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Chemistry Internal Assessment

The Effect of Halogen Atom Substitution on Bond Angles in Halogenated Compounds

Research Question

In this investigation I will look at whether the radius and number of halogen atoms bonded to a central atom such as carbon will have a significant on the bond angle compared to that predicted by VSEPR Theory. If the effect is significant I try to see if there is a relationship between halogen atom identity and the bond angles around tetrahedral centres.

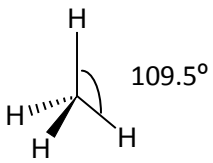
Introduction

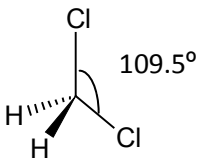
We have learned in our IB Chemistry class that Valence Shell Electron Pair Repulsion (VSEPR) theory can be used to predict molecular geometries and bond angles. According to Brown and Ford[1] the key principles of VSEPR theory are:

- Electron pairs found in the outer energy level or valence shell of atoms repel each other and thus position themselves as far apart as possible.
- The repulsion applies to both bonding and non-bonding pairs of electrons.
- Double and triple bonded electron pairs are orientated together and so behave in terms of repulsion as a single unit known as a "negative charge centre".
- The total number of charge centres around the central atom determines the geometrical arrangement of the electrons
- Non-bonding (lone) pairs of electrons have a higher concentration of charge than a bonding pair because they are not shared between two atoms and so they cause more repulsion than bonding pairs. The repulsion decreases in the order:

lone pair-lone pair > lone pair-bond pair > bond pair-bond pair

So according to the VSEPR theory described by Brown and Ford the molecular geometry and bond angles are only affected by the number of bonding pairs and lone pairs of electrons around the central atom.

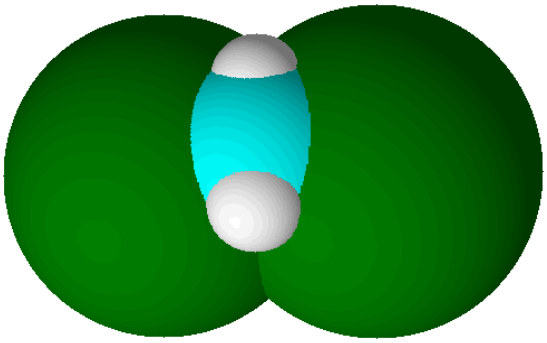




What doesn't seem to have any effect according to VSEPR Theory is the identity of the atom or functional group attached to the central atom. So for example methane, CH_4 and dichloromethane, CH_2Cl_2, will have the same tetrahedral geometry and 109.5° bond angles since they both have four bonding pairs and no non-bonding pairs of electrons around the central carbon.

When looking at some three dimension space filling diagrams like that below for CH_2I_2 from ChemSketch I saw that the large iodine atoms overlapped. I would expect that the greater number

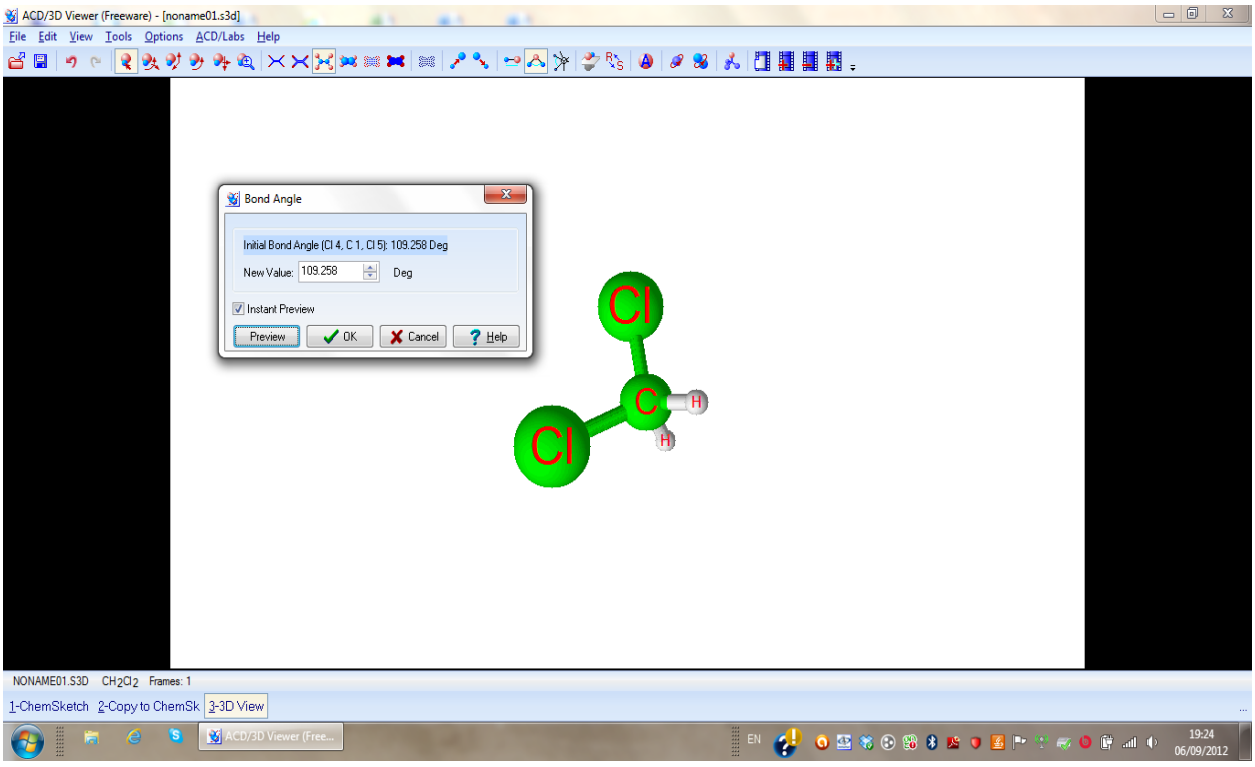
of shells of electrons and the large atomic radius would cause the iodine atoms to repel each other more than the iodine atoms would repel the hydrogen atoms. So I expect the iodine-carbon-iodine bond angle to be greater than the symmetric tetrahedral bond angle of 109.5°.



In this investigation I will look at the effect of halogen-halogen repulsion on the bond angles in halogenated methane compounds.

Methodology

The bond angles for the tetrahedral centred molecules were determined using the Chemsketch software downloaded from http://www.acdlabs.com.

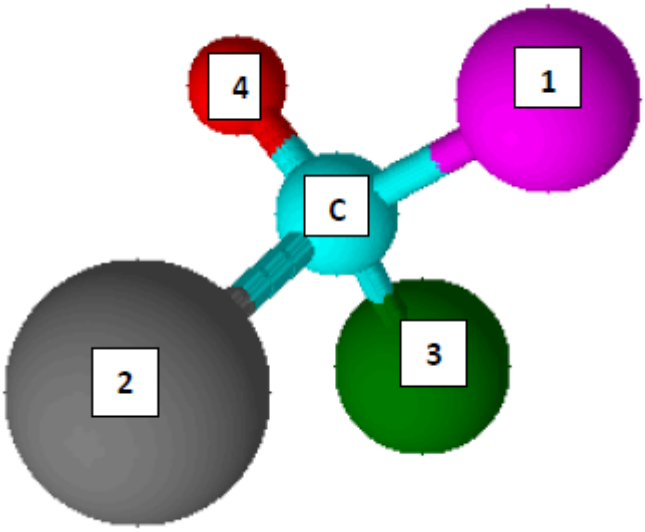


The Help Facility on the ChemSketch Software describes under 3D Optimisation Algorithm how it calculates the bond angles using a 3D Optimisation algorithm based on modified molecular mechanics. It does state that the "3D-optimizer is NOT a full-scale molecular mechanics engine. Its

design aims to reliably reproduce reasonable conformations from (possibly very unreasonable) 2D drawings, rather than to precisely optimize 3D structures."

Once the ACD/3D Viewer ChemSketch software was loaded the following procedure was followed for each compound.

1. The ChemSketch page opened and the target molecule drawn in.
2. Click on the Tools menu and select 3D-structure Optimisation
3. Click on 3D Viewer icon on top tool bar to enter 3d-Viewer
4. Select 3D-optimization
5. Rotate 3D image into orientation as shown below



6. Select Bond Angle icon on Tool bar
7. Click on image in order of substituent atom1 – central atom – substituent atom. Record bond angle stated in dialogue box
8. Repeat for all six bond angles 1-C-2, 1-C-3, 1-C-4, 2-C-3, 2-C-4, 3-C-4

Raw Data

The raw data is given by ChemSketch to three decimal places which I repeat in the tables below.

Table 1: Bond Angles in Halogenated Methane Compounds of General Formula CH_4 and CX_4

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average Bond Angle (±0.001°)
					1-C-2	1-C-3	1-C-4	2-C-3	2-C-4	3-C-4	
CH_4	H	H	H	H	109.454	109.454	109.473	109.478	109.450	109.450	109.460
CF_4	F	F	F	F	109.454	109.480	109.482	109.467	109.470	109.464	109.470
CCl_4	Cl	Cl	Cl	Cl	109.471	109.472	109.469	109.474	109.469	109.473	109.471
CBr_4	Br	Br	Br	Br	109.488	109.466	109.448	109.469	109.482	109.475	109.471
CI_4	I	I	I	I	109.473	109.476	109.474	109.470	109.463	109.472	109.471

Table 2: Bond Angles in Halogenated Methane Compounds of General Formula CH_3X

Formula	3D Optimisation	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average Bond Angle (±0.001°)
						1-C-2	1-C-3	1-C-4	2-C-3	2-C-4	3-C-4	
CH_3F	1st	F	H	H	H	109.991	109.002	109.989	109.437	108.969	109.440	109.471
CH_3Cl	1st	Cl	H	H	H	110.640	110.624	108.481	108.437	109.319	109.319	109.470
CH_3Br	1st	Br	H	H	H	110.854	110.847	108.300	108.295	109.209	109.252	109.460
CH_3I	1st	I	H	H	H	111.073	111.038	108.139	108.193	109.188	109.179	109.468

Table 3: Bond Angles in Halogenated Methane Compounds of General Formula CH_2X_2

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average Bond Angle (±0.001°)
					1-C-2	1-C-3	1-C-4	2-C-3	2-C-4	3-C-4	
CH_2F_2	F	F	H	H	110.510	108.968	109.450	108.958	109.461	109.476	109.471
CH_2Cl_2	Cl	Cl	H	H	111.937	108.223	109.523	108.228	109.518	109.364	109.466
CH_2Br_2	Br	Br	H	H	112.424	109.570	107.957	109.574	107.965	109.280	109.462
CH_2I_2	I	I	H	H	112.964	107.634	109.670	107.618	109.661	109.197	109.457

Table 4: Bond Angles in Halogenated Methane Compounds of General Formula CHX_3

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average Bond Angle (±0.001°)
					1-C-2	1-C-3	1-C-4	2-C-3	2-C-4	3-C-4	
CHF_3	F	F	F	H	110.038	109.428	108.987	109.385	108.983	110.007	109.471
$CHCl_3$	Cl	Cl	Cl	H	109.113	110.781	108.511	109.103	110.805	108.527	109.473
$CHBr_3$	Br	Br	Br	H	108.929	108.941	111.107	111.026	108.435	108.411	109.475
CHI_3	I	I	I	H	108.715	108.719	111.468	111.240	108.370	108.349	109.477

Data Analysis

In this section I am going to look at the trends in bond angles revealed by the data tables above plus I will look at the trends in the average bond angle data for each bond angle type.

Analysis Comment 1:

All the molecules in tables 1 to 4 above show that the average bond angle within each molecule agrees with the ideal tetrahedral angle of 109.5°.

The smallest average is 109.460° for CH_4 in Table 1 and the largest is 109.477° for CHI_3 in Table 4. This means that when one bond angle is distorted to more than 109.5° then the other bond angles are reduced to compensate by exactly the right amount to keep the average close to the ideal angle.

Analysis Comment 2:

The data in Table 1 shows that if all four atoms bonded to the central carbon are the same (all of general formula CX_4) then the bond angles are all close to being equal and close to the ideal angle of 109.5°.

This makes sense because all the molecules are perfectly symmetrical. Although I think that Iodine, with its many electrons, will be repelling more than a small hydrogen or fluorine all the other atoms in the molecule are "pushing back" equally strongly and the overall net repulsion is the same

Analysis Comment 3

The effect of a single halogen substitute in molecules of general formula CH_3X on the average H-C-Hal and H-C-H bond angles can be seen in Table 5 below

Table 5 Average Bond Angles of Each Type in Compounds of General Formula CH_3X

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average H-C-Hal Bond Angle (±0.001°)		Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average H-C-H Bond Angle (±0.001°)
					1-C-2	1-C-3	1-C-4	Average		2-C-3	2-C-4	3-C-4	Average
CH_3F	F	H	H	H	109.991	109.002	109.989	**109.661**		109.437	108.969	109.440	**109.282**
CH_3Cl	Cl	H	H	H	110.640	110.624	108.481	**109.915**		108.437	109.319	109.319	**109.025**
CH_3Br	Br	H	H	H	110.854	110.847	108.300	**110.000**		108.295	109.209	109.252	**108.919**
CH_3I	I	H	H	H	111.073	111.038	108.139	**110.083**		108.193	109.188	109.179	**108.853**

The average bond angle data shows that there is a small increase in H-C-Hal bond angle as the halogen atom gets bigger. The total effect is small with the large iodine atom causing only about 0.6° increase compared to the symmetrical methane bond angle. But the trend in the data is observable and we can say that increasing the size of a single halogen substitute causes greater repulsion of the adjacent hydrogens.

The average H-C-H bond angles reduce a little so as to compensate for the increased H-C-Hal bond angle as would be expected.

Analysis Comment 4

The effect of increasing halogen substitute size on the Hal-C-Hal bond angle is shown in Tables 6 and 7 below

Table 6 Average Bond Angles of Each Type in Compounds of General Formula CH_2X_2

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Hal-C-Hal Bond Angle (±0.001°)		Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average H-C-Hal Bond Angle (±0.001°)
					1-C-2		1-C-3	1-C-4	2-C-3	2-C-4	3-C-4	Average
CH_2F_2	F	F	H	H	110.51		108.968	109.45	108.958	109.461	109.476	109.2626
CH_2Cl_2	Cl	Cl	H	H	111.937		108.223	109.523	108.228	109.518	109.364	108.9712
CH_2Br_2	Br	Br	H	H	112.424		109.57	107.957	109.574	107.965	109.28	108.8692
CH_2I_2	I	I	H	H	112.964		107.634	109.67	107.618	109.661	109.197	108.756

The effect of halogen size on the Hal-C-Hal bond angle is very clear. If the substitutes are fluorine then the halogen-carbon-halogen bond angle is 1 whole degree above the symmetric tetrahedral angle. The trend carries on and the iodine-carbon-iodine bond angle is a full 3.5° above the symmetric tetrahedral angle. This is a very important result that shows that the size of the halogen atom **does** have a major influence on bond angles.

The Halogen- Carbon- Hydrogen bond angles are reduced in order to compensate for the increased halogen – carbon – halogen angle.

Table 7 Average Bond Angles of Each Type in Compounds of General Formula CHX_3

Formula	Substituent 1	Substituent 2	Substituent 3	Substituent 4	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average Hal-C-Hal Bond Angle (±0.001°)		Bond Angle (±0.001°)	Bond Angle (±0.001°)	Bond Angle (±0.001°)	Average H-C-Hal Bond Angle (±0.001°)
					1-C-2	1-C-3	2-C-3	Average		1-C-4	2-C-4	3-C-4	Average
CHF_3	F	F	F	H	110.038	109.428	109.385	109.617		108.987	108.983	110.007	109.326
$CHCl_3$	Cl	Cl	Cl	H	109.113	110.781	109.103	109.666		108.511	110.805	108.527	109.281
$CHBr_3$	Br	Br	Br	H	108.929	108.941	111.026	109.632		111.107	108.435	108.411	109.318
CHI_3	I	I	I	H	108.715	108.719	111.240	109.558		111.468	108.370	108.349	109.396

When a third halogen is substituted into the molecule then the effect on bond angles gets smaller again. I think this is because the third halogen is large and stops the first two halogens repelling each other as much as in the CH_2X_2 molecules. The effect is not symmetrical and one of the halogen-carbon-halogen bond angles is much bigger than the other two.

Conclusion

Overall the conclusions were that

1. The average bond angle within each molecule agrees with the ideal tetrahedral angle of 109.5°.

2. If all four atoms bonded to the central carbon are the same (all of general formula CX_4) then the bond angles are all close to being equal and close to the ideal angle of 109.5°.

3. In molecules of general formula CH_3X increasing the size of a single halogen substitute causes greater repulsion of the adjacent hydrogens and hydrogen-carbon-halogen bond angle increases steadily

4. In molecules of general formula CH_2X_2 increasing the size of a single halogen substitute causes great repulsion of the adjacent halogen and the halogen-carbon-halogen bond angle increases greatly. This is the biggest effect that I observed and confirms that atomic size does affect bond angles.

5. When a third halogen is substituted into the molecule then the effect on bond angles gets smaller again. I think this is because the third halogen is large and stops the first two halogens repelling each other as much as in the CH_2X_2 molecules.

Evaluation

There was no experimental data used in this investigation so there is no experimental uncertainty to consider. The precision in the data generated by Chemsketch was very good and given to three decimal places.

Suggestions for Further Study

The effect of atom or functional group size on the bond angles can be studied further. If I continued the study I would look at the effect of different alkyl groups on the bond angles around a tetrahedral carbon atom.

Sources

1. C. Brown and M. Ford, Higher Level Chemistry, pp 120-121, Pearson Baccalaureate, 2009
2. ChemSketch Software, http://www.acdlabs.com Last accessed 29-2-2012