

VSEPR and Central Atom Size Effects

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One of the criticisms frequently leveled at the valence-shell electron-pair repulsion or VSEPR model is its apparent inability to give a convincing rationale for the anomalously small bond angles (Table 1) observed in AX_3E (where A is a Group V element) and AX_2E_2 (where A is a Group VI element) species as one replaces A with heavier members of their respective groups (1). Gillespie has rationalized this phenomenon using the rule that the bond angles decrease as the electronegativity difference between A and its ligands increases. Leaving X constant and replacing A with heavier members of a group increases the relative electronegativity difference between A and X and so leads to smaller angles. This is consistent with the trends among the AX_3E halides given in Table 1.

However, a comparison between the halides and the hydrides for a given central atom A shows that the bond angle contractions are greater for the hydrides than for the halides, a trend which is not consistent with the relative electronegativity argument. The rationale in this case is based on the unique ability of the proton, due to the absence of any core electrons, to penetrate the electron cloud of its bonding pair (2, 3). This causes the bonding-pair electron clouds to contract, thus allowing for closer approach and smaller bond angles than one would expect on the basis of electronegativity differences alone.

The degree of penetration and contraction will, in turn, depend on the repulsions between the A core and the proton. The larger A, for a given net core charge, the smaller its positive charge density and the less the repulsion. Thus one

Table 1. Bond angles (in degrees) for some typical AX_3E and AX_2E_2 species. R represents the methyl group. All data from reference 2.

AX_3E Species							
NH ₃	107.8	PH ₃	93.8	AsH ₃	91.8	SbH ₃	91.3
NF ₃	102.1	PF ₃	97.8	AsF ₃	96.2	SbF ₃	88.0
NCl ₃	—	PCl ₃	100.3	AsCl ₃	98.5	SbCl ₃	99.5
NCl ₃	—	PBr ₃	101.5	AsBr ₃	99.6	SbBr ₃	97.0
NI ₃	—	PI ₃	102.0	AsI ₃	100.2	SbI ₃	99.1
AX_2E_2 Species							
H ₂ O	104.5	H ₂ S	92.2	H ₂ Se	91.0	H ₂ Te	89.5
Cl ₂ O	111.0	SCl ₂	98.0	SeCl ₂	—	TeBr ₂	98.0
R ₂ O	111.5	R ₂ S	105.0	R ₂ Se	98.0	R ₂ Te	—
ROH	109	RSH	99.4	RSeH	—	RTeH	—

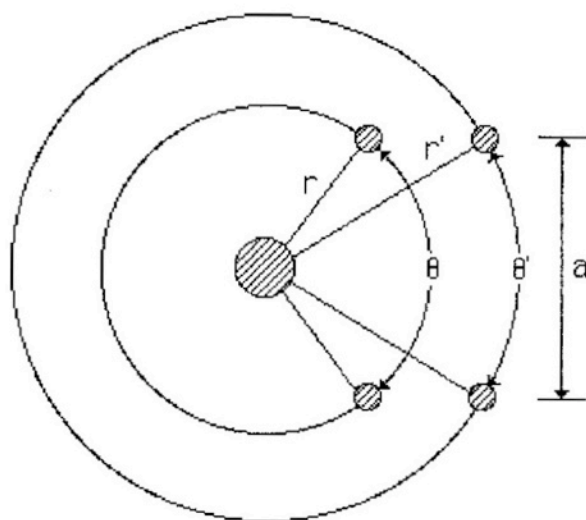
would predict greater contractions and smaller bond angles as A increases in size. Gillespie has also suggested that central atom size effects play an important role in these angle changes in yet another way. He equates an increase in the size of A with an incomplete valence shell on A and allows the lone pairs on A to expand into this extra space, pushing the bonding pairs closer together in the process.

The purpose of this note is to stress the importance of such central atom size effects in generating the anomalous angles in Table 1. Although changes in relative electronegativity doubtlessly play a role in determining the small angle variations observed when X is changed for a given A, it will be shown that the major angle changes observed when A is changed for a given X can be rationalized almost completely in terms of such central atom size effects. The argument used here is a variation of Gillespie's, but by maintaining a clear distinction between the angle of separation and the actual distance of separation, it shows, using simple trigonometry, that the bonding pairs actually move further apart as A is replaced by heavier and heavier group members, even though their angle of separation decreases.

As one replaces A with heavier group members, the effective size of the valence electron-pair repulsion sphere increases due to the increasing size of A. One can imagine two extreme ways in which the electron pairs can utilize this increased area to lower the electron-electron repulsion energy. They can use it to proportionally decrease the interorbital repulsions between all of the electrons pairs (model 1). This would result in the bond angles remaining relatively constant as A is changed. Many textbooks seem to believe that this result is necessarily implied by the VSEPR model and, in fact, this behavior is observed for most AX₄ species in which all of the electrons are in bonding pairs.

However, in the cases under consideration, where one or more of the electron pairs is a lone pair, a second extreme is possible. Here one freezes the distances of separation between the bonding pairs and allows the electrons in the lone pairs, which are not constrained to remain together near the core of a ligand, to spread apart (model 2). The bonding pair - bonding pair interorbital repulsions remain the same as the size of A increases but the total electron repulsion energy is still lowered due to the decrease in the intraorbital repulsion energy of the lone pairs.

Note, however, that even though the distance of separation, and consequently the repulsion, between the bonding pairs remains constant in this model, their relative



$$(\sin \theta'/2)/\sin \theta/2 = (a/2r')(a/2r) = r/r'$$

Figure 1. The relation between the change in the angle of separation (from θ to θ') and the change in the radius (from r to r') of the repulsion sphere for a constant distance of separation (a) between two valence electrons.

Table 2. Covalent radii (in ångströms) for Group V and VI elements. Data from reference 2.

N	0.70	O	0.66
P	1.10	S	1.04
As	1.21	Se	1.17
Sb	1.41	Te	1.37

angle of separation will decrease as a natural result of the increased size of the repulsion sphere. This is illustrated in figure 1, where, for a constant separation distance (a), simple trigonometry leads to following relation between the change in the angle of separation (from θ to θ') and the change in the radius of the repulsion sphere (from r to r'):

$$(\sin \theta'/2)/(\sin \theta/2) = r/r' \quad [1]$$

Using the radii in Table 2 and the bond angles in NH₃ and H₂O to set the value of "a" in each case, one can use equation 1 to calculate the expected bond angles for other Group V and Group VI hydrides on the basis of this second model. These are shown in Table 3, where they are compared with the angles expected according to the first model and with the experimentally observed angles. As can be seen, the angles calculated according to model 2 are all smaller than the experimentally observed angles, whereas those based on model 1 are all larger. What this implies is that these molecules adopt neither of these extremes, but take a compromise position instead in which the increased area is partly used to decrease the bonding pair - bonding pair interorbital repulsions by increasing their distance of separation over that observed for the lightest member of the group and partly to decrease the intraorbital electron - electron repulsions within the lone pairs. A similar result can be obtained for the other members of Table 1.

The enormous change in angles on going from period 2 to period 3 in each case is a direct reflection of the enormous change in the size of A. Between period 2 and period 3 this change is more than twice ($\sim 0.4A$) that observed between the other periods ($\sim 0.1 - 0.2A$). Thus one sees a correspondingly large decrease in the bond angles between period 2 and period 3, and a relatively smaller rate of decrease between the other periods.

In summary, the anomalous bond angles in Table 1 can be qualitatively rationalized in a manner consistent with the postulates of the VSEPR model, which, if necessary, could account for even smaller angles, and are due primar-

Table 3. Bond angles (in degrees) calculated using model 1 and model 2 as compared with the experimentally observed angles.

Species	Model 1	Model 2	Experiment
NH ₃	107.8	107.8	107.8
PH ₃	107.8	61.9	93.8
AsH ₃	107.8	55.7	91.8
SbH ₃	107.8	47.3	91.3
H ₂ O	104.5	104.5	104.5
H ₂ S	104.5	60.2	92.2
H ₂ Se	104.5	53.0	91.0
H ₂ Te	104.5	44.8	89.5

ily to changes in the size of A and, consequently, in the size of the resulting repulsion sphere. Whether or not this is the

“true” reason for these effects is, of course, another question and is bound up in the larger, and still unresolved, question of why the VSEPR model works as well as it does.

Reference and Notes

1. R. S. Drago, *J. Chem. Educ.*, **1973**, *50*, 244.
2. R. J. Gillespie, *Molecular Geometry*, Van Nostrand Reinhold: New York, NY, 1972, pp 56-58, 138-139, 151-153.
3. J. W. Linnett, *Wave Mechanics and Valency*, Methuen: London, 1969, pp 160-161.
4. Covalent radii are used because, on the basis of the tangent sphere model used in reference 2, the distance from the center of A to the center of a valence electron domain is given by the sum of the core radius and the electron-pair domain radius and the sum of latter two is equal to the central atom's covalent radius.

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