An Introduction to Symmetry Operations, Symmetry Elements, and Point Groups

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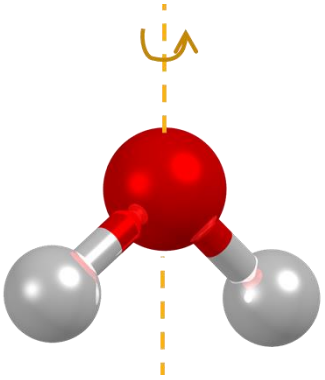
Introduction

Hello everyone, I'm Rosie Lester from the CCDC and today we're going to learn about how chemists describe symmetry.



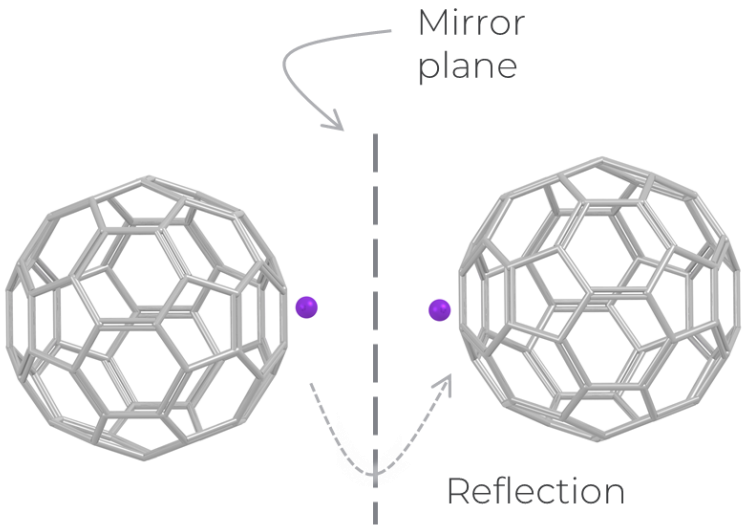
We'll start by discussing what *point groups*, *symmetry elements*, and *symmetry operations* are, before seeing how a point group is decided by identifying symmetry elements. We'll use a flow chart to decide what point group a molecule belongs in and then there is a chance for you to practise with some examples.

Let's get into it!

What is a point group?

In the field of crystallography, a point group is **"a list of the ways in which the orientation of a crystal can be changed without seeming to change the positions of its atoms"** – in other words, what *symmetry operations* can be applied to a crystal and leave it unchanged? This is useful for scientists because in 1830 a German mineralogist, Johann Hessel, proved there were only 32 distinct combinations of these symmetry operations. This means by characterising the symmetry of one crystal or molecule, scientists can learn about many others, because lots of properties depend on the underlying symmetry.

What are symmetry operations and symmetry elements?



A *symmetry operation* is the actual movement of a body, such that after the movement it appears the same as before, like a rotation or a reflection.[1]

A *symmetry element* is a geometrical entity about which a symmetry operation is performed, such as a point, axis, or plane.

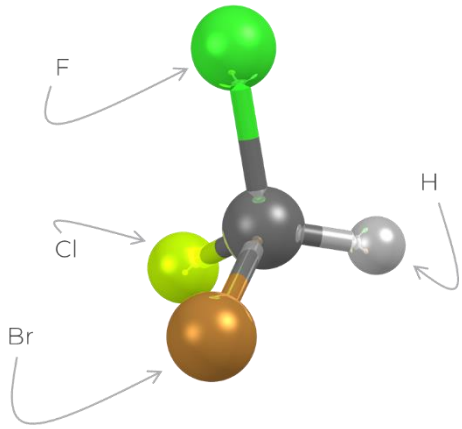
We'll note elements and operations as they appear in later sections.

[1] Note: the image above has the only scope to provide an example of the operation and element of immediate visualisation, even though the result of the operation does not make the molecule appear same as before.

Symmetry Operations

The operations we'll focus on today are reflections, rotations, inversions, and the identity operator. Although we discussed crystals earlier, we're going to look at the effect of operations on individual molecules so they're a little easier to visualise. You can spot symmetry elements in other objects too – keep watching for ideas of where to spot them in the world around you!

Identity

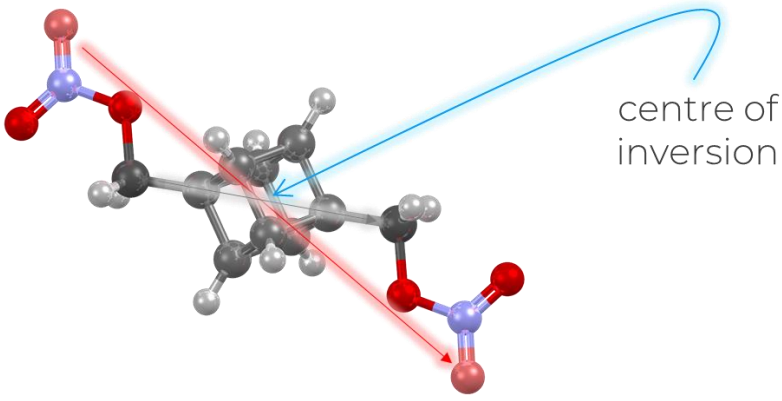


The identity operator means we do nothing to our crystal, so it stays the same – this is like adding 0 or multiplying by 1 in Maths. As you might have guessed, this means it applies to every object! It's included as part of a mathematical way to describe point groups and symmetry, and there are lots of molecules which have no other symmetry – such as CHBrClF.

The identity operator is a bit of an odd one out, since it doesn't have a symmetry element corresponding to it. It is given the symbol *E*.

Inversion

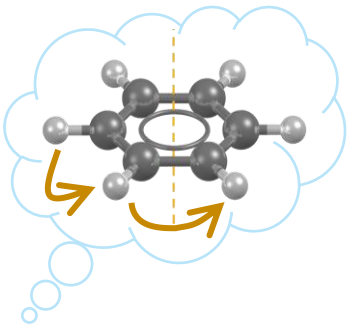
Mathematically, inversion is described as moving whatever is at the point **(x, y, z)** to **(-x, -y, -z)**. This means every point is passed through the centre of the molecule and out the same distance from the centre it started at.



The centre doesn't have to have an atom at it – just like in this example, and we can find it by checking where the arrows of motion intersect. The symbol *i* identifies a centre of inversion.

Rotation

Rotation takes place around an axis and can be described as an *n*-fold rotation, where *n* is the number of rotations which fit in 360°. As an example, if the molecule can be rotated by 180° and look the same, we call it a 2-fold rotation, because we can fit 2 rotations in 360° (as seen in water).



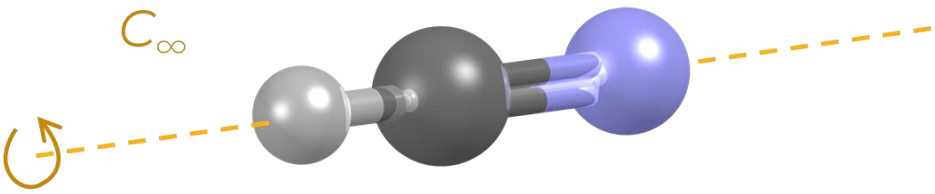
The symbol for a rotation is C_n, where the *n* is this *n*-fold number.

Question Time – Question 1

Benzene can fit 6 rotations in 360° giving it a C_6 axis, but a molecule can have more than one axis of rotation, and they don't have to have the same value of *n* either. Can you spot any other axes of rotation in benzene?

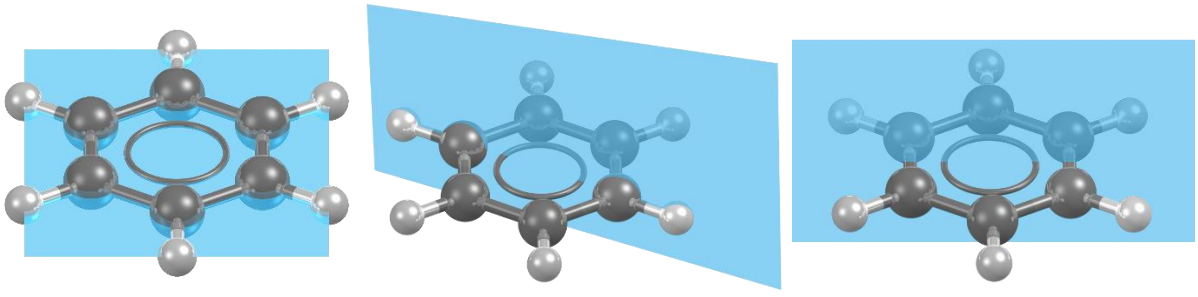
Head to the end of this document for answers!

Linear molecules like hydrogen cyanide can rotate around an axis that goes right through it, so they get an infinity sign instead of a discrete number.



Reflection

Reflections are familiar from real life, and the element associated with them is a mirror plane. Mirror planes are given the symbol σ (sigma), a Greek letter. They can also have a subscript to help tell us more about them. An **h** tells us this plane is horizonal with respect to the main rotation axis – if there's more than one rotation axis, like in benzene, we take the highest order of rotation as the most important. In this case, that's the C_6 axis shown above.

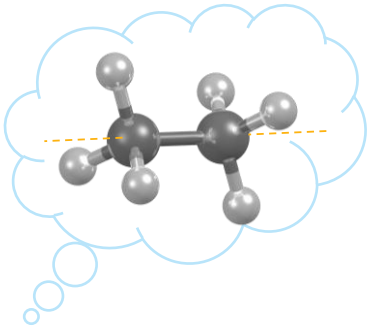


σ_h σ_v σ_d

Benzene also has two sets of mirror planes which include this principal rotation axis. One is called **v** for vertical, and we can see these must all be in one set because as soon as we find one, the rotation axis creates the other two for us (total of 3).

There is another set of 3 mirror planes which include the rotation axis, which get the letter **d**, for dihedral, since they intersect bonds.

Improper Rotation



This is a combination of a rotation and a reflection. The rotation happens as normal, and then the object is reflected in a plane perpendicular to the rotation axis (σ_h). Improper rotations are given the symbol S_n with *n* still describing the rotations within 360°.

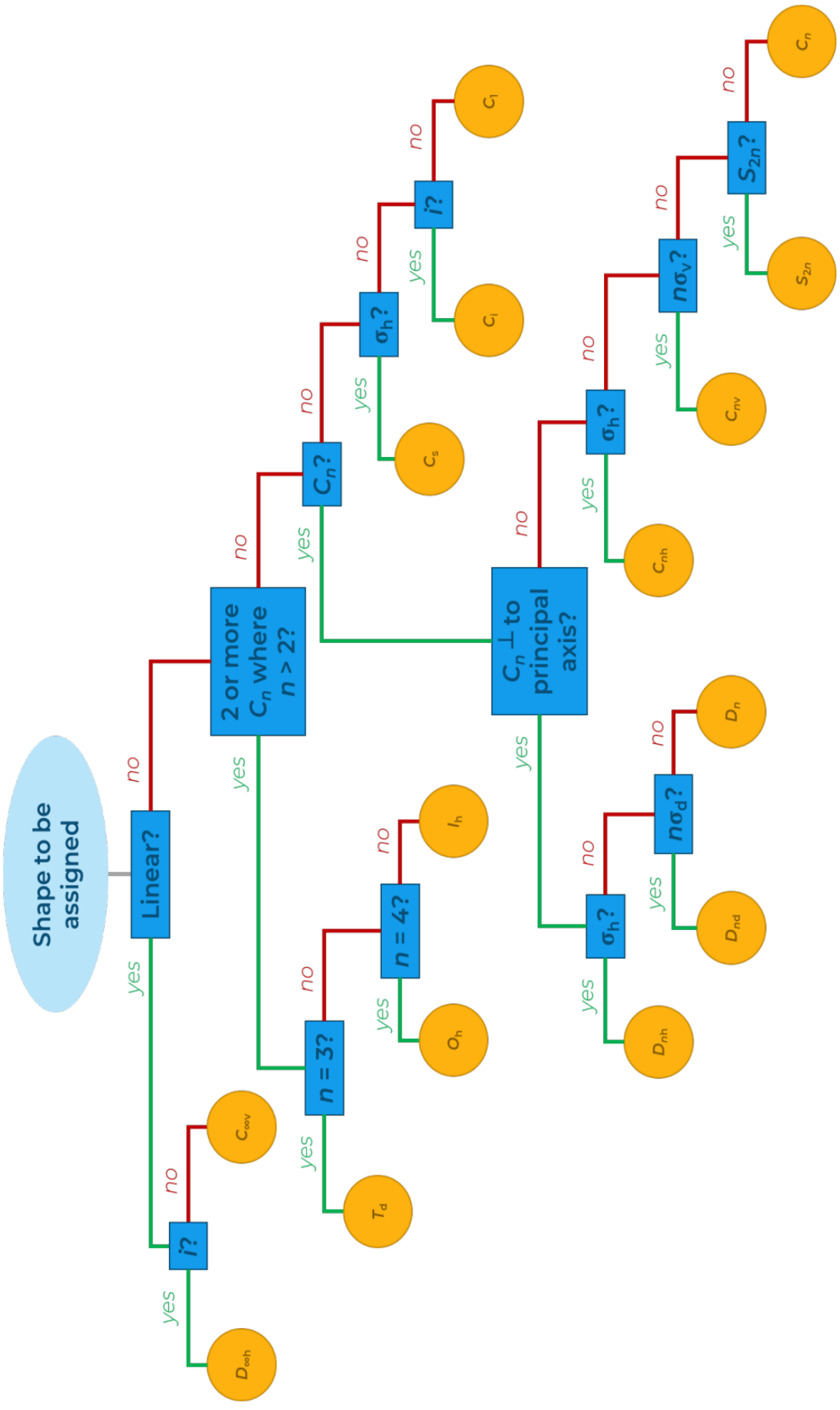
Question Time – Question 2

Ethane has a proper axis of rotation and an improper one, coincident on each other. What order do you think each one is?

Head to the end of this document for answers!

Identifying Point Groups

Earlier we learned that a point group was a list of symmetry elements, so to identify the point group what we need to do is identify symmetry elements in our object. To be systematic about it, we'll be using a flowchart to help us decide what symmetry a molecule has, which is available on the next page and as a separate document on our website.

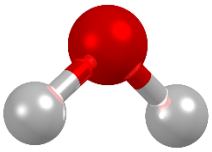

Shape to be assigned
Linear?
yes
no
i?
yes
$D_{\infty h}$
no
$C_{\infty v}$
2 or more C_n where $n > 2$?
yes
$n = 3$?
yes
T_d
no
$n = 4$?
yes
O_h
no
I_h
C_n?
yes
$C_n \perp$ to principal axis?
yes
σ_h?
yes
D_{nh}
no
$n\sigma_d$?
yes
D_{nd}
no
D_n
no
σ_h?
yes
C_{nh}
no
$n\sigma_v$?
yes
C_{nv}
no
S_{2n}?
yes
S_{2n}
no
C_n
no
σ_h?
yes
C_s
no
i?
yes
C_i
no
C_1

It's your turn!

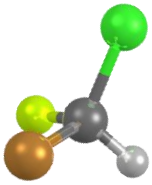
To put into practice what we've learned, have a go assigning the point groups of the molecules mentioned in this worksheet – if you get stuck, have a peek at the answers, or check out the video.

Hydrogen cyanide:

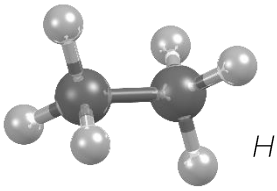
Water:



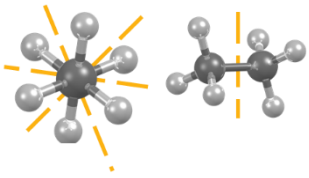
Bromochlorofluoromethane (CHBrClF):



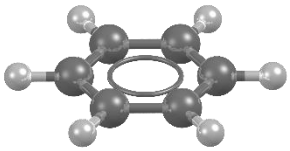
Ethane:



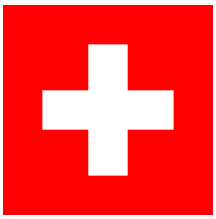
Hint: don't forget about the C_2 rotation axes:



Benzene:



Where next?



If you'd like more practice, why not try spotting symmetry elements in the world around you? Flowers, flags, and tiles are great places to start!

- Visit https://www.ccdc.cam.ac.uk/Community/educationalresources/teaching-modules/ - Learning point-group symmetry through 3D printed models for more example to practice asisgning point groups.
- Move onto https://symotter.org/challenge if you want some more complex examples!

Now you're an expert in point groups, the next step is to explore what symmetry exists in crystals, where molecules pack together in repeating patterns.

Visit https://www.xtal.iqfr.csic.es/Cristalografia/parte_03-en.html for a chance to see more symmetry in nature and learn how what we've learned today applies to crystals

Resources

The molecules used to demonstrate these concepts are available in the Cambridge Structural Database (CSD). In particular, we used CSD Entries: FULLER, BENZEN, AYALOC.

You can visualise and download the structures for free from CCDC's Access Structures service: https://www.ccdc.cam.ac.uk/structures/

Water, hydrogen cyanide, CHFBrCl, and ethane were instead manually sketched in Mercury, but you can use ConQuest, the CSD searching software (licenced), or Access Structure (free) and WebCSD (licenced), to find structures containing these molecules.

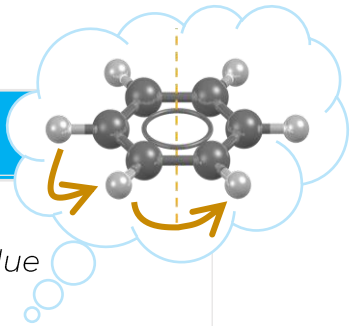
The images and animation frames of these molecules are prepared using Mercury. Mercury visualisation software is available to download for free https://www.ccdc.cam.ac.uk/Community/csdcommunity/FreeMercury/

In free Mercury you can also visualise symmetry elements on the crystal structure.

More advanced functionality from the CCDC enables you explore molecules and structures in more detail. To find out how to access more advanced functionality with a CSD-Core license see https://www.ccdc.cam.ac.uk/solutions/csd-core/

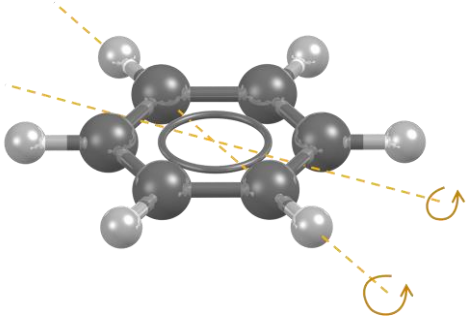
Answers

Answer Time – Question 1

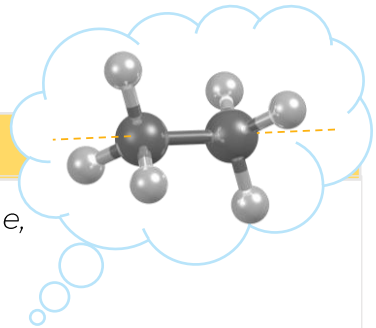


Benzene can fit 6 rotations in 360°, but a molecule can have more than one axis of rotation, and they don't have to have the same value of n either – can you spot any other axes of rotation in benzene?

Well done if you found a C_2 axis – benzene has 6 of them, 3 going through atoms and 3 going through bonds!

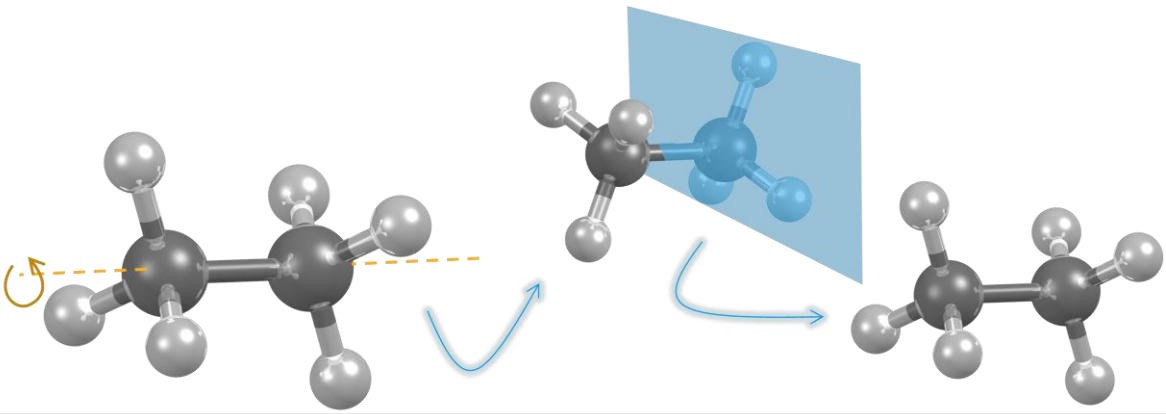


Answer Time – Question 2



Ethane has a proper axis of rotation and an improper one, coincident on each other. What order do you think each one is?

Ethane has a C_3 and an S_6 axis - both are shown here with a yellow line. The S_6 is made from a rotation of 60°, followed by a reflection in the plane perpendicular to our axis, shown in blue. C_3 is just a rotation of 120°.



Point group answers

Hydrogen cyanide - $C_{\infty v}$

- Linear? Yes.
- i? No.

Water – C_{2v}

- Linear? No.
- 2 or more C_n where n > 2? No, highest order of rotation = 2.
- C_n? Yes, n = 2.
- C_2 perpendicular to principal axis? No, C_2 is the only axis.
- σ_h? No, the mirror planes contain the principal axis.
- $n\sigma_v$? Yes.

CHBrClF – C_1

- No symmetry elements except the identity. No to all questions.

Ethane – D_{3d}

- Linear? No.
- 2 or more C_n where n > 2? No, only one C_3 axis.
- C_n? Yes, n = 3.
- C_2 perpendicular to principal axis? Yes.
- σ_h? No.
- $n\sigma_d$? Yes, 3.

Benzene – D_{6h}

- Linear? No.
- 2 or more C_n where n > 2? No, only one C_6 axis of higher order than two.
- C_n? Yes, n = 6.
- C_2 perpendicular to principal axis? Yes.
- σ_h? Yes.