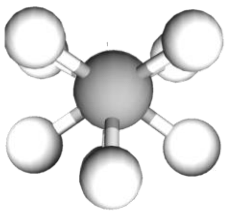
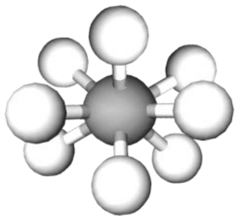
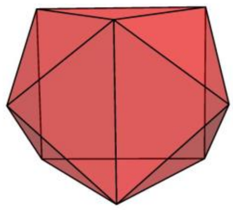
B. Removing one of the H atoms (making OH^-)

C. Replacing the oxygen with a sulfur atom.

D. Decreasing the H-O-H bond angle

At the start of the question, we considered the electron and molecular geometry of molecules consisting of a central atom connected to up to six electron domains. In the next part of the question, we use the symmetry elements discussed above to determine the molecular geometry of XeI_8^{2-}, an ion with eight electron domains around the central xenon atom. Its Lewis structure is provided below:

We consider four possible molecular geometries for XeI_8^{2-}: cubic, hexagonal bipyramidal, square antiprismatic, and bicapped trigonal prismatic, each pictured below.

Molecular Geometry	**Top View**	**Side View**	**Polyhedron**
Cubic			
Hexagonal Bipyramidal			
Square Antiprismatic			
Bicapped Trigonal Prismatic			

Replacing one iodine atom in XeI_8^{2-} with chlorine gives a number of different molecules. How many different molecules would this result in for each of the possible geometries?

Molecular Geometry	**Number of molecules formed**
Cubic	
Hexagonal Bipyramidal	
Square Antiprismatic	
Bicapped Trigonal Prismatic	

4 marks

The following information is given about the structure of XeI_8^{2-}:

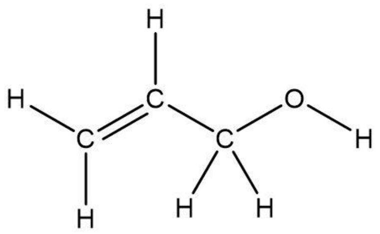
- When one of the iodine atoms is replaced with chlorine, giving $XeClI_7^{2-}$, only one molecule is produced.
- When two of the iodine atoms are replaced with chlorine atoms, giving $XeCl_2I_6^{2-}$, none of the molecules are non-polar.

(n) What is the structure of XeI_8^{2-}?

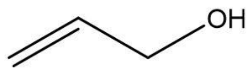
Question 18

When representing organic compounds, skeletal formula notation is often used for simplicity. In this notation, bonds are still represented by lines, but the symbol for carbon atoms is not used. Hence, the end of a line segment or the meeting point of line segments indicate carbon atoms.

Hydrogen atoms connected to carbon atoms are implied rather than explicitly shown. Any other elements are shown.

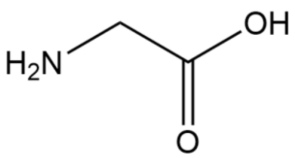


is equivalent to

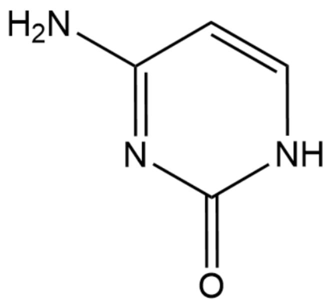


(b) How many hydrogen atoms are present in the following organic compounds?

(i)



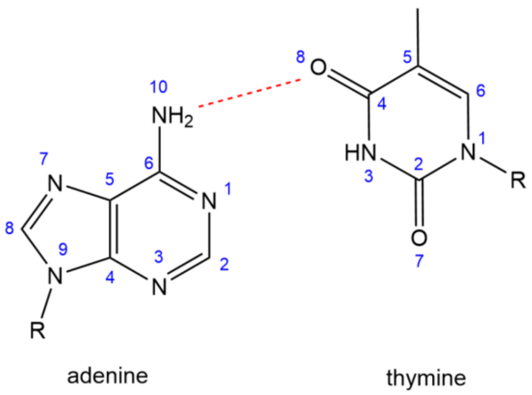
(ii)



Nucleotides are the building blocks of nucleic acid macromolecules such as DNA and other forms of genetic material. Nucleotides have three main components; a five-membered sugar, a phosphate group, and a nucleobase. There are different types of nucleobases which produce different nucleotides.

Adenine and thymine are examples of nucleobases, and their structure is shown below. (The 'R' group is shorthand notation for the rest of nucleotide chain that the base is attached to, which has no relevance to this question.)

One example of an intermolecular interaction between these two nucleobases has been shown with a dashed line:



When identifying hydrogen bond interactions, **a group that can be either a hydrogen bond donor or acceptor, will first and foremost, be a hydrogen bond donor.**

(c) Identify the type of intermolecular force interactions that can occur at the following positions:

Adenine N-1

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Adenine C-2

(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

Adenine N-10

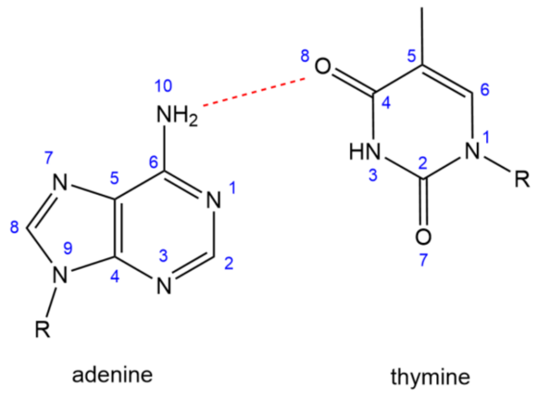
(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

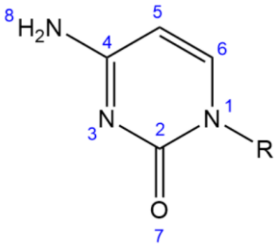
The intermolecular interaction depicted in the previous question (and below) is known as base pairing, and is responsible for holding nucleotide strands together in DNA.



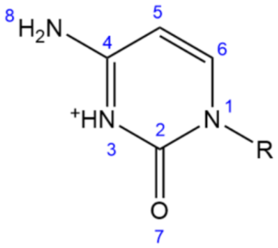
Base pairing is only possible if there are feasible intermolecular interactions between the nucleobases. This depends on their type of intermolecular interactions possible, and whether the groups are close enough to interact. In the diagram, there is a base pairing interaction between adenine N-10 and thymine O-8.

(d) Identify another feasible base pairing interaction between adenine and thymine.

Cytosine is another nucleobase, two different forms of which have been shown below, denoted structure **1** and structure **2**.



1



2

Recall that when identifying hydrogen bond interactions, **a group that can be either a hydrogen bond donor or acceptor, will first and foremost, be a hydrogen bond donor**.

(e) Identify the type of intermolecular force interactions that can occur at the following positions:

Structure 1 N-3

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Structure 2 N-3

(i) Can it be a hydrogen bond donor?

☐ yes

☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

☐ NA

☐ hydrogen bond acceptor

☐ no significant interaction

Structure 1 O-7

(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

Structure 1 N-8

(i) Can it be a hydrogen bond donor?

- ☐ yes
- ☐ no

(ii) Can it form any of the following interactions? Select NA if you answered "yes" to the hydrogen bond donor question above.

- ☐ NA
- ☐ hydrogen bond acceptor
- ☐ no significant interaction

The two forms of cytosine shown in the previous question differ in their protonation state. Protonation refers to the addition of a proton (H^+) to a molecule.

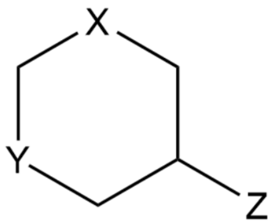
A proton acceptor, A, can exist in one of two different protonation states:

- A
- AH^+

Each protonated species has an associated acid dissociation constant (pK_a), which describes how the pH of its environment will affect its protonation state.

- When pH is equal to pK_a, the two forms will be present in equal concentrations.
- When pH is less than pK_a, the predominant species will be AH^+.
- When pH is greater than pK_a, the predominant species will be A.

Consider the generic organic compound, and its associated pK_a data.



Group	pK_a
X	6.5
Y	11.0
Z	3.0

(f) Predict the protonation state that each group will be in at pH 10.

(i) **X:**

☐ X

☐ XH^+

(ii) **Y:**

☐ Y

☐ YH^+

(iii) **Z:**

☐ Y

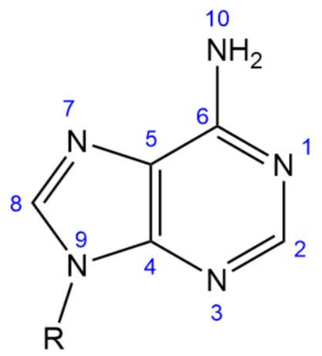
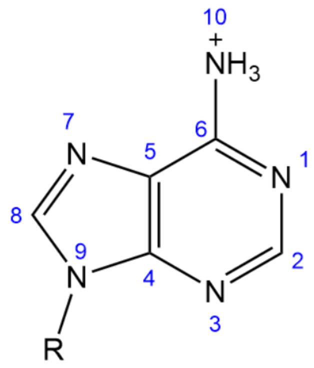
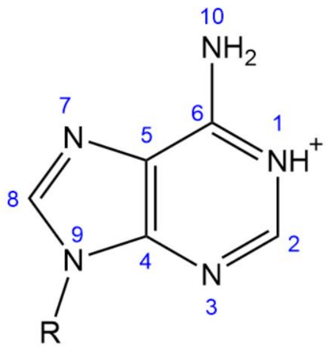
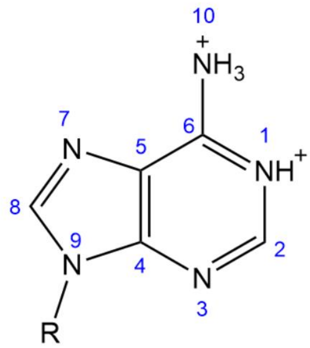
☐ YH^+

The table below shows pK_a data for N-1 and N-10 positions of the nucleobase, adenine.

Group	**pK_a**
N-1	4.15
N-10	9.80

Multiple forms of adenine are shown below.

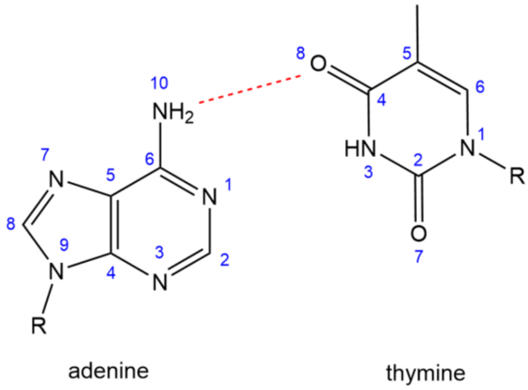
(g) Choose the most abundant form of adenine at pH 4.

(i)		(ii)	
(iii)		(iv)	

Adenine regularly base pairs with thymine, by interacting with both:

1. ideal base pairing interactions
2. appropriate protonation states

One example of a correct combination has been provided below:

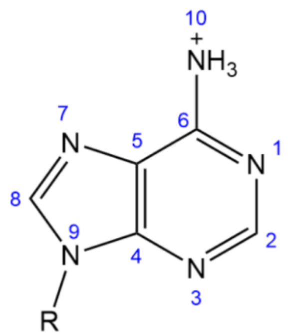
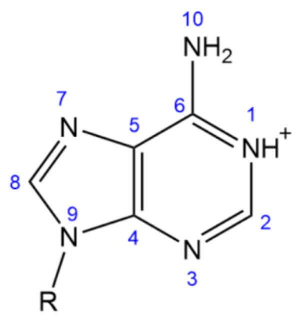
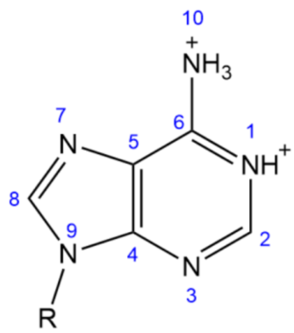


The table below shows pK_a data for N-1 and N-10 positions of adenine.

Group	**pK_a**
N-1	4.15
N-10	9.80

(h) Choose the form or forms of adenine that can interact with thymine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

(i) 	(ii) 	(iii) 

The table below shows pK_a data for N-1 and N-10 positions of adenine.

Group	pK_a
N-1	4.15
N-10	9.80

(i) Select the option that best describes the pH range where both adenine and thymine can form feasible base pairing interactions.

(i) The pH must be less than 4.15.

(ii) The pH must be greater than 4.15 and less than 9.8.

(iii) The pH must be greater than 4.15, with no upper limit.

(iv) The pH must be less than 9.8, with no lower limit.

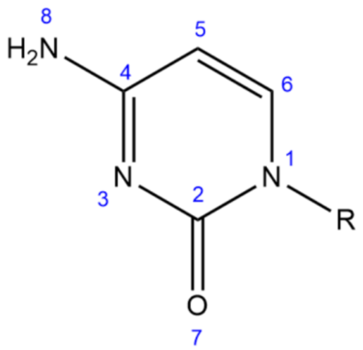
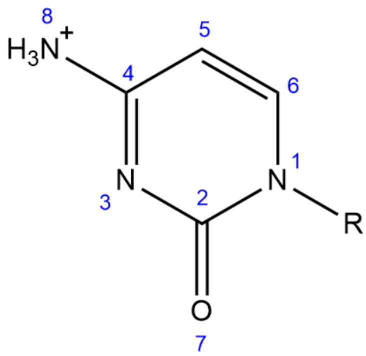
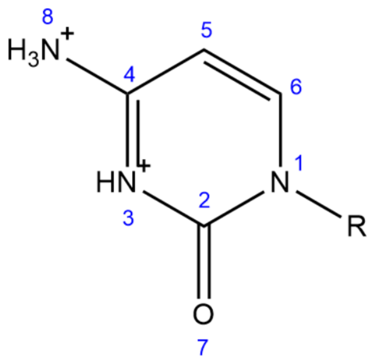
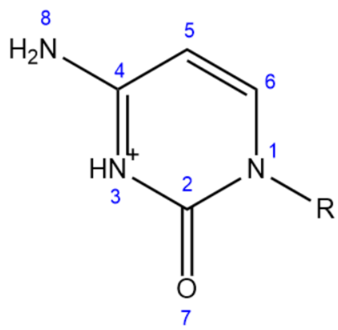
(v) The pH must be greater than 9.8.

The table below shows pK_a data for N-3 and N-8 positions of the nucleobase, cytosine.

Group	**pK_a**
N-1	4.6
N-10	12.2

Multiple forms of cytosine are shown below.

(j) Choose the most abundant form of cytosine at pH 4.

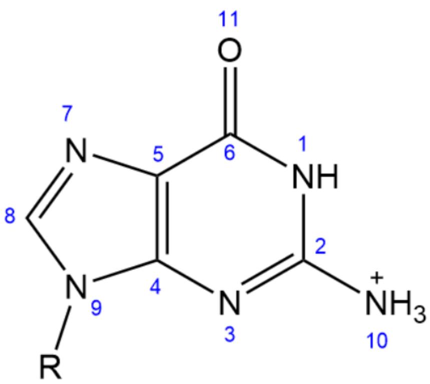
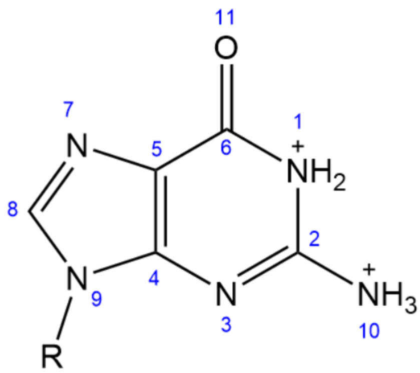
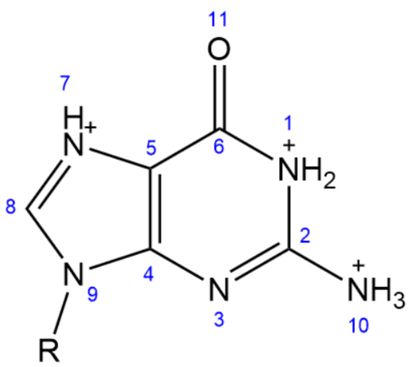
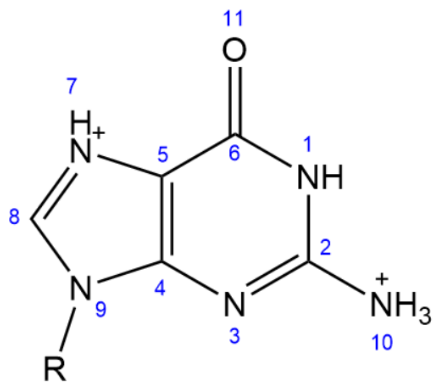
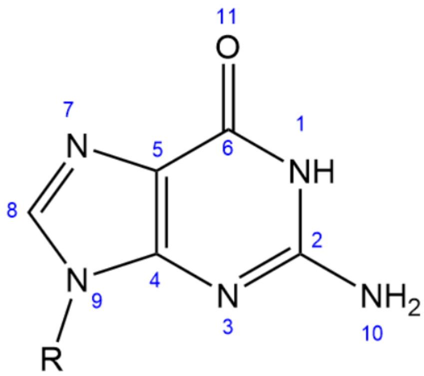
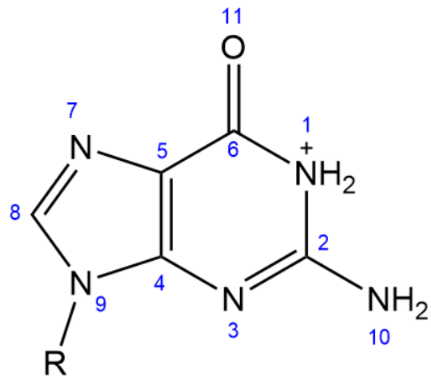
(i)		(ii)	
(iii)		(iv)	

The table below shows pK_a data for N-1, N-7 and N-10 positions of the nucleobase, guanine.

Group	**pK_a**
N-1	3.3
N-7	9.4
N-10	12.6

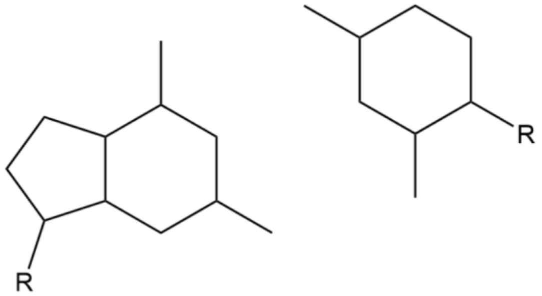
Multiple forms of guanine are shown below.

(k) Choose the most abundant form of guanine at pH 4.

(i) 	(ii) 
(iii) 	(iv) 
(v) 	(vi) 

Cytosine regularly base pairs with guanine.

The template below has been provided to indicate the orientation of the nucleobases when they undergo base pairing (guanine on the left, cytosine on the right). The actual structures of these nucleobases are shown in the question options.

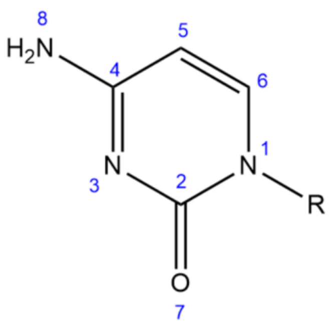
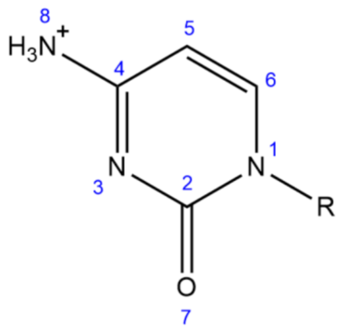


The table below shows pK_a data for N-3 and N-8 positions of cytosine.

Group	**pK_a**
N-3	4.6
N-8	12.2

(l) Choose the form or forms of cytosine that can interact with guanine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

<table>
<tr><td>(i)</td><td>
</td><td>(ii)</td><td>
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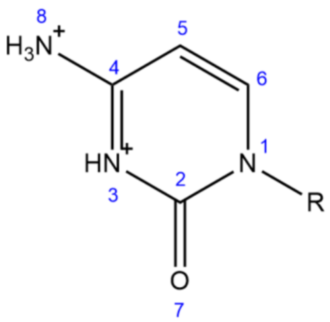
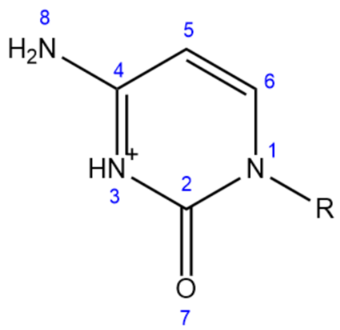
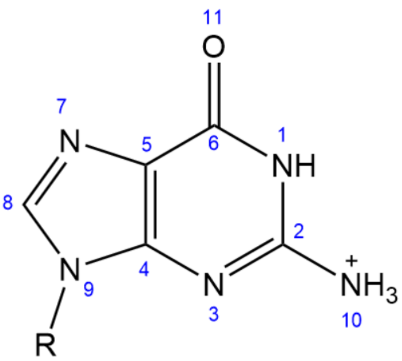
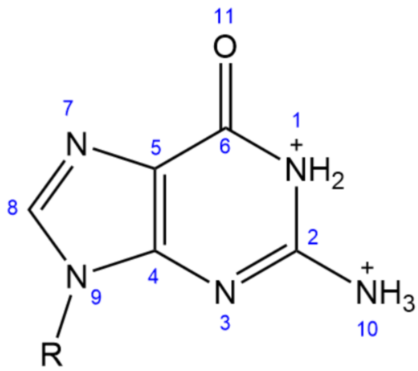
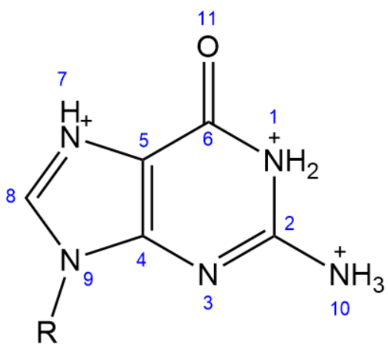
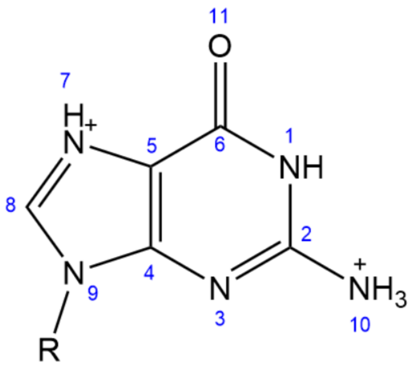
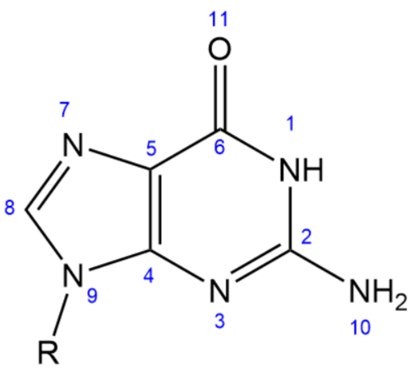
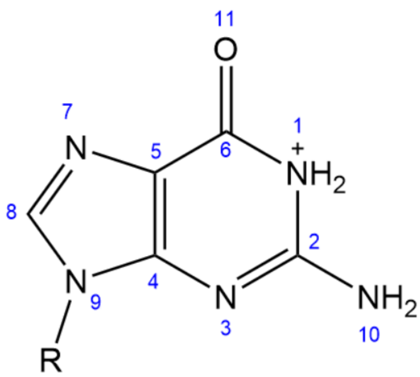
<tr><td>(iii)</td><td>
</td><td>(iv)</td><td>
</td></tr>
</table>

The table below shows pK_a data for N-1, N-7 and N-10 positions of the nucleobase, guanine.

Group	**pK_a**
N-1	3.3
N-7	9.4
N-10	12.6

(m) Choose the form or forms of cytosine that can interact with guanine and have both:

1. ideal base pairing interactions
2. appropriate protonation states

(i) 	(ii) 
(iii) 	(iv) 
(v) 	(vi) 

Complete the following sentence with the appropriate choice.

(n) For cytosine and guanine to form feasible base pairing interactions, the pH must be **greater than**:

- (i) No lower limit
- (ii) 3.3
- (iii) 4.6
- (iv) 9.4
- (v) 12.2
- (vi) 12.6

AND less than:

- (i) No upper limit
- (ii) 3.3
- (iii) 4.6
- (iv) 9.4
- (v) 12.2
- (vi) 12.6

<u>END OF EXAM</u>