

Edge Inversion in Tricoordinated Main Group IV Anions

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ABSTRACT

The inversion barriers for SiF_3^- , GeF_3^- , SnF_3^- , SnCl_3^- , and $\text{SnCl}_2\text{NH}_2^-$ have been calculated by ab initio molecular orbital theory with large basis sets and have included the effects of electron correlation. The anions are predicted to invert by the edge inversion process. The edge inversion barriers in kcal/mol are 40.3, 34.3, 27.8, 27.8, and 14.2 in the order given above. Geometric effects and the charge distributions are discussed.

INTRODUCTION

It has recently been shown experimentally [1] that appropriately substituted tricoordinate pnictogens (main group V elements) can invert by the edge inversion mechanism as opposed to the traditional vertex inversion mechanism exemplified by NH_3 . This experimental verification followed the prediction of the edge inversion process by ab initio molecular orbital theory [2]. These calculations were prompted by the discovery of novel structural and electronic effects in ADPO (5-aza-2,8-dioxo-1-phosphabicyclo[3.3.0]octa-2,4,6-triene) compounds [3]. Further calculations on compounds with tetra-coordinate main group IV elements suggested that

this mechanism would also occur for appropriate sets of substituents [4, 5]; this prediction was also subsequently verified experimentally [6]. There is significant interest [7] in novel tin species, and we have extended our theoretical studies of inversion processes to the tricoordinate Sn(II) anions (SnF_3^- and SnCl_3^-). In particular, recent experimental results in one of our laboratories [8] has prompted calculations on $\text{SnCl}_2\text{NH}_2^-$. We have also studied the periodic trends in the main group IV trifluoroanions by performing calculations on SiF_3^- and GeF_3^- .

COMPUTATIONAL METHODS

The calculations were done with the program GRADSCF [9] on CRAY-1A and CRAY X-MP/28 computers. Geometries were gradient optimized [10] in C_{3v} , D_{3h} and C_{2v} symmetries for the trifluorides and trichlorides and in C_1 and C_{2v} symmetries for $\text{SnCl}_2\text{NH}_2^-$. Force fields were calculated analytically [11] at the self-consistent field (SCF) level. Correlation corrections were made at the second order Møller-Plesset perturbation (MP-2) level [12] for the valence electrons. The calculations were done with at least polarized double ζ basis sets. For F and N, the basis set has the form (9s5p1d)/[3s2p1d] and the H basis set has the form (4s1p)/[2s1p] with coefficients and exponents from Dunning and Hay [13]. For Si, the basis set has the form (11s7p1d)/[6s4p1d] [13]. The basis set for Cl has the form (12s9p1d)/[5s3p1d] and is from McLean and Chandler [14]. We employed the Ge basis set that we developed previously [5, 15] and it has the form

Dedicated to Professor Dr. Leopold Horner on the occasion of his eightieth birthday.

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TABLE 1 Molecular Geometries^a for the Ground State (gs), Vertex (V), and Edge (E) Inversion Transition States

Anion	$r(\text{gs})$	$\theta(\text{gs})$	$r(\text{V})^b$	$r(\text{E})_{\text{ax}}$	$r(\text{E})_{\text{eq}}$	$\theta(\text{E})$
SiF_3^-	1.661	96.3	1.605 ^c	1.732	1.653	171.3
GeF_3^-	1.792	94.6	1.749	1.914	1.763	168.0
SnF_3^-	1.978	93.6	1.925	2.072	1.944	163.4
SnCl_3^-	2.495	96.1	2.397	2.691	2.434	176.0
$\text{SnCl}_2\text{NH}_2^-^d$	2.518(Sn—Cl ¹) 2.560(Sn—Cl ²) 2.073(Sn—N)	95.7(Cl ¹ SnCl ²) 91.6(Cl ¹ SnN) 97.2(Cl ² SnN)	2.409	2.740		164.6
			2.059		2.001	

^a Bond distances in Å. Bond angles in degrees.^b pl = vertex inversion planar structure.^c $r(\text{Si—F}) = 1.722$ Å for the "s" orbital structure.^d See Figure 1 for atom labels. $r(\text{N—H}^1) = 1.002$; $r(\text{N—H}^2) = 1.003$; $\theta(\text{SnNH}^1) = 116.2$; $\theta(\text{SnNH}^2) = 116.1$; $\theta(\text{H}^1\text{NH}^2) = 108.4$.

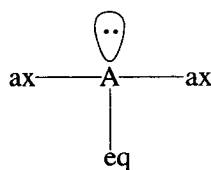
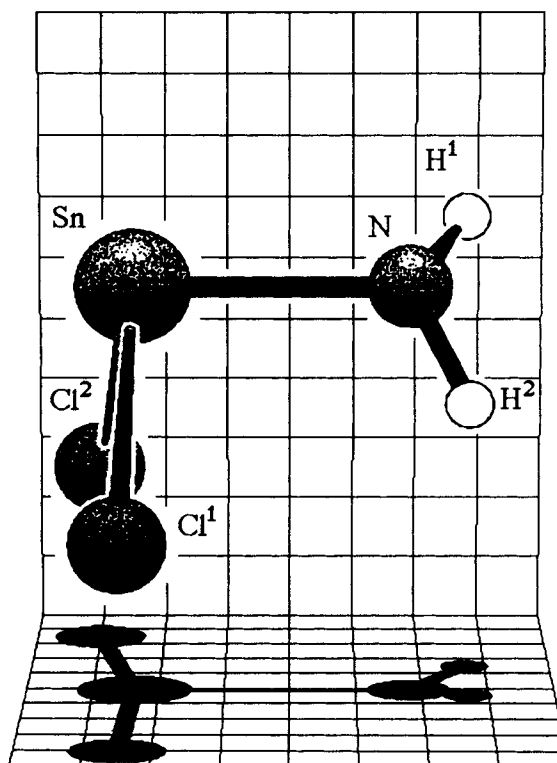
(14s11p6d)/(10s8p3d]. For Sn, we used our previously generated basis set [5, 16] augmented by diffuse p functions (exponent = 0.025) which has the form [16s12p8d)/(11s8p5d].

RESULTS AND DISCUSSION

The geometries are reported in Table 1. The bond angle $\theta(\text{F—A—F})$ decreases with increasing atomic number for A for the pyramidal (C_{3v}) structures just as found in the pnictogen trifluorides [2b]. In the Sn series, substitution of Cl for F leads to a slight increase in $\theta(\text{Hal—Sn—Hal})$. The structure of $\text{SnCl}_2\text{NH}_2^-$ has C_1 symmetry as shown in Figure 1. The Sn—Cl bond distances are both increased from the value for $r(\text{Sn—Cl})$ in SnCl_3^- . The value of $\theta(\text{Cl—Sn—Cl})$ is about the same in the two compounds.

The transition state for the edge inversion process under consideration has a T-shape of C_{2v} symmetry and is characterized by one negative direction of curvature leading to one imaginary frequency. The orbital configuration of the T-shaped structure is such that the lone pair on the central Group IVA atom is in the molecular plane, that is, it has substantial "s" orbital character. The transition state can be described as having two axial (ax) substituents and one equatorial (eq) substituent (Scheme I). The axial substituents for the AR_3^- compounds have A—R bond lengths longer than $r(\text{A—R})$ in the pyramidal forms and the equatorial A—R bond is shorter. For the fluorides the increase in the apical bond length is significantly larger than the decrease in the equatorial value. For SnCl_3^- the increase in

the apical bond length is 0.2 Å, and a comparable increase is found in $\text{SnCl}_2\text{NH}_2^-$ with the Cl's in the apical positions. The T-shaped structures have $\theta(\text{ax—A—ax})$ bond angles that are less than 180°; they are bent back toward the equatorial substituent. These bond angles range from 163° for SnF_3^- to 176° for SnCl_3^- .

FIGURE 1 KANVAS [17] drawing of the ground state structure of $\text{SnCl}_2\text{NH}_2^-$.**SCHEME I**

The transition states for the vertex inversion process should have D_{3h} symmetry for AR_3^- and C_{2v} symmetry for $SnCl_2NH_2^-$, following the model for inversion in NH_3 where the lone pair on the central atom is in a "p"-type orbital of a_2' symmetry that is orthogonal to the molecular plane. It was previously shown [2, 18] that the lowest energy structure for PF_3 in D_{3h} symmetry has the lone pair on phosphorus in an orbital of a_1' symmetry with pronounced "s" character as opposed to a "p" orbital. The structure with the "s" orbital lone pair is not a minimum or a transition state as it has three imaginary frequencies and represents a highly distorted T-shaped structure [3]. The structure with a "p" lone pair is much higher in energy. This behavior is found in SiF_3^- where the structure with the lone pair in a "p" orbital is, indeed, a transition state although it is much higher in energy than the structure with an "s" orbital lone pair. The major difference in the D_{3h} geometries for these two orbital configurations is that the bond lengths in the structure with an "s" orbital lone pair are longer than those in the pyramidal form (due to mixing of the axial and equatorial bond length parameters), whereas the structure with a "p" orbital lone pair has shorter bond lengths. This latter result is consistent with previous studies on vertex inversion barriers in compounds such as PH_3 [19]. For the remainder of our discussion, we focus on the structures with a "p" orbital lone pair. The bond lengths in the D_{3h} structures are 0.04–0.13 Å shorter than the pyramidal bond lengths with the largest effect found for the Sn–Cl bonds. For SiF_3^- and GeF_3^- , the D_{3h} structures are transition states characterized by an imaginary frequency of large magnitude. For SnF_3^- and $SnCl_3^-$, the D_{3h} structures are not transition states but are actually minima on the potential energy surface and thus correspond to $^1A_1'$ excited states. The D_{3h} -type structure for $SnCl_2NH_2^-$ has two imaginary frequencies that correspond to out-of-plane motion of the NH_2 group. The imaginary frequency of higher magnitude (817i cm^{-1}) corresponds to a symmetric motion, inversion of the NH_2 fragment, and the lower magnitude value (633i cm^{-1}) corresponds to an asymmetric motion, rotation about the Sn–N bond. This structure is like that of the other tin compounds and does not correspond to a transition state for vertex inversion at tin.

The inversion barriers calculated in this work are given in Table 2. The results clearly show that the edge inversion process is lower in energy than the vertex inversion process for all of the anions considered in this study. From our previous work, we would expect the inversion barriers in the series AF_3^- to decrease with increasing atomic number and indeed this is what is calculated. The correlation correction to the barriers of the AF_3^- species is not inconsequential, ranging from 9.0 kcal/mol for A = Si to 6.6 kcal/mol for A = Sn. The edge inver-

TABLE 2 Edge (E) and Vertex (V) Inversion Barriers in kcal/mol

Structure	SCF	MP-2	$i\nu(cm^{-1})^a$
$SiF_3^- (E)^b$	49.3	40.3	293
$SiF_3^- (V)^{b,g}$	159.3	147.3	1395
$GeF_3^- (E)^c$	42.1	34.3	189
$GeF_3^- (V)^c$	174.3	161.5	2113
$SnF_3^- (E)^d$	34.3	27.8	153
$SnF_3^- (V)^d$	153.1	140.4	0
$SnCl_3^- (E)^e$	28.0	27.8	86
$SnCl_3^- (V)^e$	125.2	113.0	0
$SnCl_2NH_2^- (E)^f$	13.3	14.2	46
$SnCl_2NH_2^- (V)^f$	174.3	161.5	817,633

^a $i\nu$ is imaginary frequency.

^b SiF_3^- : E(SCF) = -587.533933; E(MP-2) = -588.135887.

^c GeF_3^- : E(SCF) = -2373.906482; E(MP-2) = -2373.507490.

^d SnF_3^- : E(SCF) = -6320.448383; E(MP-2) = -6320.967657.

^e $SnCl_3^-$: E(SCF) = -7400.509812; E(MP-2) = -7400.974125.

^f $SnCl_2NH_2^-$: E(SCF) = -6996.601691; E(MP-2) = -6997.114532.

^g Inversion barrier of SiF_3^- with the "s" orbital lone pair is 70.3 kcal/mol at the MP-2 level. The imaginary frequencies are 687i and 287i(e) cm^{-1} .

sion barrier for $SnCl_3^-$ is the same as that for SnF_3^- . It is important to note that there is essentially no correlation correction to the inversion barrier for $SnCl_3^-$. The edge inversion barrier for $SnCl_2NH_2^-$ is significantly lower than that for $SnCl_3^-$ in agreement with our simple models that suggest that pi electron pair donors are stabilizing in the equatorial position [20]. The NH_2 group should be better able to donate an electron pair as compared to the Cl.

The Mulliken charge distributions are given in Table 3 for the pyramidal and T-shaped structures. The structures become more ionic as the atomic number of the central atom increases for the pyramidal fluorides. The fluorines are quite negative with charges ranging from -0.61e (e = elementary charge of a proton) for A = Si to -0.76e for A = Sn. There are small shifts of charge going from the pyramidal to the T-shaped structures for the fluorides with the central atom becoming more positive. The axial fluorines gain negative charge and the equatorial fluorine loses negative charge as compared to the charges in the pyramidal structure. However, these changes are at most 0.04e. The behavior of the tin chlorides is quite different. The pyramidal structures of the chlorides have less charge separation than the fluorides. There is a much larger charge transfer in the T-shaped structure with the tin becoming more positive by 0.14–0.15e. The axial chlorines become more negative by about 0.1e, and the equatorial substituents lose between 0.05–0.07e.

TABLE 3 Charge Distributions (e)^a for the Ground State (gs) and Edge (E) Inversion Transition State

Atom	SiF ₃ ⁻	GeF ₃ ⁻	SnF ₃ ⁻	SnCl ₃ ⁻	SnCl ₂ NH ₂ ⁻
A(gs)	0.82	0.98	1.28	0.60	0.69
R(gs)	-0.61	-0.66	-0.76	-0.53	-0.56, -0.58, -0.55 ^b
A(E)	0.83	1.02	1.32	0.74	0.84
R _{ax} (E)	-0.62	-0.70	-0.79	-0.63	-0.67
R _{eq} (E)	-0.58	-0.62	-0.75	-0.48	-0.48 ^c

^a e is the elementary charge of a proton.

^b In the order Cl¹, Cl², NH₂ group charge (charge on N is -1.04 e).

^c NH₂ group charge (charge on N is -1.06 e).

SUMMARY

In conclusion, we predict that the edge inversion process should be observable in tricoordinated main group IV anions. The results clearly show that the edge inversion process should predominate over the vertex inversion process at centers bearing electronegative substituents. As expected, the edge inversion barriers decrease with increasing atomic number as we previously predicted for the pnictogen trifluorides [2b] and the Group IVA tetrafluorides [5]. However, increasing the atomic number of the substituent does not lead to a decrease in the barrier for substitution at tin. Although this is similar to previous predictions for PF₃ and PCl₃ and for AsF₃ and AsCl₃ [21], our prediction of comparable barriers is found only when correlation corrections are included, whereas Clotet et al. find such a result without correlation although their basis sets are much smaller than ours. Substitution of an NH₂ group in the equatorial position for a Cl leads to a dramatic decrease in the barrier suggesting that the edge inversion process should be quite facile in appropriately substituted Sn derivatives.

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