Predicting the Shapes of Molecules: the VSEPR Model

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1 Introduction

The shapes of molecules tend to be controlled by the number of electrons in the valence shell of the central atom. The valence-shell electron-pair repulsion (VSEPR) model provides a simple method for predicting the shapes of such species. The Cambridge Structural Database (CSD) contains a wealth of diverse molecular geometries and provides the ability to visualise and manipulate molecules in three-dimensions. This is vitally important in order to study and understand the shapes adopted by particular molecules.

1.1 Learning outcomes

At the end of this module, you will:

- be able to investigate the shapes of molecules by analysing experimental crystal structure data
- understand the factors that determine the preferred shape adopted by particular molecules
- be able to use the valence-shell electron-pair repulsion (VSEPR) model to predict the shapes of given molecules

1.2 Materials

The structures needed to complete this module are available from the online Web service Access Structures. The majority are from the CSD, with a few examples taken from the Inorganic Crystal Structure Database (ICSD, https://icsd.products.fiz-karlsruhe.de/). The ICSD can also be searched via the Access Structures online portal.

https://www.ccdc.cam.ac.uk/structures/

This provides you with all the features required to complete this teaching module. Alternatively, you may prefer to use the structure visualization program Mercury, which you can download for free. Instructions for obtaining this software and links to resources to support you using it are given at the end of this document. This teaching module uses entries in the Teaching Subset; you can find out more about the Teaching Subset here: https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/.

1.3 Pre-required skills

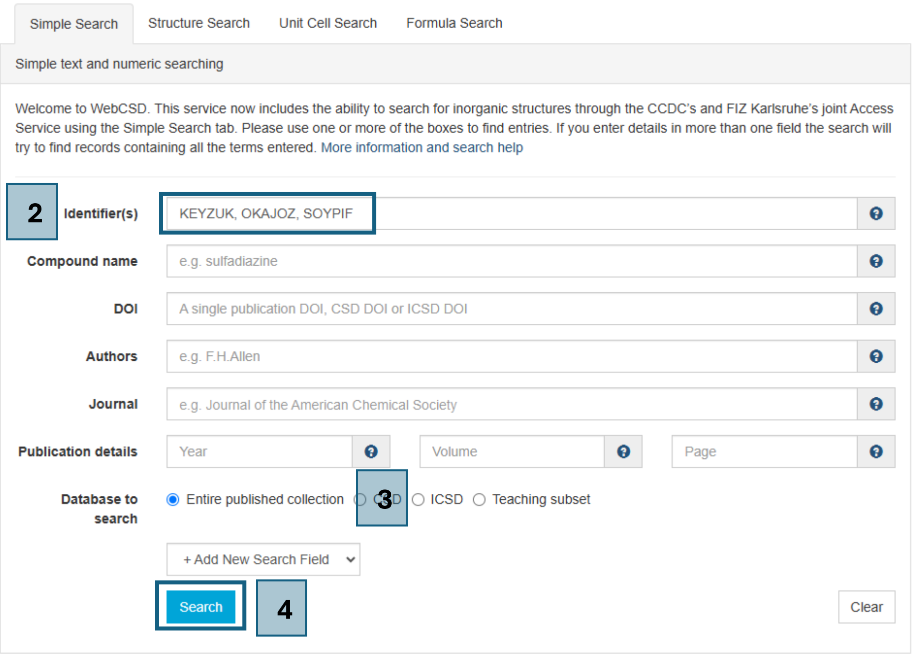
This teaching module assumes no prior knowledge of crystallography. A basic understanding of atomic structure is assumed.

2 Predicting molecular geometry

We will begin by posing a question: what shapes would you expect $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$ to take? Without even considering atomic structure, we know that atoms surrounded by electrons, which, having the same charge, will repel one another. So, what shapes would maximise the space between the Cl atoms in this series of mercury complexes and hence minimise that repulsion. We can search for these complexes in the CSD to find out.

1. To get started, navigate to Access Structures at https://www.ccdc.cam.ac.uk/structures.

2. In the *Identifier(s)* section, type “KEYZUK, OKAJOZ, SOYPIF” (the commas are optional). These six letter codes are called *refcodes*; they are used to identify structures in the CSD.



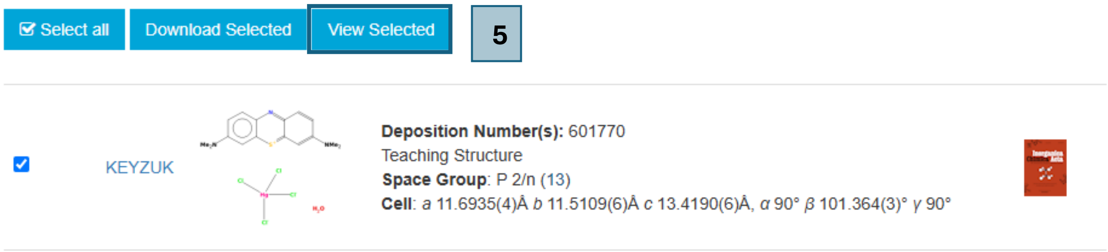
Welcome to WebCSD. This service now includes the ability to search for inorganic structures through the CCDC's and FIZ Karlsruhe's joint Access Service using the Simple Search tab. Please use one or more of the boxes to find entries. If you enter details in more than one field the search will try to find records containing all the terms entered. More information and search help

Identifier(s): KEYZUK, OKAJOZ, SOYPIF
Compound name: e.g. sulfadiazine
DOI: A single publication DOI, CSD DOI or ICSD DOI
Authors: e.g. F.H.Allen
Journal: e.g. Journal of the American Chemical Society
Publication details: Year; Volume; Page
Database to search: ● Entire published collection ○ CSD ○ ICSD ○ Teaching subset

3. Next to *Database to search*, select **Entire published collection**

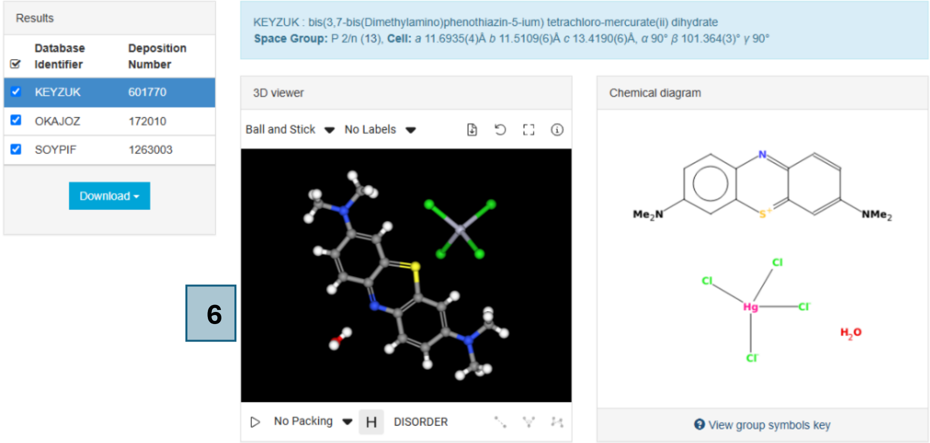
4. Press **Search**.

5. In the results page, ensure the tick boxes next to the entries are enabled (click **Select all** if they are not) and click **View Selected**.



☑ KEYZUK
Deposition Number(s): 601770
Teaching Structure
Space Group: P 2/n (13)
Cell: *a* 11.6935(4)Å *b* 11.5109(6)Å *c* 13.4190(6)Å, *α* 90° *β* 101.364(3)° *γ* 90°

6. To manipulate the structure in the 3D viewer:
    a. Left click and drag to rotate the structure.
    b. Right click and drag to translate the structure.
    c. Scroll up/down with the mouse wheel to zoom in/out.
    d. At any time, hit ⟲ to reset the viewer.



Results

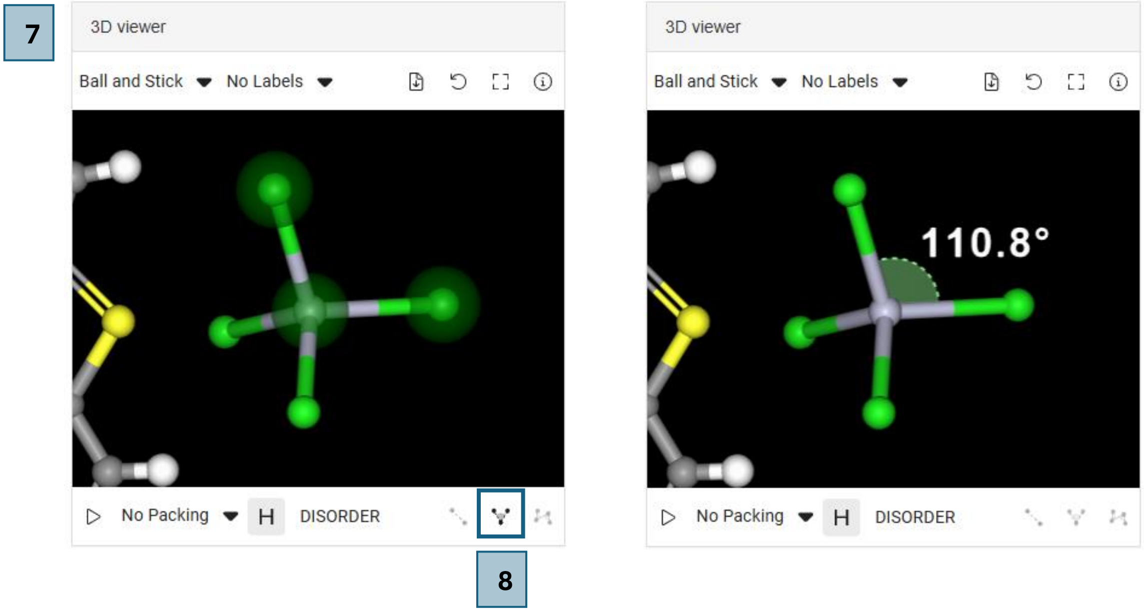
☑	Database Identifier	Deposition Number
☑	KEYZUK	601770
☑	OKAJOZ	172010
☑	SOYPIF	1263003

KEYZUK : bis(3,7-bis(Dimethylamino)phenothiazin-5-ium) tetrachloro-mercurate(ii) dihydrate
Space Group: P 2/n (13), **Cell:** *a* 11.6935(4)Å *b* 11.5109(6)Å *c* 13.4190(6)Å, *α* 90° *β* 101.364(3)° *γ* 90°

Do the molecular geometries match your expectations? We can assess the geometry more precisely by measuring the Cl–Hg–Cl bond angles.

7. With KEYZUK selected, zoom in on the $HgCl_4^{2-}$ ion. To measure the Cl–Hg–Cl angle, click on a Cl, Hg and another Cl in that order. The atoms will be highlighted in a translucent green sphere.

8. Click on the angle symbol in the bottom right-hand corner. The measurement will be displayed and the angle marked on with a green arc.



9. Measure the remaining five Cl–Hg–Cl bond angles and calculate the average.

10. Select refcode SOYPIF from the *Results* list, measure the Cl−Hg−Cl angles and calculate the average.

11. Select refcode OKAJOZ from the *Results* list, measure the Cl−Hg−Cl angle.

You should get the results shown in Table 1 below. You might recognise these bond angles as characteristic of tetrahedral, trigonal and linear geometries, as you would find in alkanes, alkenes and alkynes, respectively, in organic chemistry.

Table 1. Cl−Hg−Cl bond angles in selected mercury complexes.

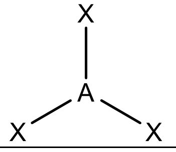
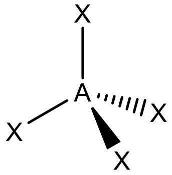
Refcode	Molecule/ion	Cl−Hg−Cl bond angle (°)
KEYZUK	$HgCl_4^{2-}$	109.5 (average)
SOYPIF	$HgCl_3^{-}$	120.0 (average)
OKAJOZ	$HgCl_2$	180.0

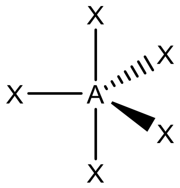
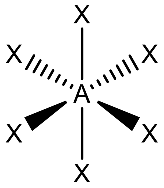
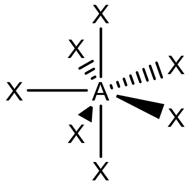
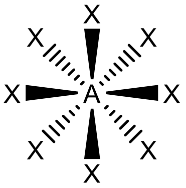
2.1 The VSEPR model

The valence shell electron pair repulsion (VSEPR) model is based upon the assumption that regions of enhanced electron density take up positions as far apart as possible to minimise repulsion. Thus, in addition to the repulsion between electrons of the outer atoms (as we saw in the series of mercury complexes previously), lone pairs and multiple bonds also need to be considered.

Let's consider the preferred geometry of a general molecule AX_m where m is the number of X ligands surrounding central atom A (Table 2).

Table 2. Common VSEPR geometries for molecules with different numbers of ligands surrounding the central atom.

Formula	Electron pairs (m)	Shape	Spatial arrangement	Ideal bond angle (°)
AX_2	2	Linear	X——A——X	180
AX_3	3	Trigonal prismatic		120
AX_4	4	Tetrahedral		109.5

AX_5	5	Trigonal bipyramidal		90 (ax-eq) 120 (eq-eq)
AX_6	6	Octahedral		90
AX_7	7	Pentagonal bipyramidal		90 (ax-eq) 72 (eq-eq)
AX_8	8	Square antiprismatic*		74.9 (adjacent, within square) 74.9 (closest between top and bottom squares) 141.5 (farthest apart between top and bottom)

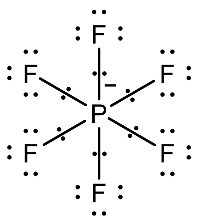
* See Kepert, D.L. (1982). Eight-Coordinate Compounds Containing only Unidentate Ligands. In: Inorganic Stereochemistry. Inorganic Chemistry Concepts, vol 6. Springer, Berlin, Heidelberg.

Note that for larger coordination geometries, it is necessary to minimise the repulsive energy with a calculation to find the optimum geometry; depending on the model used this may give slightly different inter-ligand angles. Additionally, there may be several geometries with a similar minimum energy, in such cases, the VSEPR model might be less reliable as a predictor.

2.2 How to apply the VSEPR model to predict basic shape

We will illustrate how to apply the VSEPR model to predict the shape of PF_6^-. To do so, we follow these steps:

1. Draw the Lewis structure of the molecule and identify the central atom. In the case of PF_6^-, this is phosphorus.



2. Determine the valence electrons on the central atom. Phosphorus has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^3$ and thus has 5 valence electrons. Add to this the number of electrons that are contributed by all directly bonded atoms. For PF_6^- there are 6 fluorine atoms, each contributing 1 electron. Finally, add one electron to account for the single negative charge on the phosphorus. This brings the total to 12.

3. Divide the total number of valence electrons by 2 to give the total number of electron pairs (i.e. 6) and assign the molecular geometry corresponding to this number using Table 1 in the previous section.

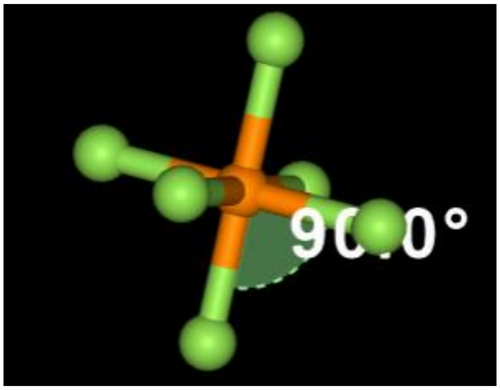
4. Hexafluorophosphate, PF_6^- is therefore expected to have an octahedral geometry.

The above points are summarised below.

Hexafluorophosphate PF_6^-

Central atom	Phosphorus
Valence electrons on central atom	5
Valence electrons from 6 F, each contributing 1 electron	6
Add 1 for negative charge	1
Total valence electrons	12
Divide by 2 to give number of electron pairs	6
Octahedral geometry for the 6 shape-determining electron pairs	

Find CSD entry WINFAA using Access Structures and measure F−P−F angles. You will see that the *cis* bonds have bond angles very close to 90° (see below).



WINFAA

Exercise 1

Use VSEPR theory to determine the geometry of the following molecules. Confirm that your answers are correct by examining the corresponding crystal structures. Comment on how closely the observed bond angles agree with the expected ideal values.

Molecule or ion	**CSD refcode**
BrF_6^-	ZAQBIC
I_3^-	RIKTAG
$In(CH_3)_3$	TRMEIN03
$[BeF_4]^-$	KIPPEE
NMe_4^+	SODVOW02
SiF_5^-	CINLEQ
SbF_6^-	FUJLAX

2.3 Modifications to basic shapes: considering the effect of lone pairs

The molecules you have encountered so far include only bonding pairs. How does the presence of lone pairs affect molecular shape?

Consider the molecular ion XeF_5^-. Xe is in group 18 and possesses 8 electrons in its valence shell. There are 5 fluorine atoms, each contributing 1 electron, this brings the electron count to 13. Finally, we add one electron to account for the single negative charge on the Xe. This brings the total to 14. Again, we divide this number by 2 to give the total number of electron pairs (7). The parent shape is therefore a pentagonal bipyramid (remember that we are describing the distribution of electron pairs *not* atoms at this stage).

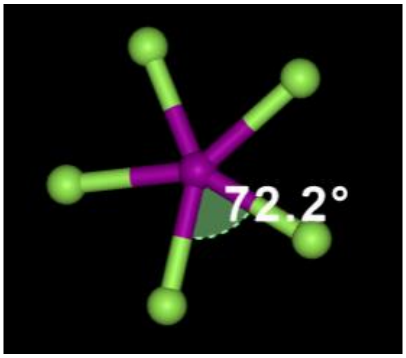
However, once the basic shape of a molecule has been identified, adjustments must be made to account for the differences in electrostatic repulsion between bonding regions and lone pairs. Repulsions lie in the order:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

The greater repelling effect of a lone pair is explained by supposing that the lone pair is on average closer to the nucleus than a bonding pair and therefore repels other electrons more strongly. Thus, for XeF_5^- the parent shape (in terms of electron pairs) is a pentagonal bipyramid with the lone pairs opposite to each other in order to minimise lone pair-lone pair repulsions. The XeF_5^- anion is therefore pentagonal planar.

Left: XeF_5^- with lone pairs displayed. Right: XeF_5^- without the lone pairs displayed, showing the pentagonal planar geometry.

You can confirm this is the case by searching for SOBWAH in Access Structures (see below).



SOBWAH

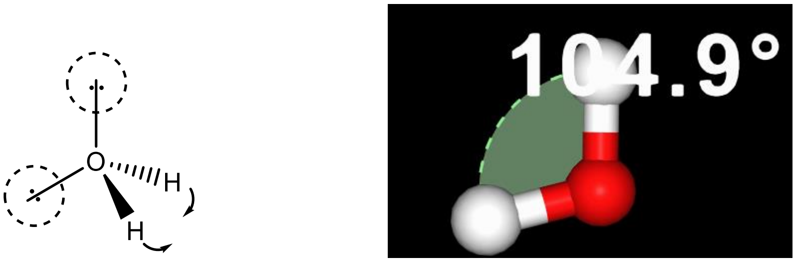
A more familiar molecule, which requires the same kind of consideration is water. Search for CYTOSM04 in Access Structures. Note that water is deuterated here (^2H = D). This does not affect its chemistry but is necessary for the neutron study used to determine this structure. Measure the D–O–D bond angle in the water molecule. How would you describe the shape?

The shape clearly is not linear but can simply be described as 'bent'. To see why this should be the case, let's find the number of valence electron pairs.

Water H_2O

Central atom	Oxygen
Valence electrons on central atom	6
Valence electrons from 2 ^2H atoms, each contributing 1 electron	2
Total valence electrons	8
Divide by 2 to give number of electron pairs	4
Tetrahedral for the 4 shape-determining electron pairs	

The electron count indicates that there should be two pairs on oxygen in water, which would occupy two vertices of a tetrahedron, hence the bent shape. However, the D–O–D bond angle, 104.9°, is considerably less than the ideal tetrahedral angle of 109.5°. This can be explained by remembering the repulsion hierarchy for lone pairs and bonding pairs. Lone pair-bonding pair repulsion > bonding pair-bonding pair repulsion, so the D–O–D bond angle compresses to increase the angle between the hydrogen atoms and the lone pairs.



The relatively greater repelling power of lone pairs decreases the D–O–D bond angle below the expected 109.5° tetrahedral angle.

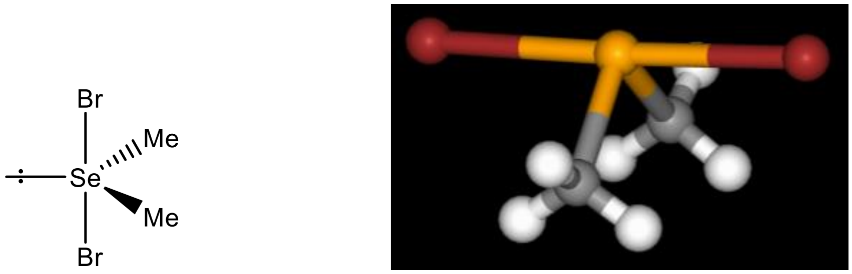
Now for slightly more complex example. Search for RIZMIW in Access Structures, which is dibromodimethylselenium. Can you explain its structure?

We can predict its parent structure (in terms of electrons pairs) as we have done previously.

Dibromodimethylselenium $SeBr_2(CH_3)_2$

Central atom	Selenium
Valence electrons on central atom	6
Valence electrons from 2 Br and 2 Me groups, each contributing 1 electron	4
Total valence electrons	10
Divide by 2 to give number of electron pairs	5
Trigonal bipyramidal for the 5 shape-determining electron pairs	

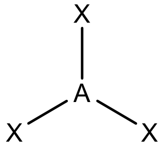
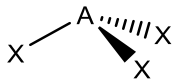
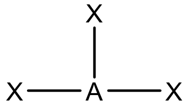
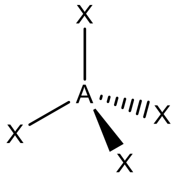
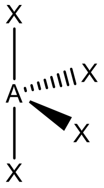
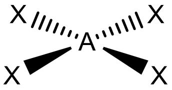
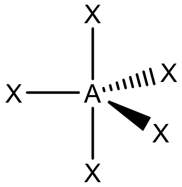
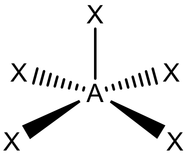
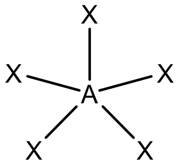
According to sums, there are 5 valence electron pairs in total, 4 of which we know must be from bonding electrons. Therefore, there is one lone pair on selenium and from the crystal structure, we can see that this lone pair is effectively occupying an equatorial site of the trigonal bipyramid. Why does the lone pair go that position rather than an axial one? According to the hierarchy of lone pair and bonding pair repulsions mentioned earlier, the lone pair causes the greatest repulsion and should go in the least crowded position, which is in the trigonal plane. A lone pair in the equator makes two 90° angles with nearest neighbour ligands, whereas an axial lone pair makes three 90° angles; putting the lone pair in the equator therefore gives the least repulsion. The overall geometry is disphenoidal or “see-saw” shaped.



Left: dibromodimethylselenium with the lone pair displayed, showing the trigonal bipyramidal parent structure. Right: the see-saw shape that the molecule adopts in RIZMIW.

Rewriting the general formula AX_m that was used in Table 2 as AX_mE_n where the lone pairs, E, are included explicitly, we can tabulate some common geometries for structures involving lone pairs (Table 3)

Table 3. Common VSEPR geometries for molecules having ligands and lone pairs on the central atoms.

AX_mE_n		*n*		
		0	1	2
m	3	 Trigonal planar	 Pyramidal	 T-shaped
	4	 Tetrahedral	 Disphenoid (see-saw)	 Square planar
	5	 Trigonal bipyramid	 Square-based pyramid	 Pentagonal planar

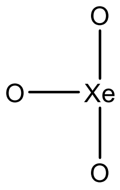
2.4 Including multiple bonds in the VSEPR model

The example we have seen so far have had either single bonds only or a combination of single bonds and lone pairs. What happens if we have double or triple bonds? How many electron pairs should we consider and how strongly do electrons in multiple bonds repel other electrons? First, let's consider the XeO_3 molecule.

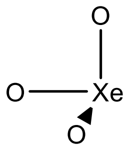
Xenon trioxide XeO_3

Central atom	Xenon
Valence electrons on central atom	8
Valence electron from 3 oxygen atoms	6
Total valence electrons	14
Divide by 2 to give number of electron pairs	7

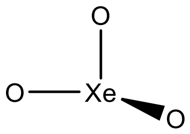
At this point, with seven electron pairs, we would expect a pentagonal bipyramidal parent structure with four vertices occupied by lone pairs. What would that look like? Depending on which positions the oxygen atoms occupied, the expected adjacent angles would be 90° (arrangement a), 90° + 72n° (n = 1, 2, arrangements b and c, respectively) or 72n° (n = 1, 2, arrangements d and e, respectively).



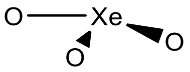
(a)



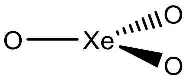
(b)



(c)

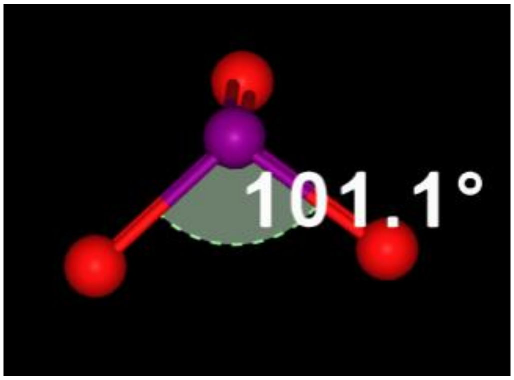


(d)



(e)

In Access Structures, search for refcode VIFKUT. Measure the O−Xe−O bond angles. You should find that the bond angles are 101.1, 101.1 and 101.7°, overall giving a pyramidal geometry. This does not fit any of the structures a-e above.



XeO_3 in VIFKUT

The solution is to treat all electrons involved in the Xe=O bonds as aligned with those bonds, i.e. there are 4 electrons per Xe=O bond, and that counts as a single region of electron density. Let's modify the electron count to account for that.

Xenon trioxide

Central atom	Xenon
Valence electrons on central atom	8
Valence electron from 3 oxygen atoms	6
Total valence electrons	14
Divide by 2 to give number of electron pairs	7
Electron pairs in 3 double bonds	6
Lone pairs	1
Tetrahedral arrangement of electron pairs (one of which is a lone pair, the remaining six in 3 double bonds). Overall geometry is **pyramidal**.	

In terms of repulsive power, a double bond repels more than a single bond but not as much as a lone pair. This explains why the O−Xe−O bond is less than the ideal tetrahedral angle of 109.5°.

Exercise 2

Look up CSD refcode QEZYUQ in Access Structures and measure the bond angles. How do they compare with expectations?

2.5 The influence of electronegativity on molecular shape

One further factor is needed to complete our understanding of the VSEPR model. VSEPR theory considers repulsion between electrons around a central atom, however, when a strongly electronegative element is bonded to the central atom, the bonding pair will be pulled closer to the electronegative element than when a less electronegative element is bonded to the central atom. This effectively take up less room in the region immediately surrounding the central atom. Where there is a clear choice of environments, the more electronegative element occupies the more crowded positions (e.g. the axial positions of the trigonal bipyramid).

Exercise 3

Look up refcodes ROGYEU and HUWREX, which are crystal structures containing NF_3 and ND_3 (D = ^{2}H, as before), respectively. Are the results consistent with the VSEPR rules on electronegativity?

Exercise 4

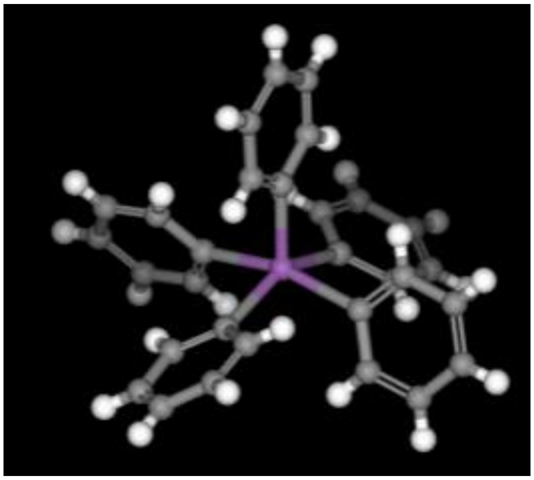
Apply the VSEPR model to the following molecules. Confirm that your predictions are correct by examining the relevant crystal structures. Comment on how closely the observed angles match those of the ideal geometry and account for any significant deviations.

Molecule/ion	**CSD refcode/ICSD identifier**
SO_2	DADXOW
$[CeCl_6]^{2-}$	CLCAME01
$(CF_3)Cl_2I$	COXYIX
$Sr(py)_5Br_2$ (py = pyridine)	TANWAG
BCl_4	PETKAB
$SePh_2Cl_2$	PHSECL01
$B(OH)_3$	JAGREP
ClF_4^-	ROLSEQ
$P(OPh)_5$	PPHOXP
$SbBr_5^-$	CLPYSB
$[Ce(OEP)_2]$ (OEP = octaethylporphyrinate)	DURLUX
XeF_8^{2-}	83701
XeO_2F_2	10203
SMe_3^+	YUTDEY

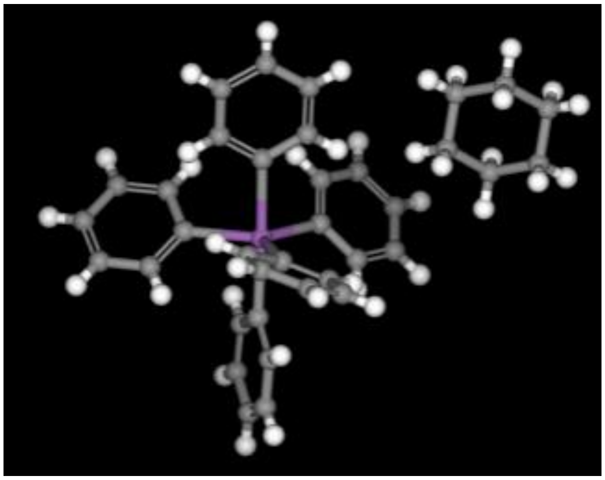
2.6 When doesn't the VSEPR model work?

The most common situation where VSEPR theory fails in transition metal compounds. This is because transition metals have varying number of electrons in d orbitals; these d orbitals are involved in covalent bonding to different degrees depending on the molecular geometry, which can only be properly understood by molecular orbital theory. Octahedral coordination geometry dominates despite varying numbers of valence electrons (e.g. $[M(H_2O)_6]^{2+}$, where M = 1st row transition metal). VSEPR theory can work for metal complexes with more ionic bonding, such as alkali metals and lanthanoids, where geometry is determined largely by electrostatic repulsion between the ligands, and metal-based electrons can be ignored.

In other cases, two geometries may actually be quite close in energy (and indeed they may interconvert under some conditions). Such an example is seen for $SbPh_5$; CSD entry PHENSB03 has a square-based pyramid geometry, whereas PPHSBC01, which contains cyclohexane in the structure, adopts a trigonal bipyramid shape. Solution NMR spectroscopy reveals only one set of resonances for the aryl groups, even at −142 °C, indicating it changes conformation very rapidly in solution.[1]



PHENSB03



PPHSBC01

Lastly, put quite simply, sometimes it just doesn't work. Consider $TeBr_6^{2-}$. The electron count would be as follows:

Tellurium hexabromide dianion	
Central atom	Tellurium
Valence electrons on central atom	6
Valence electron from 6 bromine atoms	6
2 electrons from charge	2
Total valence electrons	14
Divide by 2 to give number of electron pairs	7
Electron pairs in 6 bonds	6
Lone pairs	1
Pentagonal bipyramidal arrangement of electron pairs (one of which is a lone pair, the remaining six in 6 double bonds). Overall geometry is **pentagonal pyramidal**.	

Now look up CSD entry YUTDEY in Access Structures and assess the geometry.

The predicted geometry is pentagonal pyramidal; however, we can see from YUTDEY that the geometry is actually octahedral. This molecule would be said to have a stereochemically inactive lone pair – a phenomenon that is not unusual for heavier elements due to relativistic effects.*

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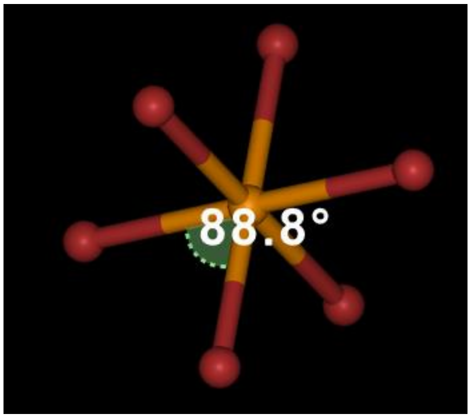
[1] B. Lindquist-Kleissler, Monica Weng, P. Le Magueres, G. N. George and Timothy C. Johnstone, *Inorg. Chem.*, 2021, **60**, 8566–8574 DOI: 10.1021/acs.inorgchem.1c00496.



$TeBr_6^{2-}$ in YUTDEY

*This is beyond the scope of this teaching module. Simplistically, it is because the increased mass of the nucleus causes some electrons to orbit close to the speed of light; it tends to affect s electrons more than p or d electrons and the result is that the s electrons become less involved in bonding.

3 Summary

In this teaching module we have seen how the geometries of many molecules can be predicted using VSEPR theory, a model based on electrostatics. Bonding and lone pair electrons are assumed to surround the central atom and to repel one another. Minimising this repulsion gives a geometry determined by the number of electron pairs present. The model is completed by considering the repulsion hierarchy lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair, with further refinements where multiple bonds and electronegativity differences are important. The model is quite successful at predicting the geometries of main group compounds and non-transition metals but does not always work for heavier elements and rarely works for transition metal complexes.

3.1 Next steps

If you would like to study the structures presented in this teaching sheet further, we suggest viewing them in Mercury, where you can customize the view of the molecules and make more advanced measurements. A free-for academic use version of Mercury is available for educational use. To learn more about Mercury, we recommend trying the online module “Visualization 101 – Visualizing Structural Chemistry Data with Mercury”. You can find the structures used in this module in the Teaching Subset, which is pre-loaded into Mercury. See the links below for more information.

https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/
https://www.ccdc.cam.ac.uk/community/training-and-learning/csdu-modules/visualization-101/
https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/

If you wish to explore the CSD further and search for structures of interest to you, you can find a number of training resources, including self-guided workshops, online courses and videos to you get started from the CCDC’s Training and Learning Web pages.

https://www.ccdc.cam.ac.uk/community/training-and-learning/

3.2 Acknowledgements

We would like to thank Professors Alice Brink and Marietjie Schutte-Smith (University of the Free State, South Africa) and Professor Sally Boss (University of Cambridge, UK) for providing helpful feedback on this teaching module.

4 Answers to exercises

Exercise 1

Molecule or ion	CSD refcode	Geometry	Angle range (°)
BrF_6^-	ZAQBIC	Octahedral	88.6–91.8
I_3^-	RIKTAG	Linear	180.0
$In(CH_3)_3$	TRMEIN03	Trigonal planar	116.2–124.1
$[BeF_4]^-$	KIPPEE	Tetrahedral	108.6–110.5
NMe_4^+	SODVOW02	Tetrahedral	109.4–109.5
SiF_5^-	CINLEQ	Trigonal bipyramidal	89.6–90.3 (eq-ax) 117.5–121.2 (eq-eq)
SbF_6^-	FUJLAX	Octahedral	89.0–91.4

Each of these examples has the geometry expected for the given number of valence electron pairs. The range of bond angles is generally small and in line with the expected geometry, although TRMEIN03 and SiF_5^-, both show a greater range on bond angles in the trigonal plane. This is likely because the space between atoms is greater in the trigonal plane, so the bond angles can vary slightly without a significant increase in repulsion.

Exercise 2

According to the rules for counting double bonds, we predict the following for $XeOF_2$

Xenon oxydifluoride $XeOF_2$

Central atom	Xenon
Valence electrons on central atom	8
Valence electron from 1 oxygen atom and 2 fluorine atoms	4
Total valence electrons	12
Divide by 2 to give number of electron pairs	6
Electron pairs in 1 double bond + two single bonds	4
Lone pairs	2
T-shaped based on a trigonal bipyramidal parent arrangement with two vertices occupied by lone pairs.	

There are two independent $XeOF_2$ molecules in QEZYUQ; we shall use the molecule containing Xe1 for this discussion. The F–Xe–O bond angles are 94.0 and 90.1°, whereas F–Xe–F is 171.9°. The molecule conforms to the expected T-shape, with oxygen occupying the equatorial position of the parent trigonal bipyramidal structure. The relative repelling power: lone pair > multiple bond > single bond is consistent with the oxygen atom in the equatorial position of the parent trigonal bipyramid structure, together with the two lone pairs. The F–Xe–O bond angles are obtuse, which is perhaps surprising as we might expect repulsion from the lone pairs to make them acute. For comparison, in the cation XeF_3^+ from ICSD entry 6034, the equivalent angles are acute (around 81°), which is consistent with this hypothesis.

Exercise 3

The bond angles in NF_3 in ROGYEU are around 102°, whereas the bond D–N–D angles in ND_3 in HUWREX are in the range 106–108° (average 107.1°). This can be explained by the relative electronegativities of fluorine (χ_P = 3.98) and hydrogen (χ_P = 2.20). The more electronegative fluorine pulls the bonding pair closer to itself than hydrogen does, reducing repulsion and along the fluorine atoms to be forced closer together by the lone pair repulsion.

Exercise 4

Molecule/ion	CSD refcode	Angles range (°)	Comments
SO_2	DADXOW	113.0–114.2	**Bent** geometry based off trigonal parent shape with 1 lone pair. O–S–O angle < 120° as lone pair-bonding pair repulsion is strongest.
$[CeCl_6]^{2-}$	CLCAME01	88.3–91.7	**Octahedral** as expected for 6 electron pairs. Ce^{4+} has no valence electrons.
$(CF_3)Cl_2I$	COXYIX	171.6 (Cl–I–Cl) 82.9-88.7 (Cl–I–C)	**T-shaped** geometry based off trigonal bipyramid with 2 lone pairs. Lone pairs occupy equator as expected and lone pair-bonding pair repulsion makes Cl–I–Cl <180°.
$Sr(py)_5Br_2$ (py = pyridine)	TANWAG	177.9 (Br–Sr–Br) 70.6–73.6 (N–Sr–N) 85.3–91.4 (N–Sr–Br)	**Pentagonal bipyramidal** geometry. Sr^{2+} has no valence electrons, and each ligand can be considered to donate a lone pair to Sr. The nitrogen atoms have a smaller radius and thus go in the equatorial sites where the inter-bond angles are < 90° allowing Br to take up the less crowded axial positions.
BCl_4^-	PETKAB	109.0–110.2	**Tetrahedral** geometry. All bonding pairs; angles are ideal.
$SePh_2Cl_2$	PHSECL01	175.0 (ax-ax) (in direction pointing away from molecule) 92.4 (ax-eq) 100.4 (eq-eq)	**See-saw** geometry based off trigonal bipyramidal parent arrangement with one lone pair. The C–Se–C angle is < 120° consistent with enhanced repulsion by the lone pair but Cl–Se–Cl is < 180° in the direction away

			from the molecule. This is unexpected based on just the sizes of C and Cl alone, though the phenyl groups as a whole take up a lot of space.
$B(OH)_3$	JAGREP	119.0–120.2	**Trigonal planar** geometry with ideal bond angle as expected for compound with three bonding electron pairs.
ClF_4^-	ROLSEQ	88.9–91.2	**Square planar** geometry based off octahedral parent arrangement with two lone pairs. Ideal bond angles. The lone pairs occupy the axial positions to minimise lone pair-lone pair repulsion.
$P(OPh)_5$	PPHOXP	176.5 (ax-ax) 114.9–126.2 (eq-eq) 88.0–92.2 (ax-eq)	**Trigonal bipyramidal** geometry as expected with only bonding pairs. Small deviations from ideal bond angles likely due to conformation of aryl rings.
$SbBr_5^{2-}$	CLPYSB	87.0–92.4 (in square plane) 87.5–92.9 (apex-square plane)	**Square-based pyramidal** geometry based off octahedral parent geometry with one lone pair. Bond angles close to the expected 90° for this geometry. No clear evidence of asymmetry from lone pair presence.
$[Ce(OEP)_2]$ (OEP = octaethylporphyrinate]	DURLUX	71.0–72.7 (in square) 77.3–81.4 (nearest neighbours between squares) 139.7–146.1(farthest between squares)	**Square antiprismatic** geometry. Ce^{4+} has no valence electrons remaining and we can consider each N atom to donate an electron pair. The 'cis' angles within the squares are compressed compared to the ideal angle (74.9°) and other angles are changed accordingly. This could be explained by repulsion between the large framework of the porphyrin ligands.
XeF_8^{2-}	83701	73.7–75.5 (in square)	**Square antiprismatic** geometry based on 8

		75.4–78.0 (nearest neighbours between squares) 140.8–143.9 (farthest between squares)	bonding pairs. In comparison to example $[Ce(OEP)_2]$ (DURLUX) above, the bond angles are closer to those expected for this geometry, which we can attribute to the constraint of the nitrogen atoms within the porphyrin in DURLUX compared to the greater freedom of the F atoms in XeF_8^{2-}
XeO_2F_2	10203	105.7 (O−Xe−O) 174.7 (F−Xe−F) 91.6 (O−Xe−F)	**See-saw** geometry based on a trigonal bipyramidal parent geometry with an equatorial position occupied by a lone pair. The positioning of the doubly bonded oxygens in the equatorial plane and the fluorine atoms in the axial positions is in line with predictions, taking into account (1) the greater repelling power of double bonds relative to single bonds and (2) the higher electronegativity of fluorine favouring the less congested axial positions. The O−Xe−O bond angle is < 120°, as predicted.
SMe_3^+	YUTDEY	101.2°	**Pyramidal** geometry based on a tetrahedral parent geometry with one vertex occupied by lone pair. Bond angle < 109.5°as expected based on lone pair-bonding pair repulsion.