

# Correspondence

## Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and $\pi$ Bonds in Trigonal-Bipyramidal Molecules

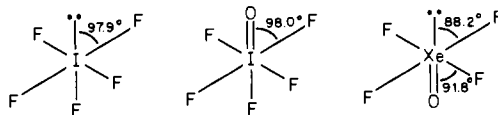
Sir:

The Gillespie-Nyholm valence-shell electron-pair-repulsion (VSEPR) theory<sup>1,2</sup> is very useful for explaining the basic structural features of many classes of inorganic compounds. The theory assumes that the geometry around a given central atom is determined by the number of electron pairs in its valence shell which are arranged as "points-on-a-sphere" in a manner to minimize the mutual repulsion energy. The finer details of the structure are predicted by assuming lone or nonbonding electron pairs to be more repulsive than single bonds, with double bonds being almost as repulsive as the lone pairs. Since the valence electron pairs are treated as points, their repulsive effect is assumed to be directionally independent. This approximation holds well for highly symmetric molecules such as octahedrons or tetrahedrons and for valence electron pairs which are cylindrically symmetric with respect to their axes. However, if a molecule possesses a structure of lower symmetry such as a trigonal bipyramid and if the valence electron pair is not cylindrically symmetric such as the  $\pi$  bonds of double bonds, directional repulsion effects can be expected which should depend on the nature of the orbital and its electron density distribution.

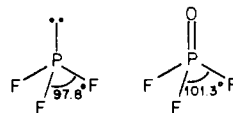
Contrary to the ligands in a tetrahedron or octahedron, those in a trigonal-bipyramidal molecule, when arranged as being equidistant from each other, are no longer on the surface of a sphere and become nonequivalent. The two axial ligands have a greater (ideally by a factor of  $2^{1/2}$ ) central atom-ligand bond length than the three equatorial ligands. Consequently, an equatorial ligand possesses two nonequivalent pairs of neighbors, one axial one of greater bond length and ideally at  $90^\circ$  angles and one equatorial one of shorter bond length and ideally at  $120^\circ$  angles.

In this correspondence, two cases are presented which are strong evidence for the existence of directional repulsion effects in trigonal-bipyramidal molecules. These two cases are (i) a comparison of the structures of  $SF_4$ <sup>3,4</sup> and  $X=SF_4$  (where X is O or  $CH_2$ )<sup>5-10</sup> and (ii) the structure of  $ClF_3O$ .<sup>11</sup> In the first case, the relative repulsion of the axial and of the equatorial fluorine ligands by either the  $\pi$  bonds of a double bond or a free valence electron pair is compared, whereas in the second case, the combined effect of a lone pair and of a doubly bonded oxygen is described.

For a meaningful comparison, we must first establish the relative repulsive strength of a lone valence electron pair and of a doubly bonded oxygen in the absence of directional effects. Inspection of the known structures of  $IF_5$ <sup>12</sup> and  $IF_5O$ <sup>13</sup> and of  $XeOF_4$ <sup>14</sup>

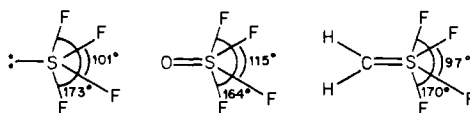


shows that in these pseudooctahedral molecules the repulsive strengths of a lone valence electron pair and of a doubly bonded oxygen are very similar and that, as demonstrated for  $XeOF_4$ , the oxygen can be even slightly more repulsive than a free valence electron pair. In the pseudotetrahedral molecules  $PF_3$  and  $PF_3O$ ,<sup>2</sup> the free valence electron pair appears to be somewhat more repulsive than oxygen:



The above examples show that, for practical purposes, the nondirectional repulsive strengths of a free valence electron pair and of a doubly bonded oxygen are comparable. For a more precise comparison, effects such as changes in the oxidation state of the central atom or in the hybridization of the orbitals should be eliminated. This is best achieved by selecting a compound such as  $XeOF_4$  containing both a free valence electron pair and doubly bonded oxygen at the same time. In this manner, their relative repulsive strengths can be compared under identical conditions.

Returning to the less symmetric case of trigonal-bipyramidal molecules, let us consider the structures of  $SF_4$ ,  $O=SF_4$ , and  $H_2C=SF_4$ :



As recently pointed out by Oberhammer and Boggs,<sup>6</sup> the FSF bond angles are surprisingly different in these molecules but could be well duplicated by ab initio MO calculations. These calculations showed that the observed differences in the structures of  $O=SF_4$  and  $H_2C=SF_4$  can be satisfactorily explained by the different population of the  $X=S$   $\pi$ -bond orbitals in the equatorial and the axial plane ( $OSF_4$ ,  $\pi_{eq} = 0.17$  au,  $\pi_{ax} = 0.12$  au;  $H_2C=SF_4$ ,  $\pi_{eq} = 0.23$  au,  $\pi_{ax} = 0.02$  au).

The comparatively small  $F_{eq}SF_{eq}$  bond angle of  $SF_4$  can be rationalized in the following manner. A lone electron pair can be delocalized rather easily, as shown, for example, by the structure of  $BrF_6^-$ <sup>15</sup> as opposed to that of  $IF_6^-$ .<sup>16</sup> Although

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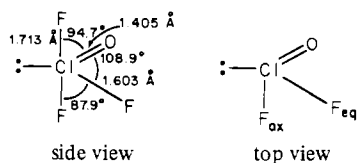
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in both ions the central atom possesses a lone valence electron pair, the size of bromine permits only a maximum coordination number of 6 (toward fluorine) and the lone pair in  $\text{BrF}_6^-$  is sterically inactive and centrosymmetric. In  $\text{IF}_6^-$ , the larger central atom can readily accept seven or eight ligands, as demonstrated by the existence of  $\text{IF}_7$  and  $\text{IF}_8^-$ ,<sup>17,18</sup> and, therefore, the lone valence electron pair becomes sterically active and acts as a ligand. On the assumption of a similar ease of delocalization of the free valence electron pair in trigonal-bipyramidal arrangements, a free valence electron pair can then be expected to possess little directional repulsive selectivity and to compress preferentially the most compressible bond angle. In an idealized  $\text{SF}_4$  structure, the  $120^\circ$  equatorial FSF angle obviously should be compressed more easily than the  $90^\circ$  angles formed between the axial ligands and the fluorine containing equatorial plane.

On the other hand, the  $\pi$  orbitals of an  $\text{S}=\text{X}$  double bond are more localized and concentrated between the sulfur and the X atom in the equatorial and the axial planes of the molecule. Depending on the relative population of these orbitals, preferential repulsion of either the axial or the equatorial fluorines is possible. Thus, the "shape" of the  $\text{S}=\text{X}$   $\pi$  bond is responsible for the preferred direction of the repulsion effect and must be considered when the structure of an unknown molecule is predicted.

In view of these directional repulsion effects, the change in a single bond angle is not a good measure for the overall repulsive strength of a ligand or a free valence electron pair. Since the repulsion of all the other ligands must be considered, the average quadruple angle<sup>10</sup> should be used for such a comparison. In  $\text{SF}_4$ ,  $\text{OSF}_4$ , and  $\text{H}_2\text{CSF}_4$ , these average quadruple angles are  $111.5^\circ$ ,  $110.3^\circ$ , and  $113.3^\circ$ , respectively, indicating that the overall repulsive strengths of a free valence electron pair and of a  $\text{S}=\text{X}$   $\pi$  bond are, within experimental error, quite similar but that they strongly differ in their directions.

Since the molecular structure of  $\text{SF}_4\text{O}$  has not yet been established beyond doubt (four models have been proposed on the basis of an electron diffraction study)<sup>5</sup> and since one might argue that secondary effects such as the difference in the oxidation state of the sulfur central atom might be of importance, the structural study of a trigonal-bipyramidal molecule containing both a lone valence electron pair and a doubly bonded oxygen atom was important. Such a molecule is  $\text{ClF}_3\text{O}$ , the structure of which was recently established:<sup>11</sup>



The fact that the axial fluorine atoms are repelled more strongly by the oxygen ligand than by the lone pair confirms the existence of directional repulsion effects in trigonal-bipyramidal molecules and supports the conclusions reached from the comparison of the  $\text{SF}_4$ ,  $\text{OSF}_4$ ,  $\text{H}_2\text{CSF}_4$  series.

In summary, in trigonal-bipyramidal molecules, cylindrically nonsymmetric valence electron pairs can result in directional repulsion effects. These effects can be rather pronounced and cannot be accounted for by simple VSEPR theory.<sup>1,2</sup>

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## Bonding in Metal Borohydride Complexes

Sir:

The borohydride ligand has been shown in various structural studies to bond to a wide variety of metal ions via bidentate,<sup>1-23</sup> tridentate,<sup>10,16,21-31</sup> and (in one instance) monodentate hy-

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