

Electronic and Substituent Effects on the Barrier to Edge Inversion

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Energy barriers for edge inversion of a tetrahedron are calculated for PF₃, SF₃⁺, SF₂O, SiF₄, PF₄⁺, and PF₃O and are shown to be energetically accessible.

We have recently presented a new mechanism for the inversion of tri-co-ordinate pyramidal main group 5 compounds, 8-Pn-3 (Pn = P, As, Sb).¹ With appropriate electronegative substituents (*e.g.*, PF₃), inversion will occur through a planar T-shaped structure with the three ligands and the lone pair in the plane. This is in contrast to the inversion process for ammonia where inversion occurs through a planar trigonal structure with the lone pair perpendicular to the molecular plane. The ammonia inversion can be described as vertex inversion of a tetrahedron while that involving a T-shaped structure can be described as edge inversion of a tetrahedron. The theoretical proposal has been verified experimentally.² Herein, we first describe how charge variation affects the barrier to edge inversion by calculating the inversion barriers for SF₃⁺ and the model sulphoxide, SF₂O. Secondly, we propose a generalization of edge inversion to a four-co-ordinate tetrahedral (*T_d*) main group 4 compound, AX₄, which suggests that the *D_{4h}* structure may be energetically accessible as a transition state. We present *ab initio* calculations on SiF₄, PF₄⁺, and PF₃O, which substantiate this proposal for second row elements.

Geometry optimizations for all structures were done at the SCF level using gradient techniques³ with either the program HONDO⁴ on an IBM-3081 computer or the program GRADSCF† on a CRAY-1A computer. Force fields and MP-2 corrections⁵ were determined with the rapid analytical techniques⁶ incorporated in GRADSCF. Only the valence electrons were included in the MP-2 calculations. The geometry optimizations on PF₃, SiF₄, SF₃⁺, and SF₂O were done with a basis set⁷ of the form [(11s7p1d)(9s5p1d)]/[(6s4p1d)(3s2p1d)]. The geometry optimizations on PF₄⁺ and PF₃O and the final energy and force field calculations on all molecules were done with a basis set of the form [(13s9p1d)(9s5p1d)]/[(6s4p1d)(4s2p1d)].^{8,9} The structures of the molecules with three ligands were optimized in the

pyramidal ground state, planar trigonal, and planar T-shaped forms (for PF₃ these structures have *C_{3v}*, *D_{3h}*, and *C_{2v}* symmetry, respectively). The molecules with four ligands were optimized in the tetrahedral and square planar forms (for SiF₄, these structures have *T_d* and *D_{4h}* symmetry).

The geometric parameters for the different structures are given in Table 1. The lowest energy structures for PF₃, SF₂O, PF₃O, and SiF₄ are in excellent agreement with the available experimental structures.^{10,11} For PF₃ and SF₃⁺, the bond lengths in the planar trigonal structures (the lone pair is in an in-plane *a₁'* orbital) are longer than those in the lowest energy pyramidal structure. For SF₂O, a pseudo *D_{3h}* structure can only be optimized with the lone pair in an out-of-plane p-type orbital. There is essentially no change in the S-F bond lengths but there is a dramatic increase in the S-O bond length of 0.24 Å as compared to the pyramidal structure. The angles for planar trigonal SF₂O show a similar variation with an increase of only 10° in θ(FSF) and an increase of 22° in θ(FSO). The T-shaped structures are all quite similar. The axial bond lengths increase significantly while the equatorial bond lengths decrease slightly. For PF₃ and SF₃⁺, the AxAEq bond angles are less than 90° so that all of the ligands are on the opposite side of the plane from the lone pair (**1a**). For SF₂O, the AxAEq bond angle θ(FSO) is greater than 90° so that the fluorines and the lone pair are on the same side of the plane and the oxygen is on the opposite side (**1b**).

The bond distances for the square planar structures all increase as compared to the *T_d* structures. For PF₃O, the two equivalent P-F bonds are slightly longer than the P-F bond to the fluorine opposite the oxygen. The F-P-O bond angle is greater than 90° so that the three fluorines are on the same side of the plane [*i.e.* the lone pair in (**1b**) is replaced by an F] which is similar to what is observed in T-shaped SF₂O.

The force fields for all of the structures have been calculated. The pyramidal structures for PF₃, SF₃⁺, and SF₂O and the tetrahedral structures for SiF₄, PF₄⁺, and PF₃O are all minima on the potential energy surface. The T-shaped structures for PF₃, SF₃⁺, and SF₂O are transition states characterized by one imaginary frequency (see Table 2). The

† GRADSCF is an *ab initio* gradient program system designed and written by A. Komornicki at Polyatomics Research and supported on grants through NASA-Ames Research Center.

Table 1. Geometry parameters^a for tri- and tetra-co-ordinate molecules.

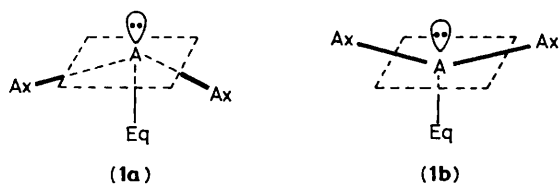
Tri-co-ordinate molecule	$r(\text{pyr})$	$\theta(\text{pyr})$	$r(\text{pl-trig})$	$\theta(\text{pl-trig})$	$r(\text{pl-T})$	$\theta(\text{pl-T})$
PF ₃	1.563(1.561) ^b	97.1(97.1) ^b	1.664	120.0	1.553(eq) 1.633(ax)	172.8 ^d 86.4 ^e
SF ₃ ⁺	1.493	99.2	1.568	120.0	1.489(eq) 1.543(ax)	175.5 ^d 87.8 ^e
SF ₂ O	(SO)1.410(1.416) ^b (SF)1.568(1.563) ^b	(FSF) 92.6(92.8) ^b (FSO)106.5(106.8) ^b	1.651 1.566	102.3 128.9	1.404 1.673	170.7 ^d 94.6 ^e
Tetra-co-ordinate molecule	$r(T_d)$	$\theta(T_d)$	$r(D_{4h})$	$\theta(D_{4h})$		
SiF ₄	1.556(1.552) ^c	109.5(109.5) ^c	1.587	90.0		
PF ₄ ⁺	1.473	109.5	1.508	90.0		
PF ₃ O	(PO)1.424(1.433) ^b (PF) 1.521(1.522) ^b	(FPF) 100.7(101.1) ^b (FPO)117.2(116.9) ^b	1.448 1.560 ^f 1.579 ^g	83.6 96.4		

^a Bond distances in Å. Bond angles in degrees. Values in parentheses are experimental values. ^b Reference 11. ^c Reference 12. ^d $\theta(\text{AxAAx})$; Ax = axial, Eq = equatorial. ^e $\theta(\text{AxAEq})$. ^f Unique P-F bond opposite to O. ^g Equivalent P-F bonds.

Table 2. Inversion barriers and vibrational frequencies^a for edge and vertex inversion.

Molecule	Edge (SCF)	Edge (MP-2)	Edge (iv) ^b	Vertex (SCF)	Vertex (MP-2)	Vertex (iv) ^b
PF ₃	68.4	53.8	365(374e) ^c	124.7	85.3	827(a),308(e)
SF ₃ ⁺	91.4	64.6	549(425e)	157.2	90.6	1589(a),376(e)
SF ₂ O	58.6	39.7	274(422,433)	141.2	143.0	1437
SiF ₄	67.7	62.6	230(268e)			
PF ₄ ⁺	92.7	81.0	295(327e)			
PF ₃ O	99.2	84.3	293(508,351e)			

^a Inversion barriers in kcal mol⁻¹ (cal = 4.184 J). Frequencies in cm⁻¹. ^b iv is the imaginary frequency at the transition state. ^c Calculated frequencies in parentheses for the optimum structures leading to edge inversion.



D_{3h} structures for PF₃ and SF₃⁺ are characterized by three imaginary frequencies and are simply distorted T-shaped structures. The trigonal planar structure for SF₂O also has only one imaginary frequency which is much larger than that found for the T-shaped structure. For SF₂O, we thus also require an energetic analysis to differentiate between the vertex and edge inversion pathways. The square planar structures for SiF₄, PF₄⁺, and PF₃O are also characterized by one imaginary frequency and are true transition states for the edge inversion motion.

In PF₃ and SF₃⁺, the motion for edge inversion is derived from the degenerate bend rather than the symmetric bend associated with vertex inversion. For PF₃, the e bending mode in the pyramidal form is similar to the imaginary frequency characterizing the edge inversion motion. In SF₃⁺, the imaginary frequency is higher than the e bending mode, while for SOF₂, this reverses and the imaginary frequency is significantly lower than the appropriate bends in the pyramidal form. For the square planar structures, the imaginary frequencies are all lower than the corresponding degenerate e bending modes in the tetrahedral form.

The inversion barriers are given in Table 2. The energetics clearly demonstrate that SF₂O will invert by edge inversion

through the T-shaped structure; the edge inversion process is ~100 kcal mol⁻¹ lower in energy than the vertex inversion process. Consistent with the vibrational analysis, PF₃ and SF₃⁺ will exhibit edge inversion instead of vertex inversion. For the tri-co-ordinate compounds, the correlation corrections to the barrier heights are significant in contrast to what is observed in the hydrides.¹² Substitution of S⁺ for P in PF₃ to form SF₃⁺ raises the edge inversion barrier by 11 kcal mol⁻¹. Subsequent substitution of O⁻ for F in SF₃⁺ to form SF₂O leads to a decrease in the edge inversion barrier height of 25 kcal mol⁻¹ relative to SF₃⁺ (14 kcal mol⁻¹ below that for PF₃). We note that the edge inversion barriers for PF₃ and SF₂O are significantly below the P-F and S-F bond dissociation energies.¹³ Furthermore, the edge inversion barrier for SF₂O is in the normal range for sulphoxide inversion barriers for sulphoxides *without* electronegative substituents.¹⁴

The substitution trends in the edge inversion barriers for the tetrahedral species are somewhat different. Substitution of P⁺ for Si in SiF₄ to form PF₄⁺ leads to an increase of 18 kcal mol⁻¹ in the edge inversion barrier. In contrast to the tri-co-ordinate molecules, substitution of O⁻ for F in PF₄⁺ to form PF₃O leads to a small increase of 3 kcal mol⁻¹ for the edge inversion barrier. Owing to electronegativity effects and the energy of the unoccupied out-of-plane orbital, the modes of stabilization of the edge inversion transition state for the tri- and tetra-co-ordinate species are different. Again the edge inversion barriers are below the appropriate bond dissociation energies¹³ so that inversion can occur without dissociation. For SiF₄, there has been a previous calculation¹⁵ on the energy difference between the square planar and tetrahedral forms. At the STO-3G level, the value for ΔE is 70 kcal mol⁻¹.

Improvement of the basis set to 3-21G(*) leads to an increase in ΔE to 75 kcal mol⁻¹ in contrast to the actual decrease in ΔE calculated with our better basis set.

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