Programme 1

Symmetry Elements and Operations

Objectives

After completing this programme, you should be able to:

1. Recognise symmetry elements in a molecule.
2. List the symmetry operations generated by each element.
3. Combine together two operations to find the equivalent single operation.

All three objectives are tested at the end of the programme.

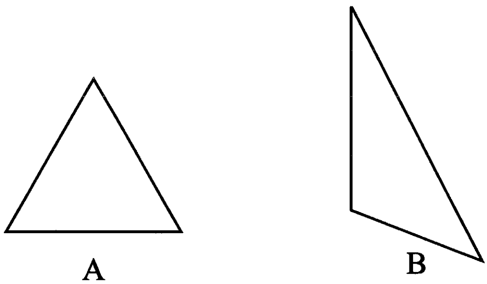
Assumed Knowledge

Some knowledge of the shapes of simple molecules is assumed.

Symmetry Elements and Operations

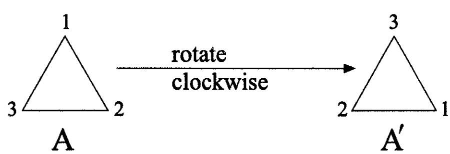
1.1 The idea of symmetry is a familiar one, we speak of a shape as being "symmetrical", "unsymmetrical" or even "more symmetrical than some other shape". For scientific purposes, however, we need to specify ideas of symmetry in a more quantitative way.

Which of the following shapes would you call the more symmetrical?



1.2 If you said A, it shows that our minds are at least working along similar lines!

We can put the idea of symmetry on a more quantitative basis. If we rotate a piece of cardboard shaped like A by one third of a turn, the result looks the same as the starting point:



Since A and A′ are *indistinguishable* (not identical) we say that the rotation is a symmetry operation of the shape.

Can you think of another operation you could perform on a triangle of cardboard which is also a symmetry operation? (Not the anticlockwise rotation!)

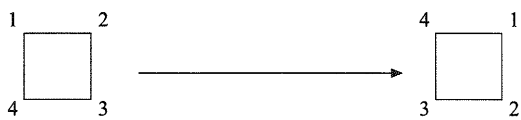
1.3 Rotate by half a turn about an axis through a vertex i.e. turn it over

How many operations of this type are possible?

1.4 Three, one through each vertex.

We have now specified the first of our symmetry operations, called a PROPER ROTATION, and given the symbol C. The symbol is given a subscript to indicate the ORDER of the rotation. One third of a turn is called C_3, one half a turn C_2, etc.

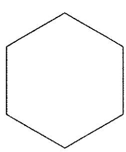
What is the symbol for the operation:



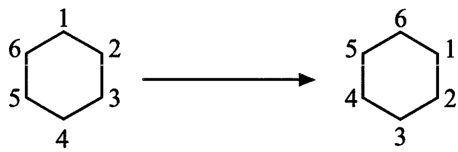
1.5 C_4. It is rotation by $\frac{1}{4}$ of a turn.

A symmetry *operation* is the operation of actually doing something to a shape so that the result is indistinguishable from the initial state. Even if we do not do anything, however, the shape still possesses an abstract geometrical property which we term a symmetry *element*. The element is a geometrical property which is said to generate the operation. The element has the same symbol as the operation.

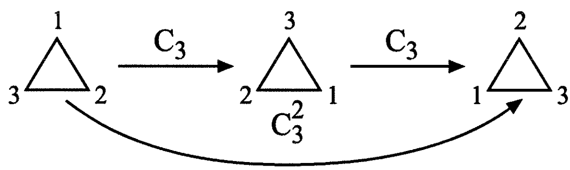
What obvious symmetry element is possessed by a regular six-sided shape:



1.6 C_6, a six-fold rotation axis, because we can rotate it by $\frac{1}{6}$ of a turn

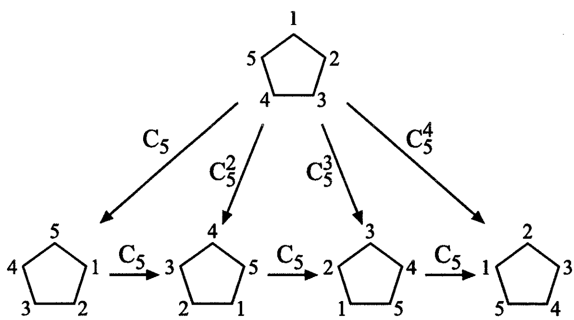


One element of symmetry may generate more than one operation e.g. a C_3 axis generates two operations called C_3 and C_3^2:



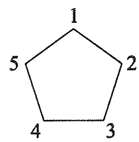
What operations are generated by a C_5 axis?

1.7 C_5, C_5^2, C_5^3, C_5^4



What happens if we go one stage further i.e. C_5^5?

1.8 We get back to where we started i.e.



The shape is now more than indistinguishable, it is IDENTICAL with the starting point. We say that C_5^5, or indeed any $C_n^n = E$, where E is the IDENTITY OPERATION, or the operation of doing nothing. Clearly this operation can be performed on anything because everything looks the same after doing nothing to it! If this sounds a bit trivial I apologise, but it is necessary to include the identity in the description of a molecule's symmetry in order to be able to apply the theory of Groups.

We have now seen two symmetry elements, the identity, E, and a proper rotation axis C_n. Can you think of a symmetry element which is possessed by all *planar* shapes?

1.9 A plane of symmetry.

This is given the symbol σ (sigma). The element generates only one operation, that of reflection in the plane.

Why only one operation? Why can't we do it twice – what is σ^2?

1.10 $\sigma^2 = E$, the identity, because reflection in a plane, followed by reflection back again, returns all points to the position from which they started, i.e. to the *identical* position.

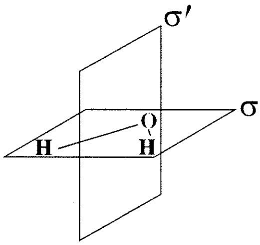
Many molecules have one or more planes of symmetry. A flat molecule will always have a plane in the molecular plane e.g. H_2O, but this molecule also has one other plane.

Can you see where it is?

AT THIS STAGE SOME READERS MAY NEED TO MAKE USE OF A KIT OF MOLECULAR MODELS OR SOME SORT OF 3-DIMENSIONAL AID. IN THE ABSENCE OF A PROPER KIT, MATCHSTICKS AND PLASTICINE ARE QUITE GOOD, AND A FEW LINES PENCILLED ON A BLOCK OF WOOD HAVE BEEN USED.

1.10a You were trying to find a second plane of symmetry in the water molecule:

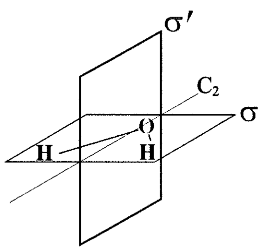
1.11



σ is the plane of the molecule, σ' is at right angles to it and reflects one H atom to the other.

The water molecule can also be brought to an indistinguishable configuration by a simple rotation. Can you see where the proper rotation axis is, and what its order is?

1.12 C_2, a twofold rotation axis, or rotation by half a turn.



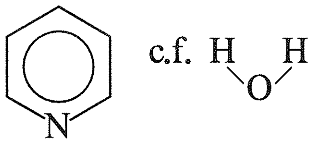
A C_2 axis passing through space is the hardest of all symmetry elements to see. It will be much easier to visualise if you use a model of the molecule.

This completes the description of the symmetry of water. It actually has FOUR elements of symmetry – one of which is possessed by all molecules irrespective of shape. Can you list all four symmetry elements of the water molecule?

1.13 E C_2 σ σ' Don't forget E!

Each of these elements generates only one operation, so the four symbols also describe the four operations.

Pyridine is another flat molecule like water. List its symmetry elements.

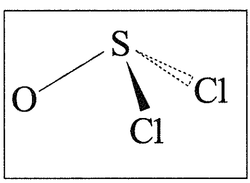


1.14 E C_2 σ σ' i.e. the same as water.

Many molecules have this set of symmetry elements, so it is convenient to classify them all under one name, the set of symmetry operations is called the C_{2v} point group, but more about this nomenclature later.

There is a simple restriction on planes of symmetry which is rather obvious but can sometimes be helpful in finding planes. A plane must either pass through an atom, or else that type of atom must occur in pairs, symmetrically either side of the plane. Take the molecule $SOCl_2$, which has a plane, and apply this consideration. Where must the plane be?

1.15 Through the atoms S and O because there is only one of each:

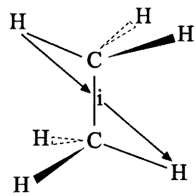


The molecule NH_3 possesses planes. Where must they lie?

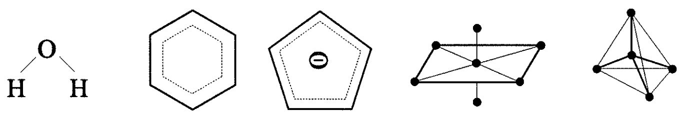
1.16 Through the nitrogen (only one N), and through at least one hydrogen (because there is an odd number of hydrogens). Look at a model and convince yourself that this is the case.

A further element of symmetry is the INVERSION CENTRE, i. This generates the operation of inversion through the centre. Draw a line from any point to the centre of the molecule, and produce it an equal distance the other side. If it comes to an equivalent point, the operation of inversion is a symmetry operation. e.g. ethane in the staggered conformation:

N.B. The operation of inversion cannot be physically carried out on a model.

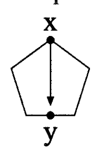


Which of the following have inversion centres



A B C D E

1.17 Only B and D e.g., for C, the operation i would take point x to point y which is certainly not equivalent:



An inversion centre may be:
a. In space in the centre of a molecule (ethane, benzene); or
b. At a single atom in the centre of the molecule (D above).

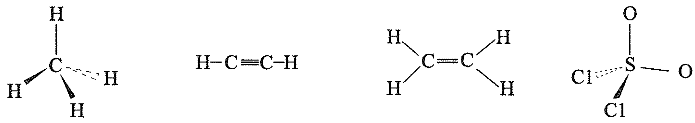
If it is in space, all atoms must be present in even numbers, spaced either side of the centre. If it is at an atom, then that type of atom *only* must be present in an odd number. Hence a molecule AB_3 cannot have an inversion centre but a molecule AB_4 might possibly have one.

Use this consideration to decide which of the following MIGHT POSSIBLY have a centre of inversion.

NH_3 CH_4 C_2H_2 C_2H_4 $SOCl_2$ SO_2Cl_2

1.18 CH_4, C_2H_2, C_2H_4, SO_2Cl_2 fulfil the rules, i.e. have no atoms present in odd numbers, or have only one such atom.

Which of these actually have inversion centres?



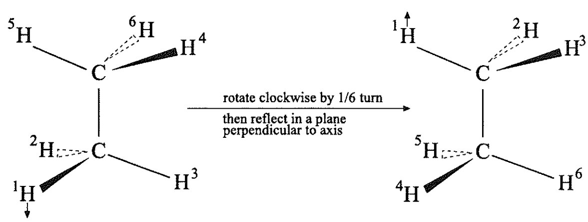
1.19 Only C_2H_2 and C_2H_4. Both have an inversion centre midway between the two carbon atoms.

What is the operation i^2?

1.20 $i^2 = E$, for the same reason that $\sigma^2 = E$ (Frame 1.10).

We now have the operations E, σ, C_n, i. Only one more is necessary in order to specify molecular symmetry completely. That is called an IMPROPER ROTATION and is given the symbol S, again with a subscript showing the order of the axis. The element is sometimes called a rotation-reflection axis, and this describes the operation very well.

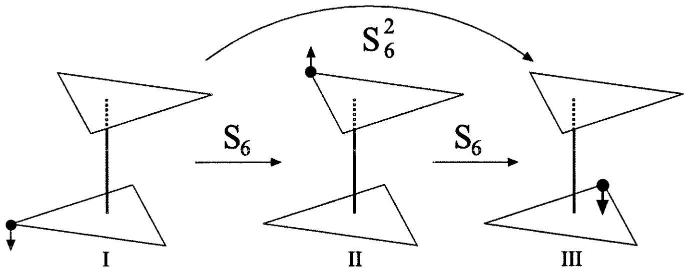
The S_n operation is rotation by 1/n of a turn, followed by reflection in a plane *perpendicular to the axis*, e.g. ethane in the staggered conformation has an S_6 axis because it is brought to an indistinguishable arrangement by a rotation of 1/6 of a turn, followed by reflection:



N.B. Neither C_6 nor σ are present on their own.

In this example the effect of the symmetry operation has been shown by labelling one corner of the drawing. Draw the position of the label after the S_6 operation is applied a second time.

1.21



Now consider what single symmetry operation will take this molecule from state I direct to state III i.e. what single operation is the same as S_6^2?

1.22 $S_6^2 = C_3$, rotation by one third of a turn, because the molecule has been rotated by 2/6 of a turn ($= C_3$) and reflected twice ($\sigma^2 = E$).

What happens to the marker if S_6 is applied once more, i.e. what single operation has the same effect as S_6^3 (use a model or the diagram above).

1.23 $S_6^3 = i$. In general $S_n^{n/2} = i$ if n is even and n/2 is odd. The operation $S_n^{n/2}$ is then not counted by convention. If S_n (n even) is present, and n/2 is odd, i is present but the converse is not necessarily true.

Now apply S_6 once more, so that it has been applied four times in all.

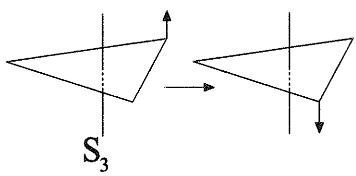
What other operation gives the same result as S_6^4?

1.24 $S_6^4 = C_3^2$ for the same reason that $S_6^2 = C_3$ (Frame 1.22) i.e. we have now rotated by 1/6 of a turn 4 times ($= C_3^2$), and reflected 4 times ($=$ E)

S_6^5 is a unique operation, and $S_6^6 = E$. This is again true for any S_n of even n.

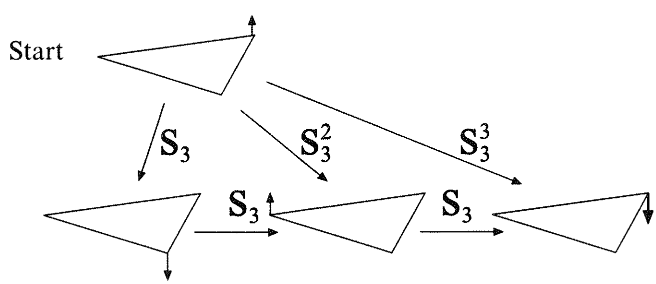
Let us now look at S_n of odd n because the case is rather different from even n. It may at first seem rather a trivial operation, because the C_n axis and a perpendicular plane must both be present, but it is necessary to include it to apply Group Theory to symmetry.

Use as the model a flat equilateral triangle with one vertex "labelled"; this label is only to help us to follow the effect of the operations, for example the application of S_3 moves the label as shown:



Write down the result of applying S_3 clockwise once, twice and then three times.

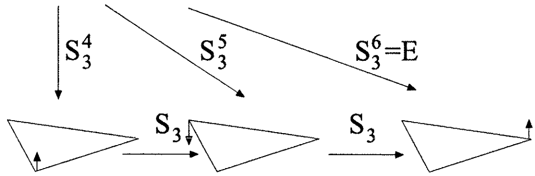
1.25



In contrast to S_6 and C_3, applying the operation n times, where n is the order of the axis does not bring us back to the identity.

Keep going, then, when do we get E?

1.26



This result is quite general, for n odd $S_n^{2n} = E$, because we have rotated through two whole circles, and reflected an even number of times.

The equilateral triangle also has E, C_3, and σ among its elements of symmetry. Many of the operations we have generated by using the S_3 element of symmetry could have been generated by using other elements e.g., $S_3^2 = C_3^2$. Write these equivalents underneath the symbol S_3^n where appropriate:

S_3	S_3^2	S_3^3	S_3^4	S_3^5	S_3^6
e.g.	C_3^2				

1.27

S_3	S_3^2	S_3^3	S_3^4	S_3^5	S_3^6
	C_3^2	σ	C_3		E

By convention, only S_3 and S_3^5 are counted as distinct operations generated by the S_3 symmetry element.

Do a similar analysis for the symmetry element C_6 (proper rotation axis) of benzene, which also has C_3 and C_2 axes colinear with the C_6. Clearly $C_6^2 = C_3$ since rotation by two sixths of a turn is the same as rotation by one third of a turn. Write the operations which have the same effect as C_6 C_6^2 C_6^3 C_6^4 C_6^5 and C_6^6.

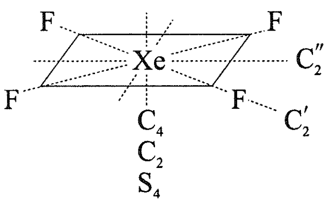
1.28 $C_6 \quad C_6^2 \quad C_6^3 \quad C_6^4 \quad C_6^5 \quad C_6^6$

$\quad\; C_3 \quad C_2 \quad C_3^2 \quad\quad E$

Again, by convention, only the operations C_6 and C_6^5 are counted, the others are taken to be generated by C_3 and C_2 axes colinear with C_6.

We have just been looking at the operations generated by a particular symmetry element, let us now turn to the identification of symmetry elements in a molecule. You must first be quite sure you appreciate the difference between a symmetry *element* and the symmetry *operation(s)* generated by the element. If you are not confident of this point, have another look at frames 1.5 to 1.13.

Some molecules have a great many symmetry elements, some of which are not immediately obvious e.g. XeF_4:

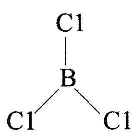


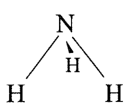
also E, i
σ_h (molecular plane)
2σ vertically through C_2'
$2\sigma'$ vertically through C_2''

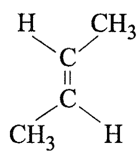
Hence the complete list of symmetry elements is:

$E \quad C_4 \quad C_2 \quad S_4 \quad i \quad 2C_2' \quad 2C_2'' \quad \sigma_h \quad 2\sigma \quad 2\sigma'$

List the symmetry elements of the following molecules:







(assume CH_3 groups spherical)

If there is a set of, say, three equivalent planes, write them as 3σ, but if there are three non-equivalent planes, write $\sigma\ \sigma'\ \sigma''$. Similarly for other elements.

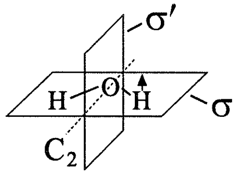
1.29 BCl$_3$: E C_3 S_3 $3C_2$ 3σ σ (a somewhat similar case to XeF_4)
NH$_3$: E C_3 3σ
Butene: E C_2 σ i

We will now look at what happens if two symmetry operations are combined, or performed one after the other. The result is always the same as doing one symmetry operation alone, so we can write an equation such as:

$$\sigma C_2 = \sigma'$$

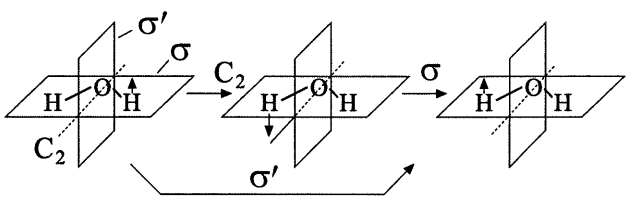
This equation means that the operation C_2 *followed* by the operation σ gives the same result as the operation σ'. Note that the order in which the operations are performed is from right to left. I apologise for the introduction of back to front methods, but this is the convention universally used in the mathematics of operators, and the reason for it will become evident when we begin to use matrices to represent symmetry operations.

Confirm that this relationship is in fact true for the water molecule. It may help to put a small label on your model to show the effect of applying the operations:



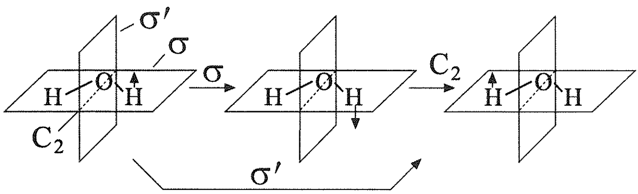
Draw the position of the arrow after applying C_2, and then after applying σ to the result. Hence confirm that $\sigma C_2 = \sigma'$.

1.30



What is the effect of reversing the order of the operations? i.e. what is the product $C_2\sigma$ (σ followed by C_2)?

1.31



In this case the two operations COMMUTE i.e., $\sigma C_2 = C_2\sigma$, but this is not always true.

Use this diagram with an arrow to set up a complete multiplication table for the symmetry OPERATIONS of the water molecule, putting the product of the top operation, then the side operation, in the spaces:

	E	C_2	σ	σ'
E				
C_2				
σ				
σ'				

1.32

	E	C_2	σ	σ'
E	E	C_2	σ	σ'
C_2	C_2	E	σ'	σ
σ	σ	σ'	E	C_2
σ'	σ'	σ	C_2	E

You should now be able to:

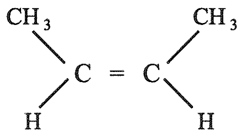
A. Recognise symmetry elements in a molecule.
B. List the operations generated by each element.
C. Combine together two operations to find the equivalent single operation.

I'm afraid the next page is a short test to see how well you have learned about elements and operations. After you have done it, mark it yourself, and it will give you some indication of how well you have understood this work.

Symmetry Elements and Operations Test

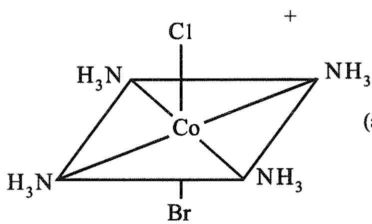
1. List the symmetry elements of the molecules.

A



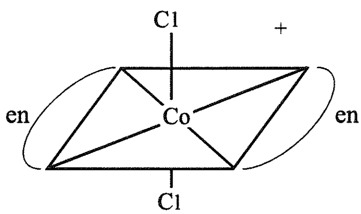
(assume CH_3 spherical)

B

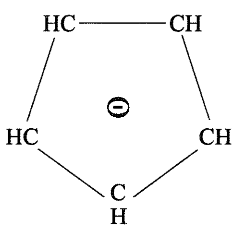


(assume NH_3 spherical)

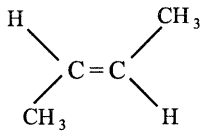
C



D



2. Set up the multiplication table for the *operations* of the molecule *trans* but-2-ene. Apply the top operation then the side operation:



	E	C_2	σ	i
E				
C_2				
σ				
i				

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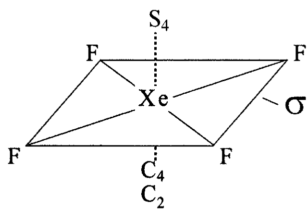
3. In this question you have to state the single symmetry operation of XeF_4 which has the same effect as applying a given operation several times. The diagram below shows the location of the symmetry elements concerned.



What operation has the same effect as:

A. S_4^2 E. C_4^3

B. S_4^3 F. C_4^4

C. S_4^4 G. σ^2

D. C_4^2 H. i^2

Answers

Give yourself one mark for each underlined answer you get right. (The others are so easy, they are not worth a mark!)

1. A. $\underline{E}$ $\underline{C_2}$ $\underline{\sigma}$ $\underline{\sigma'}$

   B. E $\underline{C_4}$ $\underline{C_2}$ $\underline{2\sigma}$ $\underline{2\sigma'}$

   C. E $\underline{C_2}$ $\underline{C_2}$ $\underline{C_2}$ $\underline{i}$ $\underline{\sigma}$ $\underline{\sigma'}$ $\underline{\sigma''}$

   D. E $\underline{C_5}$ $\underline{5C_2}$ $\underline{\sigma}$ $\underline{5\sigma'}$ $\underline{S_5}$

Total = 20

2.

	E	C_2	σ	i
E	E	C_2	σ	i
C_2	C_2	$\underline{E}$	$\underline{i}$	$\underline{\sigma}$
σ	σ	$\underline{i}$	$\underline{E}$	$\underline{C_2}$
i	i	$\underline{\sigma}$	$\underline{C_2}$	$\underline{E}$

Total = 9

3. A. $S_4^2 = \underline{C_2}$ E. $C_4^3 = \underline{C_4^3}$

   B. $S_4^3 = \underline{S_4^3}$ F. $C_4^4 = \underline{E}$

   C. $S_4^4 = \underline{E}$ G. $\sigma^2 = \underline{E}$

   D. $C_4^2 = \underline{C_2}$ H. $i^2 = \underline{E}$

Total = 8

Grand Total = 37

To be able to proceed confidently to the next programme you should have obtained at least:

Question 1 (Objective 1) 15/20 (Frames 1.1–1.20)
Question 2 (Objective 2) 7/9 (Frames 1.28–1.32)
Question 3 (Objective 3) 4/8 (Frames 1.6–1.10, 1.19–1.28).

If you have not obtained these scores you would be well advised to return to the frames shown, although a low score on question 3 is less serious than the other two.

Symmetry Elements and Operations

Revision Notes

The symmetry of a molecule can be described by listing all the symmetry elements of the molecule. A molecule possesses a symmetry element if the application of the operation generated by the element leaves the molecule in an *indistinguishable* state. There are five different elements necessary to completely specify the symmetry of all possible molecules:

E	the identity
C_n	proper rotation axis of order n
σ	a plane of symmetry
i	an inversion centre
S_n	improper (or rotation-reflection) axis of order n.

Each of the elements E, σ, i only generates one operation, but C_n and S_n can generate a number of operations because the effect of applying the operation a number of times can count as separate operations e.g., the C_3 element generates operations C_3 and C_3^2. Some such multiple applications of an operation have the same effect as a single application of a different operation. In these cases only the single case is counted, e.g., $C_4^2 = C_2$, and only C_2 is counted.

If two operations are performed successively on a molecule, the result is always the same as the application of only one different operation. It is therefore possible to set up a multiplication table for the symmetry operations of a molecule to show how the operations combine together.

When writing an equation to represent the successive application of symmetry elements it is necessary to remember that $\sigma\,\sigma'\,C_4$ means C_4 followed by σ', followed by σ.

Point Groups

Objectives

After completing this programme you should be able to:

1. State the point group to which a molecule belongs.
2. Confirm that the complete set of symmetry operations of a molecule constitutes a group.
3. Arrange a set of symmetry operations into classes.

The first of these objectives is vital to the use of group theory and is the only one tested at the end of the programme.

Assumed Knowledge

A knowledge of simple molecular shapes, and of the contents of Programme 1 is assumed.

Point Groups

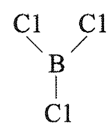
2.1 Write down the symbols of the FIVE elements needed to completely specify molecular symmetry.

2.2 E C S σ i

What are the names of these five elements of symmetry?

2.3 E — The identity element
C — Proper rotation axis
S — Improper rotation (or rotation-reflection) axis
σ — Plane of symmetry
i — Inversion centre

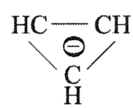
List all the symmetry elements of



2.4 E C_3 $3C_2$ σ $3\sigma'$ S_3

If you have got these three questions substantially correct you may proceed, otherwise return to Programme 1 – Symmetry Elements and Operations.

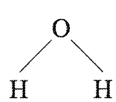
List all the symmetry elements of

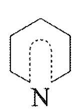


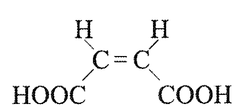
2.5 E C_3 $3C_2$ σ $3\sigma'$ S_3

i.e. exactly the same as BCl_3

There are many other examples of several molecules having the same set of symmetry elements, e.g. list all the symmetry elements of



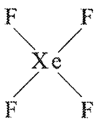


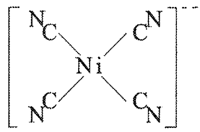


2.6 All three of these molecules (and many more!) have the elements

E C_2 σ σ'

In the same way all square planar molecules contain the elements E C_4 $C_2(=C_4^2)$ $4C_2$ σ $4\sigma'$ i S_4, regardless of the chemical composition of the molecule e.g.

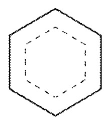




etc.

It is convenient to classify all such molecules by a single symbol which summarises their symmetry. This symbol for a flat square molecule is D_{4h}.

Can you suggest the symbol for a flat hexagonal molecule like benzene:



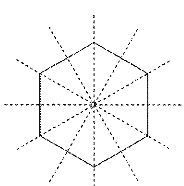
2.7 D_{6h} the symmetry is similar to that of the square planar case, but the principal axis is a 6-fold axis not a 4-fold axis.

The symmetry symbol consists of three parts:

The number indicates the order of the principal (i.e. highest order) axis. This is conventionally taken to be vertical.

The small letter h indicates a horizontal plane.

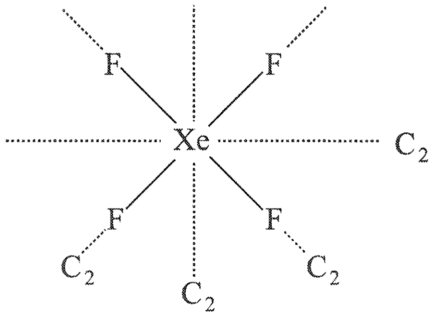
The capital letter D indicates that there are n(= 6 for benzene) C_2 axes at right angles to the principal C_n axis (C_6 for benzene):



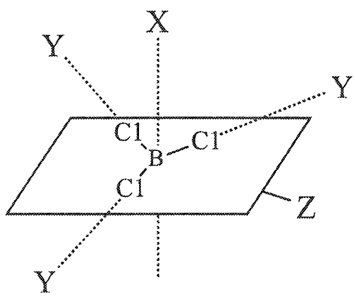
Two-fold axes

How many two-fold axes like this are there in a flat square molecule like XeF_4?

2.8 Four



Let us look now at a flat triangular molecule, say BCl_3:



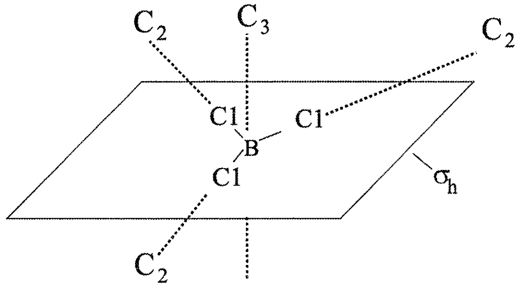
What are the symmetry elements labelled X, Y, and Z?

2.9 X = C_3 axis
Y = C_2 axes
Z = plane of symmetry

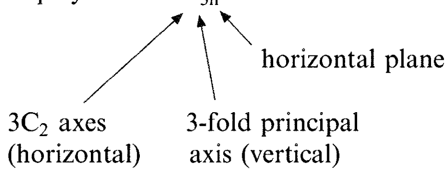
The principal C_3 axis is taken, conventionally to be vertical, so the plane is a horizontal plane (σ_h), and there are three C_2 axes at right angles to the principal axis.

What, therefore, is the symmetry symbol of the BCl_3 molecule? (frame 2.7 may help).

2.10 D_{3h}



Point group symbol: D_{3h}



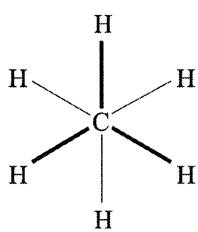
The molecule is said to belong to the D_{3h} POINT GROUP.

Let us now get a bit more general, and call the principal axis C_n, so that its order, n, can be any number.

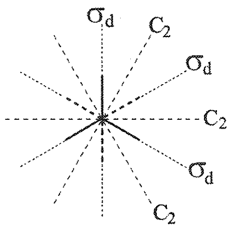
If there is no horizontal plane of symmetry, but there are n vertical planes as well as nC_2 axes, the point group is D_{nd}.

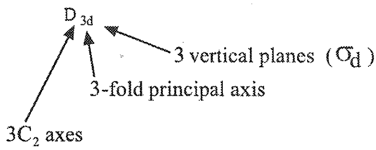
The D and the number mean the same as before but the small d stands for DIHEDRAL PLANES, because the n vertical planes lie between the nC_2 axes.

Ethane in the staggered conformation belongs to a D_{nd} point group. Decide on the value of n from the following diagram (looking down the principal axis), and hence state the point group to which ethane belongs.



2.11 D_{3d}, a model will help to convince you of the elements of symmetry in this case, but the following diagram is looking down the principal, vertical, 3-fold axis:



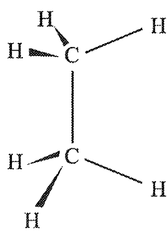


This is another case like frame 1.12 in which the C_2 axis passes through space and not along a bond. These axes are quite difficult to see and a molecular model may be necessary.

In the eclipsed conformation ethane has an additional element of symmetry. Can you see from the diagram (or a model) what the extra element is?

2.12 A horizontal plane of symmetry, σ_h

What does this make the point group of ethane in the eclipsed conformation?



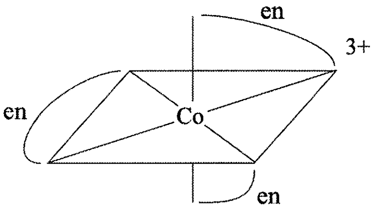
2.13 D_{3h} i.e. in the eclipsed conformation the horizontal plane takes precedence over the dihedral planes in describing the symmetry.

Some molecules have a principal C_n axis, and nC_2 axes at right angles, but no horizontal or vertical (dihedral) planes.

There is then no need to include h or d in the symmetry symbol. If the principal axis is a 3-fold axis what is the symmetry symbol in this case?

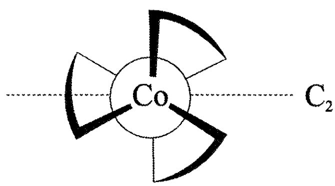
2.14 D_3 i.e., it has a 3-fold axis and three C_2 axes at right angles, hence D_3, but no σ_h or a σ_d, so no additional symbol is necessary.

An example of an ion of this symmetry is:



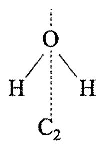
(en = $NH_2CH_2CH_2NH_2$)

You will probably need a model of the ion to see the axes, although an alternative diagram of the structure shows its symmetry very well:



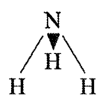
If the principal C_n axis is not accompanied by nC_2 axes, the first letter of the point group is C. A horizontal plane is looked for first, and is shown by a little h. If σ_h is not present, n vertical planes are looked for and are shown by a small v.

e.g.



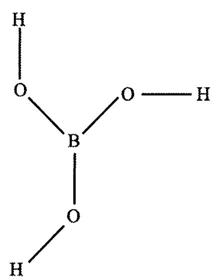
C_2, no C_2 at right angles no σ_h, but $2\sigma_v \therefore$ point group C_{2v}

What is the point group of



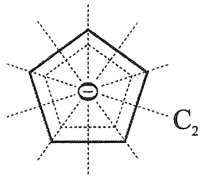
2.15 C_{3v} i.e. it has a principal C_3 axis and 3 vertical planes.

Remember that all flat molecules have a plane of symmetry in the molecular plane. Try to decide the point group of a free boric acid molecule which has no vertical planes or horizontal C_2 axes.



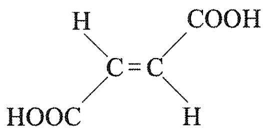
2.16 C_{3h} i.e. it has a principal C_3 axis, no horizontal C_2 axes, and a horizontal plane

What is the point group of the flat ion:



2.17 D_{5h} i.e. it has a C_5 (vertical), 5 C_2 axes at right angles, and a horizontal plane.

List the four symmetry elements of fumaric acid: (CARE! There is again a C_2 axis through space).

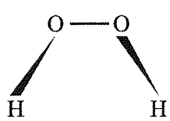


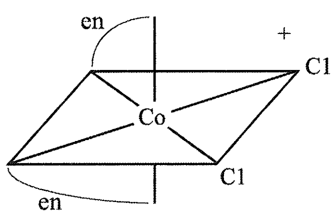
2.18 E, C_2, σ_h, i. What does this make the point group symbol?

2.19 C_{2h} i.e. it has a C_2 axis and a horizontal plane.

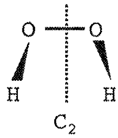
The molecule H_2O_2 and the ion *cis*$[Co(en)_2Cl_2]^+$ both have only the identity and one proper axis of symmetry. They both belong to the same point group. Can you say which one it is?

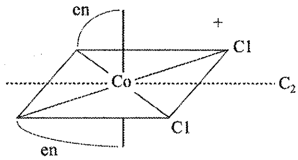
(A model, or the diagrams below, might help.)



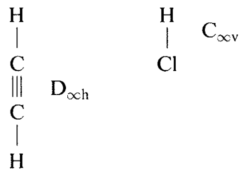


2.20 C_2. They both have a C_2 axis:



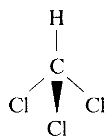


We have so far seen the point groups, D_{nh}, D_{nd} D_n, C_{nh}, C_{nv} and C_n. These groups cover many real molecules, even simple linear ones which have an infinity-fold axis e.g.



There are three additional groups for highly symmetrical molecules, octahedral molecules belong to the group O_h, tetrahedral molecules to T_d, and icosahedral structures to I_h. You must realise that T_d refers to the symmetry of the whole molecule e.g. CH_4 and CCl_4 both belong to the T_d group, but $CHCl_3$ does not.

What is the point group of $CHCl_3$?



(c.f. NH_3)

2.21 C_{3v}

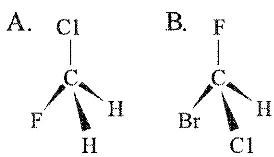
Some rather rare molecules possess only two elements of symmetry, and these are given a special symbol:

E and i only C_i
E and σ only C_s
E and S_n only S_n

Many molecules have no symmetry at all (i.e. their only symmetry element is the identity, E. Such molecules belong to the C_1 point group.

The following are examples of molecules with only one or two symmetry elements.

What are their point groups?

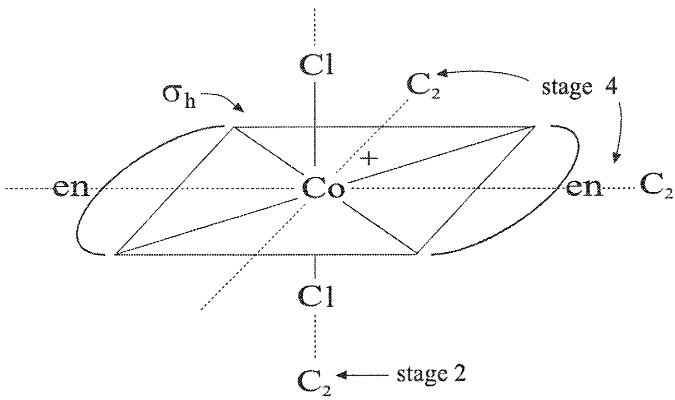


2.22 A. C_S

B. C_1

There is a simple way of classifying a molecule into its point group, and a sheet at the end of this programme gives this. You will see that the tests at the bottom of the scheme are similar to those used to introduce the nomenclature in this programme. The scheme does not test for all the symmetry elements of a molecule, only certain key ones which enable the point group to be found unambiguously.

Have a look at the sheet, and try to follow it through for the ion:

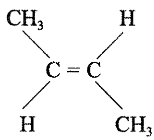


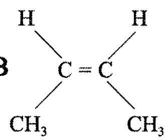
Stage 1 – it is not one of these special groups
Stage 2 – there is a C_2 axis – ∴ n = 2
Stage 3 – there is no S_4 colinear with C_2
Stage 4 – there are two C_2 axes at right angles, there is a horizontal plane.

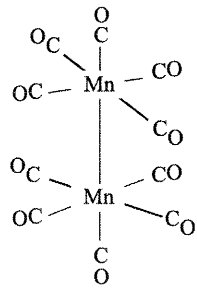
What point group have you arrived at? (Remember the value of n found in Stage 2.)

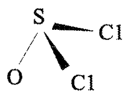
2.23 D_{2h}

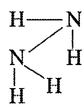
Use the scheme to find the point group of each of the following: (C, E, F and G are a bit tricky without a model, but you may get C, F and G right by analogy with ethane as discussed in frames 2.10–2.13).

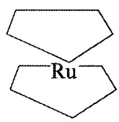
A


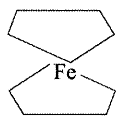
B


C


D


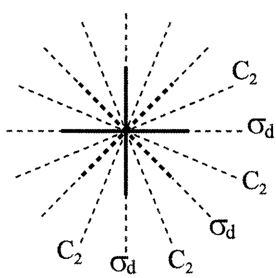
E


F


G


2.24 A. C_{2h} B. C_{2v} C. D_{4d} D. C_s E. C_2 F. D_{5h} G. D_{5d}

The hardest of these examples are probably C and G which are both D_{nd} molecules. It is often very difficult to see the n 2-fold axes on such a molecule and you may need to ask advice on this. Frame 2.11 shows the axes in the case of a D_{3d} molecule. The corresponding diagram, looking down the principal 4-fold axis of $Mn_2(CO)_{10}$ is:



A simple rule to remember is that any n-fold staggered structure (like C_2H_6, $Mn_2(CO)_{10}$ etc) belongs to the point group D_{nd}, and you may find it easier simply to remember this rule.
We have said that the symbol represents the POINT GROUP of the molecule. This is because all the symmetry elements of a molecule always pass through one common point (sometimes through a line or a plane, but always through a point).

Where is the point for examples A and G above?

2.25 A – the centre of the C=C double bond
G – the Fe atom

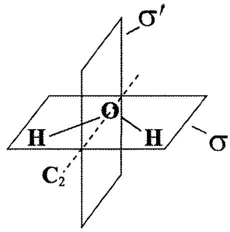
At this stage, the programme begins to look at what mathematicians call a GROUP. If you have had enough for one sitting, this is a convenient place to stop, but in any case it is not absolutely vital for a chemist to know about the rules defining a group, although I strongly recommend you to work through the rest of the programme. You should now be able to classify a molecule into its point group, which is absolutely vital to the use of Group Theory, and the test at the end of the programme tests only this classification.

The term GROUP has a precise mathematical meaning, and the set of symmetry OPERATIONS of a molecule constitutes a mathematical group. A group consists of a set of members which obey four rules:

a. The product of two members, and the square of any member is also a member of the group.
b. There must be an identity element.
c. Combination must be associative i.e. (AB)C = A(BC).
d. Every member must have an inverse which is also a member i.e. $AA^{-1} = E$, the identity, if A is a member, A^{-1} must also be.

N.B. Some texts use the word *element* for the members of a group. This convention has not been followed here in order to avoid confusion with the term *symmetry element*. It is the set of *symmetry operations* which form the group.

Let us take the C_{2v} group (e.g. H_2O) and confirm these rules. The group has four operations, E, C_2, σ, σ':



We have already seen the effect of combining two operations in the programme on elements and operations.

Set up the complete multiplication table for the group operations (in Programme 1 you used a little arrow on H to help do this).

	E	C_2	σ	σ'
E				
C_2				
σ				
σ'				

2.26

	E	C_2	σ	σ'
E	E	C_2	σ	σ'
C_2	C_2	E	σ'	σ
σ	σ	σ'	E	C_2
σ'	σ'	σ	C_2	E

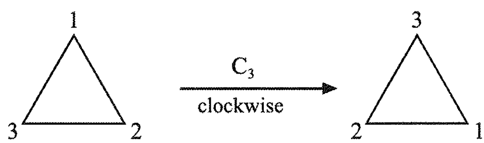
If you did not get this result, look back at the first programme, frames 1.29–1.32.

We can see immediately from this table that rules a and b are true for this set of operations.

What about rule d? What is the inverse of σ', i.e. what multiplies with σ' to give E?

2.27 σ', it is its own inverse, $\sigma'\sigma' = E$. This is true for all the operations of this group.

Consider the C_3 element in a D_{3h} molecule. What is the inverse of the C_3 operation, or what *operation* will bring the shape back to the starting point (I'd rather you didn't say C_3 in the opposite direction!).



2.28 C_3^2, i.e. apply the C_3 operation clockwise a further two times. Thus $C_3^2C_3 = C_3^3 = E$. (Remember that this means C_3 followed by C_3^2.)

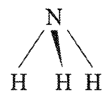
Note particularly that it is the symmetry OPERATIONS, not the elements which form a group.

Confirm rule c for the elements C_2, σ, and σ' of the C_{2v} group, i.e. work out the effect of $(C_2\sigma)\ \sigma'$ and of $C_2\ (\sigma\sigma')$.

2.29 $(C_2\sigma)\sigma' = \sigma'\sigma' = E$
$C_2(\sigma\sigma') = C_2C_2 = E$

i.e. the operations are associative.

The C_{2v} point group only has four operations, so it is a simple matter to set up the group multiplication table. There is, however, a further feature of groups which can only be demonstrated by using a rather larger group such as C_{3v}. Ammonia belongs to the C_{3v} group. Can you write down the five symmetry *elements* of ammonia?

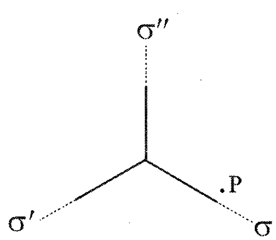


2.30 E C_3 3σ

What operations do these elements generate?

2.31 E C_3 C_3^2 σ σ' σ'' (or 3σ)

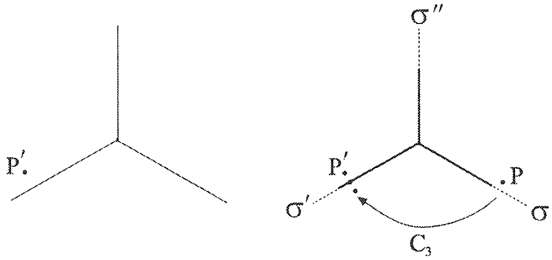
We can set up the 6×6 multiplication table for these operations by considering the effect of each operation on a point such as P in the diagram below, which has the C_3 axis perpendicular to the paper:



The C_3 and C_3^2 operations are clockwise

Draw the position of point P after applying C_3 and then σ' (call the new position P$'$).

2.32

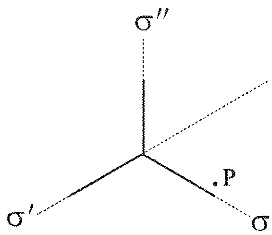


What single operation would take P to P′?

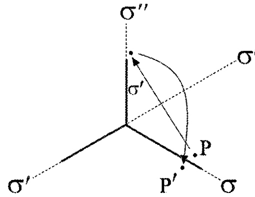
2.33 σ''

i.e. $\sigma' C_3 = \sigma''$ (remember that this means C_3 followed by σ' has the same effect as σ'' — we write the operations in reverse order).

What happens if we do it the other way round, i.e. what is σ' followed by C_3 ($= C_3\sigma'$)?



2.34 σ



In this case $\sigma' C_3$ does not equal $C_3 \sigma'$ – we say that these two operations do not COMMUTE.

Use the effect of the group operations on the point P to see which of the following pairs of operations commute:

C_3 and C_3^2 $\quad$ σ and C_3 $\quad$ σ and σ' $\quad$ E and C_3^2

2.35 $C_3C_3^2 = E$; $C_3^2C_3 = E$ i.e. C_3 and C_3^2 commute
$\sigma C_3 = \sigma'$; $C_3\sigma = \sigma''$ i.e. σ and C_3 do not commute
$\sigma\sigma' = C_3$; $\sigma'\sigma = C_3^2$ i.e. σ and σ' do not commute
$EC_3^2 = C_3^2$; $C_3^2E = C_3^2$ i.e. E and C_3^2 commute

It should be obvious that E commutes with everything – it does not matter if you do nothing before or after the operation!

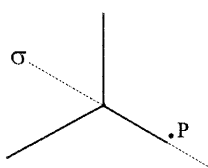
We will now consider briefly the subject of CLASSES of symmetry operations. Two operations A and B are in the same class if there is some operation X such that:

$XAX^{-1} = B$ $\quad$ (X^{-1} is the inverse of X, i.e. $XX^{-1} = E$)

We say that B is the *similarity transform* of A, and that A and B are *conjugate*.

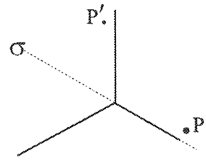
Since any σ is its own inverse we can perform a similarity transformation on the operation C_3 by finding the single operation equivalent to $\sigma C_3 \sigma$.

Work out the position of point P after carrying out these three operations.

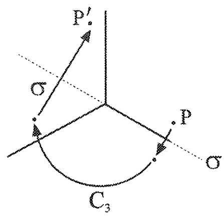


C_3 is clockwise

2.36



i.e.

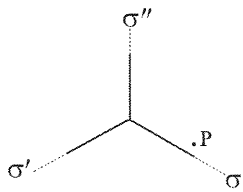


What single operation is the same as $\sigma C_3 \sigma$?

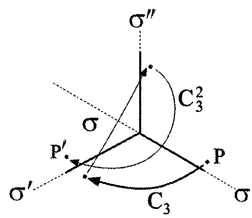
2.37 C_3^2. Thus C_3 and C_3^2 are in the same class.

What is the inverse of C_3?

2.38 C_3^2. Work out the similarity transform of σ by C_3, i.e. decide the operation equivalent to $C_3^2 \sigma C_3$.



2.39 $C_3^2 \sigma C_3 = \sigma''$



Thus σ and σ'' are in the same class

The complete set of symmetry operations of the C_{3v} point group, grouped by classes, is as follows:

E (always in a class by itself)
C_3 C_3^2
σ σ' σ''

The operations are commonly written in classes as:

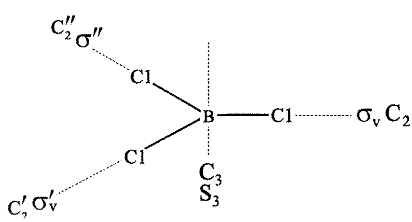
E $2C_3$ 3σ

It is not necessary to go through the whole procedure of working out similarity transformations in order to group operations into classes. A set of operations are in the same class if they are *equivalent operations* in the normally accepted sense. This is probably fairly evident for the example above.

The D_{3h} group (e.g. BCl_3) consists of the operations

E C_3 C_3^2 C_2 C_2' C_2'' σ_h S_3 S_3^5 σ_v σ_v' σ_v''

Group these operations into their six classes



2.40 E

$2C_3$

$3C_2$

σ_h

$2S_3$

$3\sigma_v$ (all equivalent but different from σ_h)

You should now be able to:

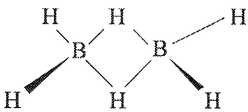
State the point group to which a molecule belongs.
Confirm that a set of operations constitutes a group.
Arrange a set of operations into classes.

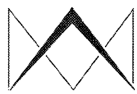
The assignment of a molecule to its correct point group is a vital preliminary to the use of group theory, and this is the subject of the test which follows. The other two objectives of this programme are not tested because it is known in all cases that the symmetry operations of a molecule do constitute a group, and the tables (character tables) which are used in working out problems show the operations grouped by classes.

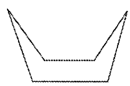
Point Groups Test

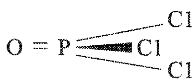
Classify the following molecules and ions into their point group. You may use molecular models and the scheme for classifying molecules.

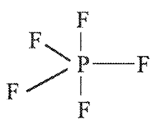
1. CH_2Cl_2

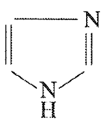
2. 

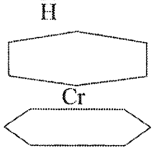
3. Cyclohexane (chair) (use a model) 

4. Cyclohexane (boat) 

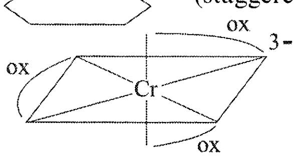
5. 

6. 

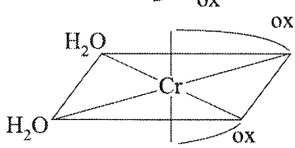
7. 

8. 

(staggered)

9. 

ox = oxalate (a model is almost essential)

10. 

(a model is valuable)

11. CBr_4
12. SF_6
13. CO_2
14. OCS

Answers

One mark each.

1. C_{2v}
2. D_{2h}
3. D_{3d}
4. C_{2v}
5. C_{3v}
6. D_{3h}
7. C_s
8. D_{6d}
9. D_3
10. C_2
11. T_d
12. O_h
13. $D_{\infty h}$
14. $C_{\infty v}$

To be able to proceed confidently to the next programme you should have obtained at least 10 out of 14 on this test, and you should understand the assignment of the point group in any cases you got wrong.

If you are in any doubt about the assignment of point groups, return to frames 2.7 to 2.24.

Point Groups

Revision Notes

The set of symmetry operations of any geometrical shape forms a mathematical group, which obeys four rules:

i. The product of two members of the group, and the square of any member, is also a member of the group.
ii. There must be an identity element.
iii. Combination must be associative, i.e. (AB)C = A(BC)
iv. Every member must have an inverse, i.e. if A is a member, then A^{-1} must also be a member, where $AA^{-1} = E$.

Symmetry operations do not necessarily commute, i.e. AB does not always equal BA.

A molecule can be assigned to its point group by a method which does not require the listing of all symmetry operations of the molecule; the method merely involves looking for certain key symmetry elements. The symbol for most molecular symmetry groups is in three parts e.g.

$$C_{4v} \quad C_{2h} \quad D_{3h} \quad D_{6d}$$

These have the following meanings:

i. The number indicates the order of the principal (highest order) axis. This axis conventionally defines the vertical direction.
ii. The capital letter is D if an n-fold principal axis is accompanied by n two-fold axes at right angles to it; otherwise the letter is C.
iii. The small letter is h if a horizontal plane is present. If n vertical planes are present, the letter is v for a C group but d (= dihedral) for a D group. (N.B. h takes precedence over v or d.) If no vertical or horizontal planes are present, the small letter is omitted.

Systematic Classification of Molecules into Point Groups

C = rotation axis
S = improper axis (alternating axis)
i = inversion centre
σ = plane of symmetry

1. Examine for special groups

   a. Linear, no σ perpendicular to molecular axis — $C_{\infty v}$
   b. Linear, σ perpendicular to molecular axis — $D_{\infty h}$
   c. Tetrahedral — T_d
   d. Octahedral — O_h
   e. Dodecahedral or icosahedral — I_h

2. Examine for a C_n axis

C_n present
Find C_n of highest n or a unique C_n — this axis is then taken to be vertical by convention → go to 3.

C_n absent
σ present — C_s
i present — C_i
no symmetry elements other than E — C_1

3. Examine for S_{2n} colinear with C_n

S_{2n} present
No other symmetry elements present, except i —— S_{2n}
Other symmetry elements present → go to 4.

S_{2n} absent → go to 4.

4. Examine for n horizontal C_2 axes

n C_2 axes present
Horizontal plane (σ_h) present — D_{nh}
n Vertical planes (dihedral planes, σ_d, bisecting angles between C_2 axes) present – D_{nd}
Absent — D_n

n C_2 axes absent
Horizontal plane (σ_h) present — C_{nh}
n vertical planes present (σ_v) —— C_{nv}
Absent — C_n