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Is VSEPR Valid?

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Summary. A chief tenet of VSEPR (valence shell electron pair repulsion theory) is that very electronegative atoms or groups attached to a central atom pull electrons toward themselves. These electron pairs, being farther apart, exert less repulsion, and consequently the bond angles involving them are decreased. A comparison of 37 pairs of common compounds shows that this rule holds only for hydrogen compounds. For other molecules, the size of the attached groups determines the bond angles.

Keywords. VSEPR; Molecular geometry; Bond angles.

VSEPR: ist es stichhaltig?

Zusammenfassung. Ein Hauptgrundsatz der VSEPR (Valenzschalen-Elektronenpaar-Repulsion) Theorie heißt: hoch elektronegative, an einem Zentralatom angelagerte Atome oder Atomgruppen ziehen Elektronen an. Da sie weiter voneinander entfernt sind, üben diese Elektronenpaare weniger Repulsion aus. Daher werden die dazugehörigen Bindungswinkel vermindert. Ein Vergleich von 37 Paaren einfacher Verbindungen zeigt, daß diese Regel nur für Wasserstoffverbindungen gilt. In anderen Molekülen bestimmt die Größe der angelagerten Gruppen die Valenzwinkel.

Introduction

The Valence Shell Electron Pair Repulsion, VSEPR, procedure for deducing structure of molecules and ions is quite popular. Aside from any question concerning its theoretical justification, the reason for its popularity is clear. It is very simple and easy to apply to main group elements, because it starts with a simple Lewis electron structure, and focuses only on the electrons in the valence shell, and essentially ignores all else [1–8]. The equilibrium structure is the one which minimizes the repulsive forces between these electrons. It is known to have some faults, especially in predicting the structure of rather complex structures, but in general is considered to be quite successful in predicting simple molecular structures.

Other alternatives have been offered [8], but these require calculations and concepts which are not considered in most chemistry texts.

Yet it is still necessary that we consider the reliability of VSEPR in predicting and describing the actual structure of molecules and ions. When we do so, we find an embarrassingly large number of very simple molecules and ions which do not fit VSEPR predictions.

This is not the place to list all the aspects of VSEPR, but the chief tenets should be considered. Basically, it focuses only on repulsion between electron pairs around the central atom. When repulsive interactions of valence shell electrons are considered, they are in the order: nonbond pairs-nonbond pairs > nonbond pairs-bond pairs > bond pairs-bond pairs. In addition, when considering bond pairs, a very electronegative atom bonded to the central atom will pull the electrons out toward itself, thereby reducing their repulsive interaction with other electron pairs. This results in a reduction in the angle involving the attached electronegative atoms.

Results: Evaluation of VSEPR

The bond angles are from Wells [9], unless otherwise stated, in Tables 1 – 3.

Let us compare several actual structures in light of the VSEPR hypotheses, Tables 4 and 5.

Table 1. Bond angles and electronegativity differences for simple hydrides $E\mathrm{H}_2$ and $E\mathrm{H}_2$ of Groups 15 and 16, and bond radii (angstroms) of the central elements

Hydride	$\mathrm{H}E\mathrm{H}$	Δx	r	Hydride	$\mathrm{H}E\mathrm{H}$	Δx	r
$\mathrm{TeH_2}$	-	0.19	1.37	$\mathrm{SbH_3}$	91.3°	0.15	1.41
$\mathrm{SeH_2}$	91°	0.35	1.17	$\mathrm{AsH_3}$	91.8°	0.02	1.21
$\mathrm{SH_2}$	92°	0.38	1.04	$\mathrm{PH_3}$	93.8°	0.01	1.10
$\mathrm{OH_2}$	104.5°	1.24	0.66	$\mathrm{NH_3}$	106.6°	0.84	0.70

Table 2. Bond angles in simple binary compounds, $E\mathrm{X}_3$, of Group 15. (*Mf* signifies trifluoromethyl, $\mathrm{CF_3}$; *Sl* is silyl)

$\mathrm{NF_3}$	102.2	$\mathrm{PF_3}$	97.8	$\mathrm{AsF_3}$	96.2	$\mathrm{SbF_3}$	-[a]	$\mathrm{BiF_3}$	-
$\mathrm{N}\mathit{Me}_3$	110.9	$\mathrm{P}\mathit{Me}_3$	98.9	$\mathrm{As}\mathit{Me}_3$	96	$\mathrm{Sb}\mathit{Me}_3$	-	$\mathrm{Bi}\mathit{Me}_3$	96.7
$\mathrm{N}\mathit{Mf}_3$	117.9[b]	$\mathrm{P}\mathit{Mf}_3$	97.2[c]	$\mathrm{As}\mathit{Mf}_3$	100	$\mathrm{Sb}\mathit{Mf}_3$	100.0	$\mathrm{Bi}\mathit{Mf}_3$	-
$\mathrm{NCl_3}$	106.8	$\mathrm{PCl_3}$	100.3	$\mathrm{AsCl_3}$	98.7	$\mathrm{SbCl_3}$	97.2	$\mathrm{BiCl_3}$	100
$\mathrm{NBr_3}$	-	$\mathrm{PBr_3}$	101.0	$\mathrm{AsBr_3}$	99.7	$\mathrm{SbBr_3}$	98	$\mathrm{BiBr_3}$	100
$\mathrm{NI_3}$	-	$\mathrm{PI_3}$	102	$\mathrm{AsI_3}$	100.2	$\mathrm{SbI_3}$	99.1	$\mathrm{BiI_3}$	-
$\mathrm{N}\mathit{Sl}_3$	120	-	-	-	-	-	-	-	-

[a] Not available in gas phase; crystal shows pseudo-octahedral coordination around Sb

[b] Burger H. (1979) J. Mol. Struct. **54**: 159

[c] Ref. [1]

Table 3. Bond angles in simple binary compounds, $E\mathrm{X}_2$, of Group 16. (*Mf* signifies trifluoromethyl, $\mathrm{CF_3}$)

$\mathrm{OF_2}$	103.3	$\mathrm{SF_2}$	98				
$\mathrm{OCl_2}$	110.9	$\mathrm{SCl_2}$	100			$\mathrm{TeBr_2}$	98
$\mathrm{O}\mathit{Me}_2$	111.5	$\mathrm{S}\mathit{Me}_2$	99	$\mathrm{Se}\mathit{Me}_2$	98		
$\mathrm{O}\mathit{Mf}_2$	119.1[a]	$\mathrm{S}\mathit{Mf}_2$	106	$\mathrm{Se}\mathit{Mf}_2$	104		

[a] Lowrey A. (1980) J. Mol. Struct. **63**: 243

Table 4. Bond angle comparisons for elements of Groups 15 and 16 bonded to hydrogen: a test of VSEPR

Upper numbers are electronegativities from Huheey (1983) Inorganic Chemistry, 3rd edn. Harper & Row, New York ($\mathit{Mf}=CF_3$)

2.2	4.0	2.2	3.2	2.2	2.3	2.2	3.4		
OH_2 *	OF_2	OH_2	OCl_2	OH_2	$\mathrm{O}\mathit{Me}_2$	OH_2	$\mathrm{O}\mathit{Mf}_2$		
104.5	103.3	104.5	110.9	104.5	111.5	104.5	119.1		
2.2	4.0	2.2	3.2	2.2	2.3	2.2	3.4		
SH_2	SF_2	SH_2	SCl_2	SH_2	$\mathrm{S}\mathit{Me}_2$	SH_2	$\mathrm{S}\mathit{Mf}_2$		
92	98	92	100	92	99	92	106		
2.2	4.0	2.2	3.2	2.2	2.3	2.2	3.4		
NH_3 *	NF_3	NH_3	NCl_3	NH_3	$\mathrm{N}\mathit{Me}_3$	NH_3	$\mathrm{N}\mathit{Mf}_3$		
106.6	102.2	106.6	106.8	106.6	110.9	106.6	117.9		
2.2	4.0	2.2	3.2	2.2	2.3	2.2	2.7	2.2	3.4
PH_3	PF_3	PH_3	PCl_3	PH_3	$\mathrm{P}\mathit{Me}_3$	PH_3	PI_3	PH_3	$\mathrm{P}\mathit{Mf}_3$
93.8	97.8	93.8	100.3	93.8	98.9	93.8	102	93.8	97.2

[a] Only pairs with asterisks follow VSEPR rules

Table 5. Bond angle comparisons for elements of Groups 15 and 16 bonded to other atoms and groups: a test of VSEPR

Upper numbers are electronegativities from Huheey (1983) Inorganic Chemistry 3rd edn, Harper & Row, New York; except silyl, which is author's estimate.) ($\mathit{Mf}=CF_3$; $\mathit{Sl}=SiH_3$; Ph=phenyl)

2.3	3.2	4.0	3.4	2.3	3.4				
$\mathrm{O}\mathit{Me}_2$ *	OCl_2	OF_2	$\mathrm{O}\mathit{Mf}_2$	$\mathrm{O}\mathit{Me}_2$	$\mathrm{O}\mathit{Mf}_2$				
111.5	110.9	103.3	119.1	111.5	119.1				
2.3	3.2	3.4	4.0	2.3	3.4	3.3	4.0		
$\mathrm{S}\mathit{Me}_2$	SCl_2	$\mathrm{S}\mathit{Mf}_2$ *	SF_2	$\mathrm{S}\mathit{Me}_2$	$\mathrm{S}\mathit{Mf}_2$	$S(CN)_2$	SF_2		
99	100	106	98	99	106	96	98		
3.4	4.0	3.2	3.4	2.1	2.3	2.3	3.0		
$\mathrm{N}\mathit{Mf}_3$ *	NF_3	NCl_3	$\mathrm{N}\mathit{Mf}_3$	$\mathrm{N}\mathit{Sl}_3$ *	$\mathrm{N}\mathit{Me}_3$	$\mathrm{N}\mathit{Me}_3$	$\mathrm{N}\mathit{Ph}_3$		
117.9	102.2	106.9	117.9	120	110.9	110.9	116		
3.4	4.0	2.3	3.2	2.3	3.0	2.3	2.7	3.3	4.0
$\mathrm{P}\mathit{Mf}_3$	PF_3	$\mathrm{P}\mathit{Me}_3$	PCl_3	$\mathrm{P}\mathit{Me}_3$	PBr_3	$\mathrm{P}\mathit{Me}_3$	PI_3	$P(CN)_3$	PF_3
97.2	97.8	98.9	100.3	98.9	101.0	98.9	102	93	97.8
		2.3	3.2	2.3	3.0	2.3	2.7	3.3	4.0
		$\mathrm{As}\mathit{Me}_3$	$AsCl_3$	$\mathrm{As}\mathit{Me}_3$	$AsBr_3$	$\mathrm{As}\mathit{Me}_3$	AsI_3	$As(CN)_3$	AsF_3
		96	98.7	96	99.7	96	100.2	92	96.2

[a] Only pairs with asterisks follow VSEPR rules

An examination of these 37 pairs shows only six which follow the VSEPR rules (marked with asterisks). There are obviously many other pairs which can be formed, especially involving Se, Te, As, and Sb. These pairs are no different from the examples in the tables: very few follow VSEPR rules.

In addition to these, other types of structures can be given.

S_2O and SO_2. The latter should have a smaller bond angle, although it is larger: 118 vs. 119.5°.

H_2O_2 and O_2F_2. The latter should have a smaller angle, although it is larger: 98 vs. 109.5°. (The situation here is the exact opposite of H_2O and OF_2).

ClO_2^- and ClO_3^-. The former has two unshared pairs, the latter has one. Therefore the Cl-O-Cl angle should be smaller for ClO_2^-. In fact, they are the same, within experimental error, 108° and 107°.

H_2O, HOBr, HOCl, and Cl_2O. The bond angles around oxygen should decrease along this series, due to an increase in electronegativity of the bonded atoms. In fact they do not. The angles are: 104.5°, 110°, 113°, and 110.9°, respectively.

We see many simple, common molecular structures which deviate from the qualitative prediction of VSEPR. Other very similar deviant compounds involving congeners of the above can be found, with only a cursory search.

Discussion

An examination of the data in the tables shows that it is size of the bonded atoms or groups which causes the deviations from VSEPR. In general, the larger the attached group, the greater the deviation from VSEPR predictions. For almost all the cases where the pairs appear to be following VSEPR – $O(CH_3)_2$, OCl_2; SF_2, $S(CF_3)_2$; NF_3, $N(CF_3)_3$; $N(SiH_3)_3$, $N(CH_3)_3$ – it can be seen that the larger atoms or groups occupy more space around the central atom.

Why have these frequent, common exceptions to VSEPR eluded us for such a long time? I think that the answer is that we have almost always used examples involving only halogens. In this case the supposed electronegativity effect is in the same direction as the size effect. As soon as halogen atoms are compared with other atoms or groups then it is clear that size actually determines the geometry.

Effect of Size of the Central Atom

It is clear that larger central atoms have more space available around them, so the angles between attached atoms or groups is smaller. This is demonstrated by the following sequences of compounds.

NH_3	PH_3	AsH_3	SbH_3
106.6°	93.8°	91.8°	91.3°
	PI_3	AsI_3	SbI_3
	102°	100.2°	99.1°
$\mathrm{N}Me_3$	$\mathrm{P}Me_3$	$\mathrm{As}Me_3$	$\mathrm{Bi}Me_3$
110.9°	98.9°	96°	96.7°

When the central atom is quite large, e. g., Sb and Bi, then the trend is unclear, due to lack of accuracy of the angle determinations. This results in *apparent* inversions of angles in the pair As-Bi. One is not surprised to find that, when the central atom is quite large, the angle is not very sensitive to change in size of attached groups.

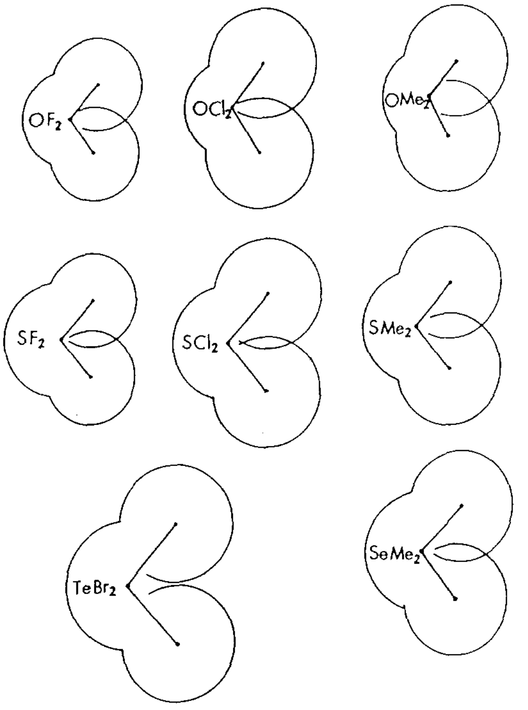

Fig. 1. Geometry of some Group 16 compounds, showing bond lengths, bond angles, and van der Waals radii to scale

The degree of interaction of attached groups or atoms, as a function of size of the central atoms, is shown in Figs. 1 and 2. These figures are drawn with actual bond lengths and angles, and the correct van der Waals radius. When the central atom is small, the attached groups interpenetrate more, producing more repulsion of nonbonded electrons. As the attached groups increase in number of electrons they become "harder", and interpenetration is less. We could say that the atoms with more electrons have a larger Born exponent, resulting in greater repulsion. The methyl group has a small number of electrons, and it can arrange the hydrogen atoms in a "gear-like" fashion to reduce steric hindrance. Consequently it interpenetrates to a great extent, and behaves as if it were rather small.

The Hydrides

When one compares the bond angles of simple hydrides with other hydrides then the story is somewhat different.

The hydrides of Group 14 are all tetrahedral, as predicted by any theory. Practically speaking, the only compounds which need to be considered are the hydrides of Groups 15 and 16, Table 1. (The hydrides of the other elements, such as B and Al, do not consist of simple molecules under ordinary conditions. Most other hydrides consist of polymeric structures which do not contain molecules. These do not fit into any simple structural theory.)

The proton is small. Therefore the valence shell pairs dominate the situation; VSEPR gives a good description of these, cf. Ref. [8]. In fact, the simple hydrides are the only class of compounds whose molecular structure is consistently predicted by VSEPR.

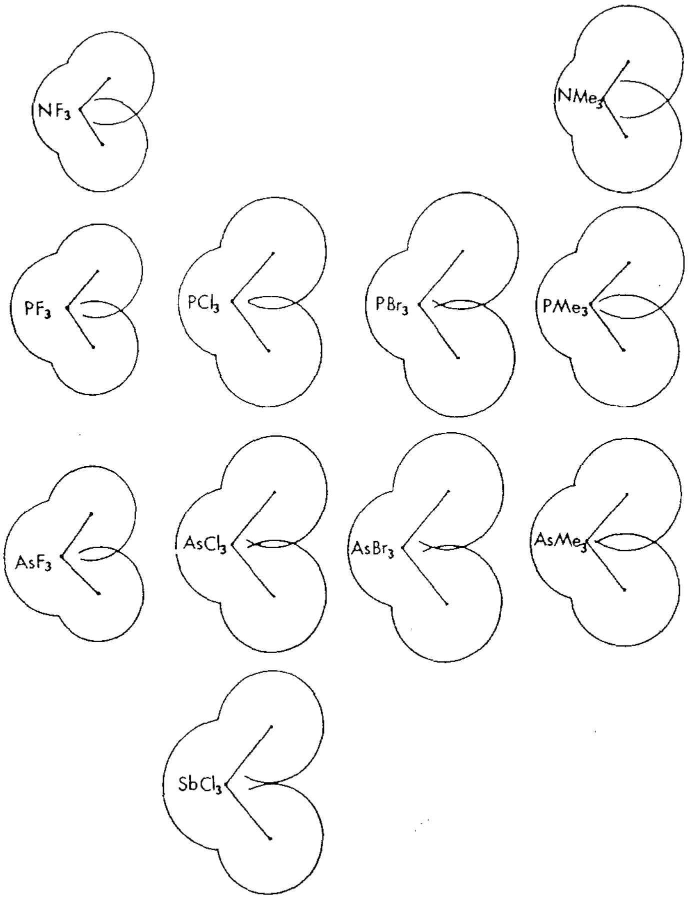

Fig. 2. Geometry of some Group 15 compounds, showing bond lengths, bond angles, and van der Waals radii to scale

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