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Structures and Stabilities of Three-Membered Rings Containing a Hypervalent Atom

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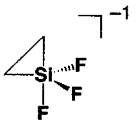
We investigated the structures and the stabilities of the three-membered rings $\mathrm{F}_n\overline{\mathrm{X}-\mathrm{CH}_2-\mathrm{Y}}$ (X = Si, P, S; Y = CH_2, NH, O; $n = 2$ or 3) containing a hypervalent atom (X) and disclosed their origins by developing and applying an electron-pair bond model for hypervalent molecules. For the rings containing a pentacoordinated Si or P atom, the (ap, eq) isomers with the ring bonds in the apical and equatorial positions are local minima, while the (eq, eq) isomers with both ring bonds in the equatorial positions are the transition states of pseudorotation reactions due to the high ring strains. In contrast, the (ap, eq) and (eq, eq) isomers for the rings containing a tetracoordinated P or S atom are both local minima. The tetracoordinated species are less strained than the pentacoordinated ones because of the effect of the lone pair on X giving rise to less antibonding properties of the electron delocalization between the geminal ring bonds on X. Moreover, the more strained (eq, eq) isomers are surprisingly more stable than the (ap, eq) isomers in most of the tetracoordinated species. The relative stabilities are controlled by the repulsion between the lone pair on X and the apical bond. The relative stabilities of the (ap, eq) isomers with Y (= NH, O) in the apical and equatorial positions are predicted and discussed.

Introduction

Recently, small ring compounds containing a hypervalent atom have attracted chemists' interest.[1−11] Some three-membered ring compounds containing a hypervalent silicon, phosphorus, or sulfur atom have been suggested as intermediates for such organic reactions as the Brook rearrangements of α-silylcarbinols,[1] singlet oxygen oxidation of trivalent phosphorus,[2] decomposition of phosphite ozonide and bisphosphinic peroxides,[3] photooxidation of diethyl sulfide,[4] and addition of a 1,3,2-dioxaphospholane to benzaldehyde.[5] Among the characterized three-membered ring molecules are included azaphosphorizine,[6] phosphorizine,[7] phosphirenes,[8] and thiaphosphirane[9] with pentacoordinated phosphorus, dioxaphosphirane[10] with hexacoordinated phosphorus, and thiasiliirane[11] with pentacoordinated silicon. In this paper, we investigated the structures and the stabilities of the three-membered rings **1**−**12** containing a hypervalent silicon, phosphorus, or sulfur atom.

The concept of the three-center four-electron bond was suggested by the application of the molecular orbital theory to hypervalent molecules to understand the violation of the octet rules.[12] However, the concept has not dramatically contributed to designing hypervalent molecules and their reactions. We previously proposed a bond model for molecules[13−16] and transition states[17] to analyze the electronic structures in terms of the interactions of chemical bonds. The chemical bonds investigated thus far include only electron pair (two-center two-electron) bonds. We here propose a new method for the analysis of the bond interactions and show that the electron-pair bond model is applicable and useful for understanding and designing hypervalent molecules.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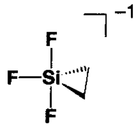
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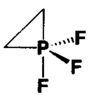
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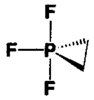
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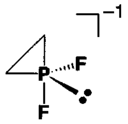
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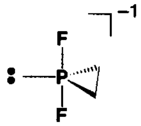
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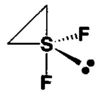
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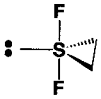
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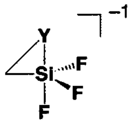
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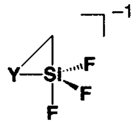
6a-ap, Y = O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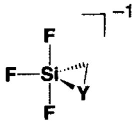
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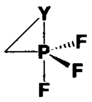
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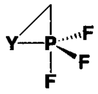
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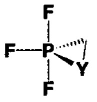
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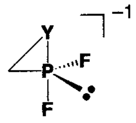
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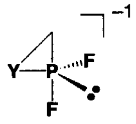
10a-ap, Y = O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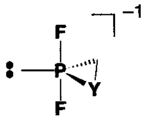
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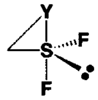
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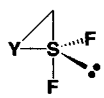
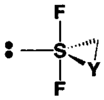
12a-ap, Y = O


11a-eq, Y = NH
12a-eq, Y = O


11b, Y = NH
12b, Y = O

Bond Orbitals and Bond Interactions

We propose a new definition of bond orbital for studying the bond interactions in molecules. Chemists have very often understood and predicted chemical phenomena on the basis of the concept of the chemical bond so far. A chemical bond is usually considered in organic chemistry to be formed between a pair of atoms by a pair of electrons. A bond orbital is here

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represented by a linear combination of atomic orbitals on the bonded atoms or a two-center bond orbital. Bonds interact with one another. The bonding orbitals lose some of the paired electrons, while the antibonding orbitals accept electrons. A desirable set of bonding orbitals should occupy paired electrons as much as possible. In contrast, the antibonding orbitals should occupy electrons as little as possible. We can obtain such bond orbitals by maximizing the populations of bonding (nonbonding) orbitals or by minimizing those of antibonding orbitals.

Molecular orbitals (ψ_{m}), obtained by the Hartree–Fock method, are expressed by a linear combination of bonding, antibonding, nonbonding, and vacant orbitals (ϕ_i^{b}, $\phi*_i^{\mathrm{b}}$, ϕ_j^{n}, and $\phi*_k^{\mathrm{v}}$, respectively):

$$\psi_{\mathrm{m}} = \sum_i c_{\mathrm{m}i}\phi_i^{\mathrm{b}} + \sum_i c_{\mathrm{m}i}^{*}\phi*_i^{\mathrm{b}} + \sum_j c_{\mathrm{m}j}\phi_j^{\mathrm{n}} + \sum_k c_{\mathrm{m}k}^{*}\phi*_k^{\mathrm{v}} \quad (1)$$

The bonding and antibonding orbitals, ϕ_i^{b} and $\phi*_i^{\mathrm{b}}$, of the ith bond are expressed by linear combinations of the atomic hybrid orbitals $\chi_{i\alpha}$ and $\chi_{i\beta}$ on the bonded atoms α and β:

$$\phi_i^{\mathrm{b}} = d_{i\alpha}\chi_{i\alpha} + d_{i\beta}\chi_{i\beta} \quad (2)$$

$$\phi*_i^{\mathrm{b}} = d_{i\alpha}^{*}\chi_{i\alpha} + d_{i\beta}^{*}\chi_{i\beta} \quad (3)$$

The coefficients $d_{i\alpha}$, $d_{i\beta}$, $d_{i\alpha}^{*}$, and $d_{i\beta}^{*}$ of the hybrid orbitals in the bonding and antibonding orbitals of each bond are obtained by the diagonalization of the 2 × 2 Fock matrix on the basis of the hybrid orbitals. Each of nonbonding and vacant atomic orbitals is given as a hybrid orbital. The sum (P) of the populations of the bonding and nonbonding orbitals and that (P*) of the antibonding and vacant orbitals are calculated as follows.

$$P = \sum_i \sum_m n_m (c_{mi})^2 + \sum_j \sum_m n_m (c_{mj})^2 \quad (4)$$

$$P* = \sum_i \sum_m n_m (c_{mi}^{*})^2 + \sum_k \sum_m n_m (c_{mk}^{*})^2 \quad (5)$$

where n_m is occupation number of electrons in the mth molecular orbital. A set of bond orbitals, i.e., hybrid orbitals, gives the P and P* values. The hybrid orbitals, first given by the Schmidt orthogonalization of atomic basis functions, are optimized[18] by the 2 × 2 orthogonal transformation to give the maximum P value or the minimum P* value.

To estimate the interaction of the bond orbitals, i and j, we employed the interbond population, IBP(i,j),[13−15] and the interbond energy, IBE(i,j),[16] defined previously:

$$\mathrm{IBP}(i,j) = 2P_{ij}S_{ij} \quad (6)$$

$$\mathrm{IBE}(i,j) = P_{ij}(H_{ij} + F_{ij}) \quad (7)$$

where P_{ij}, F_{ij}, H_{ij}, and S_{ij} are the elements of the density, Fock, core Hamiltonian, and overlap matrixes, respectively. Furthermore, to estimate the interaction of the bonds, A and B, we employed the interbond energy, IBE(A,B):

$$\mathrm{IBE(A,B)} = \sum_{i,j} \mathrm{IBE}(i,j)$$

where i and j are bond orbitals of the bonds A and B, respectively.

TABLE 1: Comparison between the Methods of the *P*-Maximization and the *P-Minimization for the H_2 Molecule**

items	*P*-maximization	*P**-minimization
P	2.044	2.000
$P*$	0.020	0.000
P_{σ}	2.044	2.000
$P_{\sigma*}$	0.000	0.000
$P_{\mathrm{s}*}$	0.010	0.000
IBP(σ,s*)	−0.036	0.000
IBP(s*,s′*)	0.008	0.000

We applied the methods of the P-maximization and the P*-minimization to the H_2 molecule to examine which of the methods is more suitable to represent the electronic structure of the molecule by the double occupation of each bonding (nonbonding) orbital. The H_2 molecule has only one σ bond. It is most preferable that the electronic structure should be represented only by the σ-bonding orbital occupied by paired electrons ($P = 2$ and $P* = 0$). We used the geometry and the wave function obtained by the RHF/6-31G calculations. The P and P* values, the population of the bond orbitals, and the interbond populations are listed in Table 1. The P*-minimization gave the ideal P ($P = 2$) and P* ($P* = 0$) values, while the P-maximization gave $P = 2.04$ and $P* = 0.02$. The interbond populations showed that the P-maximization leads to the negative population (IBP = −0.04) between the $\sigma_{\mathrm{H-H}}$ bonding orbital and vacant orbitals, $\mathrm{s}_{\mathrm{H}}^{*}$, on hydrogens to increase the population of the $\sigma_{\mathrm{H-H}}$ bonding orbitals. The P*-minimization method is preferable and employed in the present study.

Electron-Pair Bond Model for Hypervalent Molecules

We here propose an electron-pair bond model for the three-center four-electron bonds in the hypervalent molecules to analyze the electronic structures. The bonds between a hypervalent atom and the ligands are supposed to be two-center two-electron bonds.

We applied the electron-pair bond model to the hypervalent SiF_5 anion and SiF_4 as a reference molecule by the calculations with the RHF/6-31G* basis set. The contour maps of the apical and equatorial bond orbitals in SiF_5 anion were found to be similar to those of the bond orbitals in SiF_4 (Figure 1). The bonds in SiF_5^- and SiF_4 are polar σ bonds. The bond polarities, $|d_{\mathrm{Si}}/d_{\mathrm{F}}|$, indicated that the Si−F bonds in SiF_5^- are more polar than those (0.316) in SiF_4 (Table 2). The apical bond (0.254) is more polar than the equatorial one (0.266). This is in agreement with the fact that the apical fluorine atoms have more negative charges than the equatorial ones (−0.570e and −0.537e, respectively, in total atomic charges). The p- and d-characters of hybrid orbitals on silicon atoms increase in the following order: the bond ($\mathrm{sp}^{2.3}\mathrm{d}^{0.3}$) in SiF_4 is lower than the equatorial one ($\mathrm{sp}^{2.5}\mathrm{d}^{0.8}$) in SiF_5^- which is lower than the apical one ($\mathrm{sp}^{4.4}\mathrm{d}^{2.5}$) in SiF_5^-. The Si−F bond lengths increase in the same order: the bonds (1.557 Å) in SiF_4 are shorter than the equatorial one (1.619 Å) in SiF_5^- which is shorter than the apical one (1.653 Å) in SiF_5^-. The high polarity and the long distance of the apical bonds are interpreted in terms of the high p- and d-characters. The σ and σ* orbital energies of the apical bond are −0.703 and 0.536 au, respectively, while those of the equatorial bond are −0.977 and 0.628 au, respectively. The energies of the bond orbitals suggest that the apical bonds are more electron-donating and -accepting than the equatorial ones. We expect that the electron-pair bond model for hypervalent molecules is helpful to understand and disclose the properties of hypervalent molecules.

Three-Membered Rings 1−4

We investigated at the MP2/6-311+G** level the structures, the relative energies, and the ring strains of the three-membered

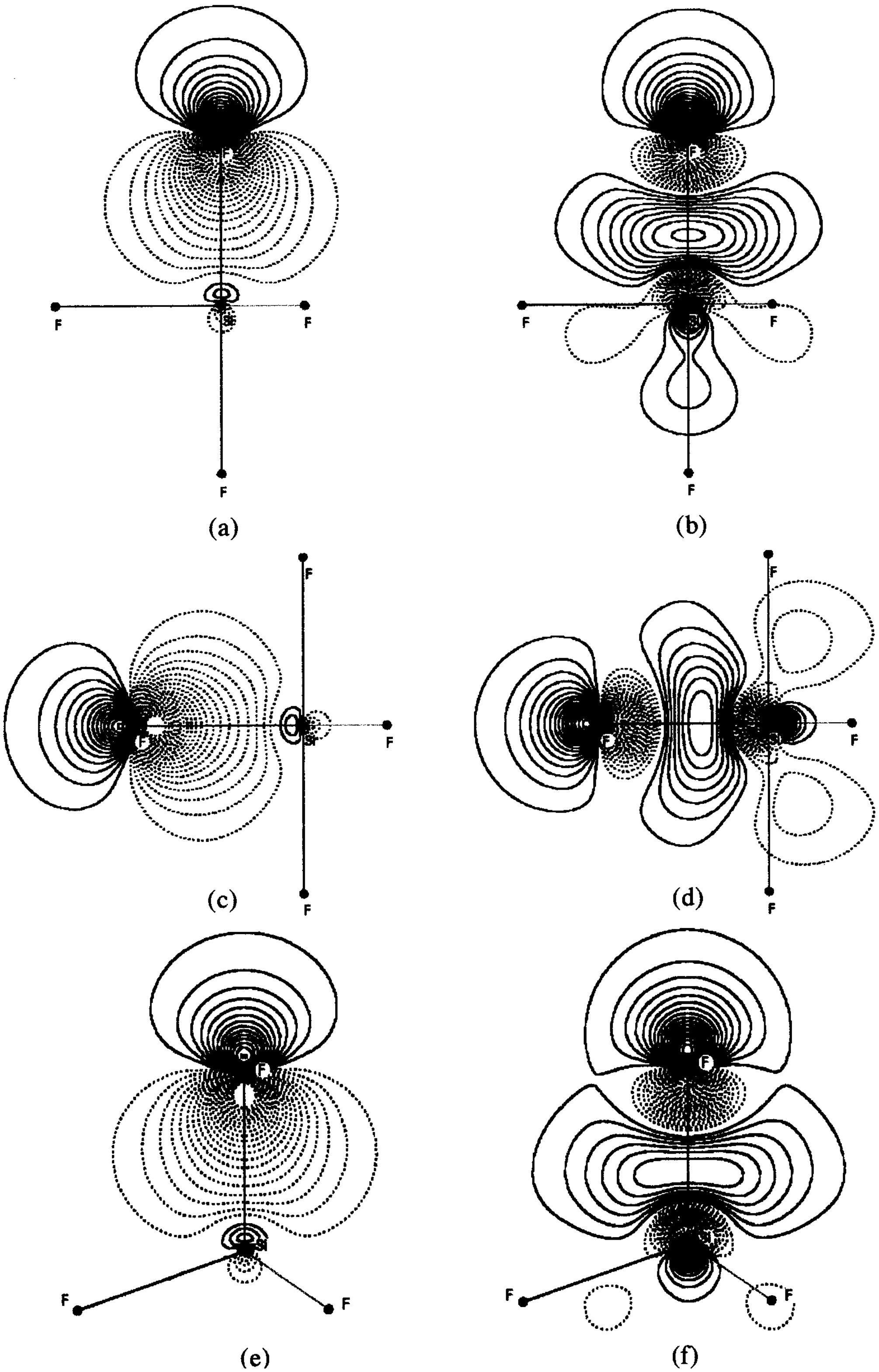


Figure 1. Electron-pair bond orbitals: (a) apical bonding, (b) apical antibonding, (c) equatorial bonding, and (d) equatorial antibonding orbitals in the SiF_5 anion and (e) bonding and (f) antibonding orbitals in SiF_4. The absolute value of the lowest contour line is 0.04 au. The heights of adjacent contours differ by 0.04 au.

rings **1**−**4** containing a hypervalent silicon, phosphorus, or sulfur atom.[19,20] The rings are formed by apical and equatorial bonds on the hypervalent atoms in the (ap, eq) isomers **1a**−**4a** and by two equatorial bonds in the (eq, eq) isomers **1b**−**4b**. The strain energies were calculated from the homodesmotic reactions[21] as shown in Scheme 1.

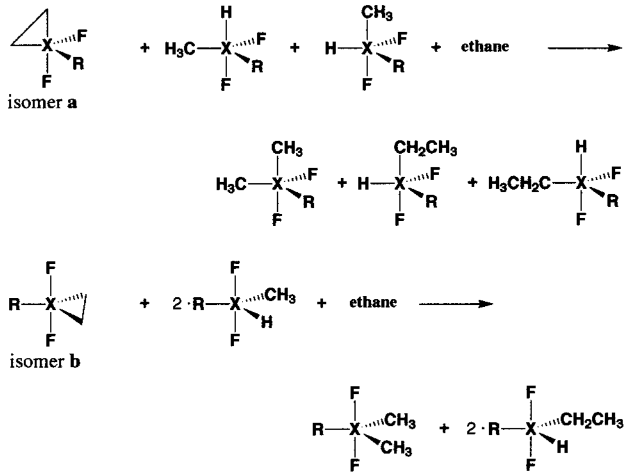
The ring structures[22,23] are shown in Figure 2 and the relative and strain energies are listed in Table 3. For the three-membered rings containing a pentacoordinated atom, the (ap, eq) isomers **1a** and **2a** are local minima, while the (eq, eq) isomers **1b** and **2b** are the transition states of pseudorotation reactions (the reaction-coordinate vectors of **1b** and **2b** are illustrated in Figure 3). The difference can be readily understood in terms of the bond angles in the trigonal bipyramid, i.e., 90° between the apical and equatorial bonds and 120° between the equatorial bonds. The bond angle in the three-membered ring is close to

TABLE 2: Selected Information about the Bonds of SiF_5^- and SiF_4

	SiF_5^-		
	apical bond	equatorial bond	SiF_4
$\|d_{Si}/d_F\|^a$	0.254	0.266	0.316
sp^md^n on Si^b	$sp^{4.4}d^{2.5}$	$sp^{2.5}d^{0.8}$	$sp^{2.3}d^{0.3}$
$\epsilon_\sigma{}^c$	−0.703	−0.977	−1.333
$\epsilon_{\sigma^*}{}^d$	0.536	0.628	0.210

[a] The bond polarity or the coefficent ratio of the hybrid atomic orbitals of the Si−F bonding orbitals. [b] The hybridization on the Si atom calculated as the summations of the squares of the coefficients of s-, p-, and d-type basis functions. [c] The energy (au) of the Si−F bonding orbital. [d] The energy (au) of the Si−F antibonding orbital.

SCHEME 1: Homodesmotic Reactions for Calculating the Strain Energies of the Three-Membered Rings 1−4



1, X = Si, R = F
2, X = P, R = F
3, X = P, R = lone pair
4, X = S, R = lone pair

the apical−equatorial bond angle. The three-membered ring strain was expected to be lower in **1a** and **2a** than that in **1b** and **2b**, respectively. In fact, the calculated strain energies showed that **1a** (29.6 kcal/mol) and **2a** (36.8 kcal/mol[24]) are less strained than **1b** (45.5 kcal/mol) and **2b** (52.9 kcal/mol), respectively.

The (ap, eq) isomer **1a** containing the pentacoordinated silicon atom in the ring is less strained than silirane. This can be interpreted in terms of the apical−equatorial bond angle (ca. 90°) in the trigonal bipyramidal structure and the C−Si−C angle (110.8°) in dimethylsilane. In contrast, the (ap, eq) isomer **2a** containing the pentacoordinated phosphorus atom in the ring is more strained than phosphirane. This may be attributed to the lack of a lone pair on the phosphorus atom in **2a**. The lone pair of the ring atoms tends to have high s-character, to leave the high p-character for the ring bonds, and to relax the ring strain by making the geminal delocalization (Chart 1) less antibonding or more bonding.[14] In fact, the lone-pair effect is supported by the high p-character of the X−C bonds in phosphirane and the low p-character of those in **2a** and **2b** (Table 4). The (ap, eq) and (eq, eq) isomers of the tetracoordinated species **3** and **4** are both local minima. The (ap, eq) isomers **3a** and **4a** are less stable than the (eq, eq) isomers **3b** and **4b**, while the (ap, eq) isomers are less strained than the (eq, eq) isomers. The relative stabilities are surprisingly opposite to those of the pentacoordinated species **1** and **2** expected from the ring strains. The strain energies of the tetracoordinated species are much lower than those of the pentacoordinated species. The low strains result from the effect of the lone pair on the tetracoordinated phosphorus and sulfur atoms.[14] The ring strains of **3** and **4** are relaxed by the lone-pair effect. In fact, the lone-pair effect is supported by the high p-character of the apical X−C bonds in **3a** and **4a** bearing the lone pairs on the hypervalent atoms (Table 4). The relative stabilities of the tetracoordinated species are controlled by other factors than the ring strains.

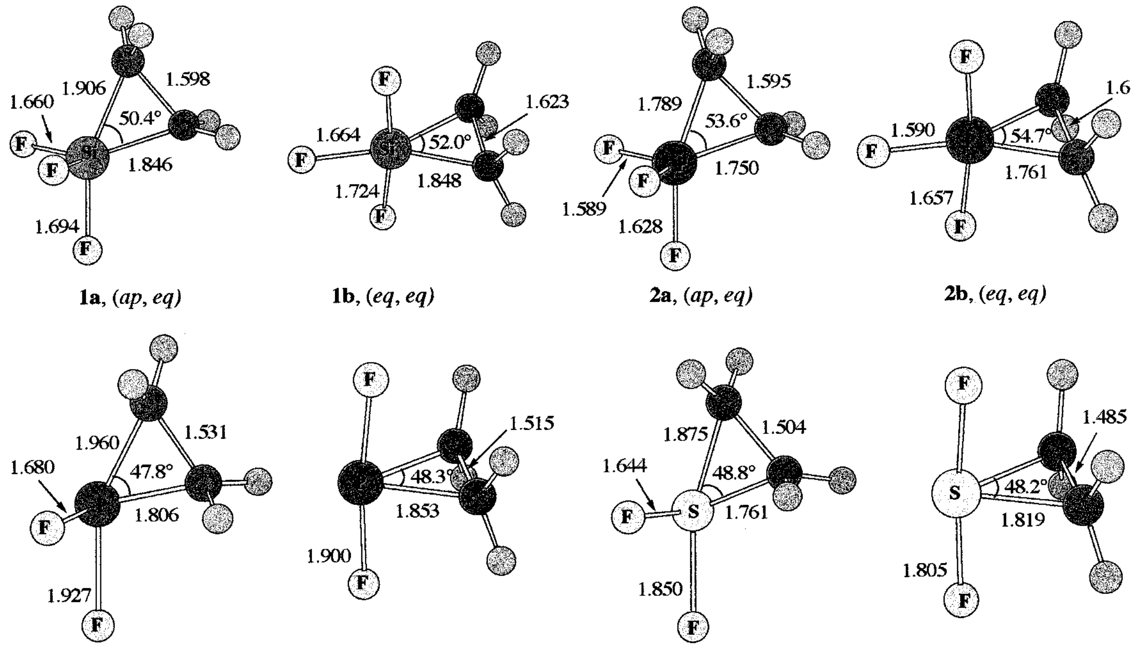
It is interesting that the more strained (eq, eq) isomers of **3** and **4** are more thermodynamically stable. We investigated the origins of the relative stabilities of **3** and **4**. The interbond energies (Table 5) showed a general feature that the apical and equatorial bonds are more repulsive than the equatorial bonds, as was expected from the narrow bond angle leading to great overlap of the occupied bonding orbitals. The (ap, eq) isomer **3a** is most destabilized relative to the (eq, eq) isomer **3b** by the greater repulsion (3.203 au) of the lone pair on the phosphorus atom with the apical P−C1 bond in **3a** than that (0.719 au) with the equatorial P−C1 bond in **3b**. The apical position is occupied by the P−F3 bond in **3b**. The repulsion of the lone pair with the P−F3 bonds is much weaker (0.734 au in **3a** and 1.466 au in **3b**) than that with the P−C bond, because the orbital on the fluorine atom has small spatial extension of orbitals (Figure 4). Similarly, the (ap, eq) isomer **4a** is most destabilized relative to the (eq, eq) isomer **4b** by the repulsion of the lone pair on the sulfur atom with the S−C1 bond (3.725 au in **4a** and 0.709 au in **4b**). The destabilization of **3a** and **4a** results from the repulsion of the lone pair on the phosphorus or sulfur atom with the apical bond containing the less-electronegative carbon atom than the fluorine atom.

For the tetracoordinated phosphorus compounds, the calculated strain energies increase in the order **3a** less than phosphirane less than **3b**. This can be interpreted in terms of the apical−equatorial bond angle (ca. 90°) in the trigonal bipyramidal structure and C−P−C angle (99.3°) in dimethylphosphane. For the tetracoordinated sulfur compounds, the strain energies increase in the order thiirane less than **4a** less than **4b**. The (ap, eq) isomer **4a** is more strained than thiirane. This cannot be interpreted in terms of the apical−equatorial bond angle (ca. 90°) and the C−S−C angles (98.1°) in dimethyl sulfide but can be interpreted in terms of the lone-pair effect. The number of lone pairs decreases from two to one on going from thiirane to **4**, while phosphirane and **3** have the same number (one) of lone pairs. The relative energies of the pentacoordinated (**1** and **2**) and the tetracoordinated species (**3** and **4**) are illustrated in Chart 2.

Pentacoordinated Species 5−8

The (ap, eq) isomers of the pentacoordinated species **1** and **2** are local minima, while the (eq, eq) isomers are the transition states of the pseudorotation reactions due to the high ring strains. Replacement of CH_2 in the ring by a NH or O gives rise to an interesting question about the relative stabilities of the (ap, eq) isomers with the heteroatom in the apical and equatorial ring bonds. We investigated the structures and the relative stabilities of the isomers of the three-membered rings **5**−**8** containing the pentacoordinated silicon or phosphorus atom with a nitrogen or oxygen atom in the rings.

The features of the stationary points of the pentacoordinated species **5**−**8**[22,23] with the heteroatom are similar to those of **1** and **2** (Table 3). The (ap, eq) isomers are local minima except **7a-ap** containing the hypervalent phosphorus atom with the nitrogen atom in the apical position. The (eq, eq) isomers are the transition states of pseudorotation reactions as in **1b** and **2b**. The geometries at the nitrogen atoms in the equatorial



1a, (*ap*, *eq*) **1b**, (*eq*, *eq*) **2a**, (*ap*, *eq*) **2b**, (*eq*, *eq*)

3a, (*ap*, *eq*) **3b**, (*eq*, *eq*) **4a**, (*ap*, *eq*) **4b**, (*eq*, *eq*)

Figure 2. MP2/6-311+G** structures of three-membered rings **1**−**4**. Bond lengths are given in angstroms and bond angles in degrees. The rings **1a** and **2a** have C_s symmetry, and **1b**−**4b** have C_{2v} symmetry.

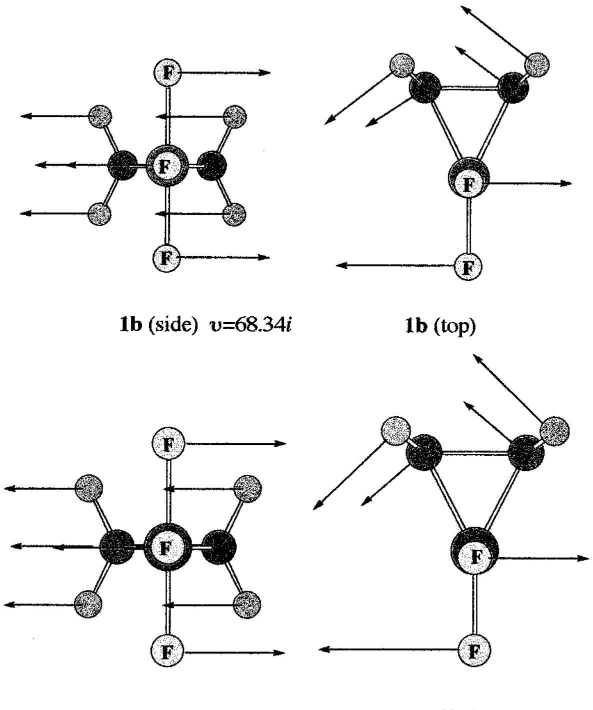
TABLE 3: Relative Energies[a] (Δ*E*, kcal/mol) and Strain Energies[a] (SE, kcal/mol) of the Three-Membered Rings 1−12

rings	NIF[b]	Δ*E*[c]	SE	rings	NIF[b]	Δ*E*[c]	rings	NIF[b]	Δ*E*[c]
1a	0	−11.7	29.6	**5a-ap**	0	−21.0	**9a-ap**	0	5.5
1b	1	0.0	45.5	**5a-eq**	0	−24.3	**9a-eq**	0	7.7
2a	0	−6.0	36.8[d]	**5b**	1	0.0	**9b**	0	0.0
2b	1	0.0	52.9	**6a-ap**	0	−27.6	**10a-ap**	0	−3.4
3a	0	15.1	19.2	**6a-eq**	0	−30.1	**10a-eq**	0	1.9
3b	0	0.0	22.9	**6b**	1	0.0	**10b**	0	0.0
4a	0	29.1	23.9	**7a-ap**	1	−20.3	**11a-ap**	0	14.1
4b	0	0.0	26.0	**7a-eq**	0	−26.5	**11a-eq**	0	18.3
silirane			36.3	**7b**	1	0.0	**11b**	0	0.0
phosphirane			21.0	**8a-ap**	0	−29.5	**12a-ap**	0	0.9
thiirane			19.7	**8a-eq**	0	−32.9	**12a-eq**	0	11.3
				8b	1	0.0	**12b**	0	0.0

[a] MP2/6-311+G** energies including zero-point energies. [b] Number of imaginary frequencies. [c] Δ*E* = *E*(**a**) − *E*(**b**). [d] See ref 24.

positions of the (ap, eq) isomers are more planar than those in the apical position (the sum of the bond angles at the nitrogen atom is 308.9° for **5a-ap**, 338.8° for **5a-eq**, 318.2° for **7a-ap**, and 360° for **7a-eq**). The bond model analysis showed that the lone pairs on the heteroatom in the equatorial position delocalize more than those in the apical position to the equatorial X−F bonds. The delocalization in **5a-eq** (IBP = 0.031; IBE = −0.294 au) and **7a-eq** (IBP = 0.062; IBE = −0.647 au) is greater than that in **5a-ap** (IBP = 0.017; IBE = −0.157 au) and **7a-ap** (IBP = 0.028; IBE = −0.301 au), respectively. The lone pair orbital on the heteroatom in the equatorial position has more favorable spatial extension to interact with the back lobe of the antibonding orbital of the equatorial X−F bond (Chart 3). The nitrogen atoms may tend to adopt a planar geometries to facilitate the n−σ^*_{X-F} interaction.

The calculated relative energies of the pentacoordinated species **5**−**8** (Table 3) showed that the (ap, eq) isomers with the electronegative atom in the equatorial position are more stable than those with the electronegative atom in the apical position (Chart 2). Similar relative stabilities of $FH_2\overline{Si-X-CH_2}$ (X = NH, O) were reported by Skancke et al.[23] The relative stabilities are readily understood in terms of the n−σ^*_{X-F} interactions favorable for the equatorial heteroatom.



1b (side) υ=68.34*i* **1b** (top)

2b (side) υ=11.23*i* **2b** (top)

Figure 3. Reaction-coordinate vectors corresponding to the sole imaginary frequency in cm^{-1} of **1b** and **2b** (MP2/6-311+G**).

CHART 1

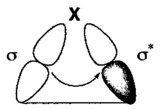
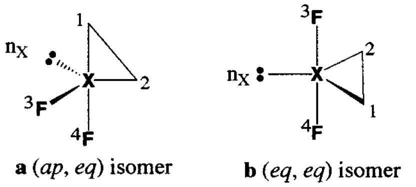


TABLE 4: Hybridization of the Hypervalent Atoms (X) in the Rings 1−4

rings	X−C$_a$[a]	X−C$_e$[a]
1a	$sp^{4.7}d^{1.5}$	$sp^{1.8}d^{0.3}$
1b		$sp^{2.2}d^{0.2}$
2a	$sp^{4.3}d^{1.0}$	$sp^{1.6}d^{0.2}$
2b		$sp^{2.3}d^{0.1}$
3a	$sp^{44.1}d^{7.2}$	$sp^{5.8}d^{0.3}$
3b		$sp^{9.8}d^{0.4}$
4a	$sp^{55.0}d^{5.4}$	$sp^{9.1}d^{0.2}$
4b		$sp^{18.3}d^{0.4}$
silirane	Si−C: $sp^{4.9}d^{0.2}$	
phosphirane	P−C: $sp^{16.6}d^{0.5}$	
thiirane	S−C: $sp^{14.2}d^{0.3}$	

[a] C$_a$ = apical carbon; C$_e$ = equatorial carbon.

TABLE 5: Interbond Energies[a] (au) in 3 and 4



	ring **3** (X = P)			ring **4** (X = S)		
interactions	a	b	ΔE[b]	a	b	ΔE[b]
n$_X$, X−C1	3.203	0.719	2.484	3.725	0.709	3.016
n$_X$, X−C2	1.421	0.719	0.702	1.068	0.709	0.359
n$_X$, X−F3	0.734	1.466	−0.732	0.694	1.895	−1.201
n$_X$, X−F4	1.100	1.466	−0.366	1.396	1.895	−0.499
n$_X$, C1−C2	0.185	−0.007	0.192	0.301	0.130	0.171
X−C1, X−C2	3.404	2.654	0.750	3.728	1.485	2.243
X−C1, X−F3	0.169	0.086	0.083	0.384	0.116	0.268
X−C1, X−F4	−0.357	0.086	−0.443	−0.500	0.116	−0.616
X−C1, C1−C2	1.042	1.196	-0.154	1.524	1.252	0.272
X−C2, X−F3	−0.037	0.086	−0.123	-0.083	0.116	−0.199
X−C2, X−F4	0.153	0.086	0.067	0.220	0.116	0.104
X−C2, C1−C2	0.678	1.196	−0.518	0.883	1.252	−0.369
X−F3, X−F4	−0.009	−0.424	0.415	−0.084	−0.757	0.673
X−F3, C1−C2	−0.050	−0.015	−0.035	−0.089	−0.017	−0.072
X−F4, C1−C2	0.003	−0.015	0.018	−0.005	−0.017	0.012

[a] The IBE values are the sums of the all bond orbital interactions between a pair of bonds. [b] ΔE = E(**a**) − E(**b**).

Tetracoordinated Species 9−12

For the three-membered rings **3** and **4** with the tetracoordinated phosphorus or sulfur atom, the (eq, eq) isomers have been shown to be surprisingly more stable than the (ap, eq) isomers. The relative stabilities are controlled by the repulsion between the lone pair on the hypervalent atom and the apical bond. The repulsion decreases with the electronegativity of the atom at the apical position. Introduction of an electronegative atom into the apical position of the ring was expected to decrease or reverse the energies of the (ap, eq) isomers relative to the (eq, eq) isomers. A heteroatom in the equatorial position was also expected to decrease the relative energies because of the orientation of the lone pairs being more favorable for the n−σ^*_{X-F} interactions in the (ap, eq) isomers than in the (eq, eq) isomers. We investigated the structures and the relative stabilities of the isomers of the three-membered rings **9−12** containing the tetracoordinated phosphorus or sulfur atom with a nitrogen or oxygen atom in the rings.

The (ap, eq) and (eq, eq) isomers of the tetracoordinated species **9−12**[22,23] are both local minima as are those of **3** and **4** (Table 3). This contrasts with the pentacoordinated species in which the (eq, eq) isomers do not exist. The geometries at the nitrogen atoms in the equatorial positions of the (ap, eq) isomers **9a** and **11a** are less pyramidal than those at the nitrogen in the apical positions (the sum of the bond angles at the nitrogen atoms is 285.0° for **9a-ap**, 316.1° for **9a-eq**, 289.7° for **11a-ap**, and 320.2° for **11a-eq**) as was found in the pentacoordinated species **5a** and **7a**.

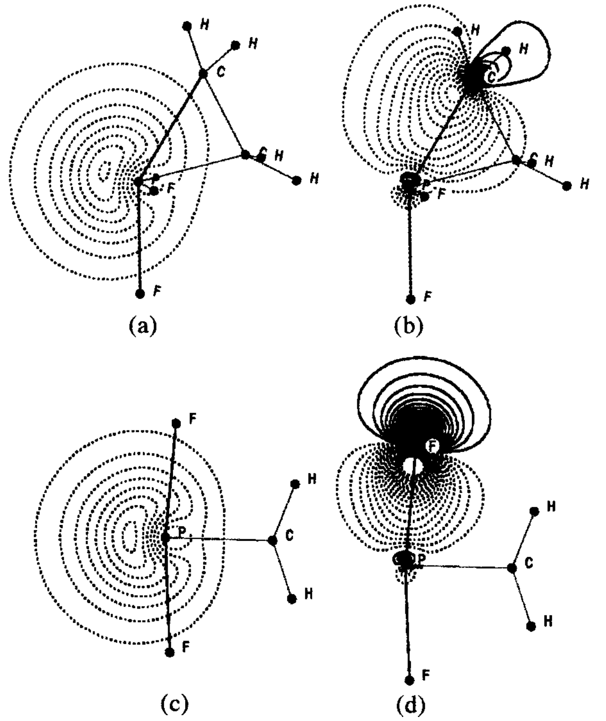


Figure 4. The lone pair orbitals on phosphorus and the apical bonding orbitals: (a) lone pair and (b) apical P−C1 bond in **3a**; (c) lone pair and (d) apical P−F3 bond in **3b**. The absolute value of the lowest contour line is 0.03 au. The heights of adjacent contours differ by 0.03 au.

CHART 2

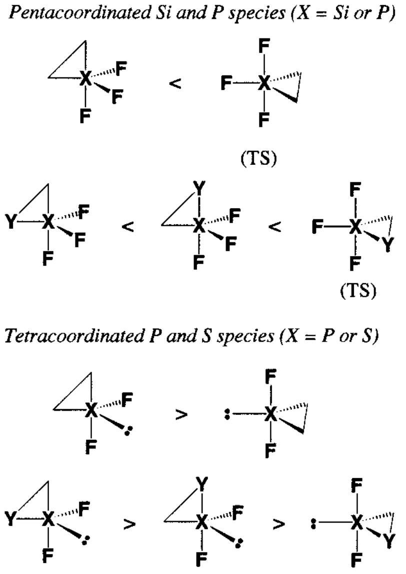
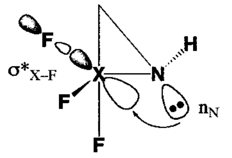


CHART 3



In fact, the instabilities of the (ap, eq) isomers relative to the (eq, eq) isomers were found to decrease or to be reversed on the introduction of the electronegative atoms (compare the relative energies of **9**−**12** with those of **3** and **4**). The relative stabilities of the phosphorus compound **10** with the oxygen atom is reversed. The (ap, eq) isomer **10a-ap** with the oxygen atom in the apical position is more stable than the (eq, eq) isomer **10b**. The instabilities of the (ap, eq) isomers of the other tetracoordinated species, **9**, **11**, and **12**, are lowered, while the (ap, eq) isomers are still more unstable than the (eq, eq) isomers (Chart 2).

The (ap, eq) isomers (**9a-ap**−**12a-ap**) with the electronegative atom in the apical ring bond are more stable than those (**9a-eq**−**12a-eq**) with the electronegative atom in the equatorial one, in contrast to the relative stabilities of the pentacoordinated species **5a**−**8a** (Chart 2). The (ap, eq) isomers of the tetracoordinated species have been shown to be significantly destabilized by the repulsion of the lone pair on the hypervalent atom with the apical bond rather than with the equatorial bond. The introduction of the heteroatom weakens the repulsion with the apical X−Y bond more than that with the equatorial X−Y bond.

Conclusion

We developed a new bond-model method for analyzing the electronic structures of molecules and proposed an electron-pair (two-center two-electron) bond model for hypervalent molecules. We investigated the molecular structures and the relative stabilities of the isomers of the three-membered rings **1**−**12** containing a hypervalent silicon, phosphorus, or sulfur atom and disclosed their origins by applying the bond-model method.

For the three-membered rings (**1**, **2**, and **5**−**8**) containing the pentacoordinated silicon or phosphorus atom, the (ap, eq) isomers are local minima while the (eq, eq) isomers are the transition states of pseudorotation reactions. The instabilities of the (eq, eq) isomers result from the high ring strains expected from the wide angle in the trigonal bipyramid for the three-membered rings. In contrast, the (ap, eq) and (eq, eq) isomers containing the tetracoordinated phosphorus or sulfur atom (**3**, **4**, and **9**−**12**) are both local minima. The relative stabilities of the (ap, eq) and (eq, eq) isomers are opposite to those of pentacoordinated species (Chart 1). The (eq, eq) isomers are, surprisingly, more stable than the (ap, eq) isomers because of the weak repulsion between the lone pair on the hypervalent atom and the apical bond in the (eq, eq) isomers. However, the relative stability of the (ap, eq) isomers (**10a-ap** and **12a-ap**) with an oxygen atom in the apical position should be noted. The tetracoordinated species are less strained than the pentacoordinated species because of the relaxation of the ring strains by the effect of the lone pair on the hypervalent atom or because of less antibonding (more bonding) property of the delocalization between the geminal ring bonds on the hypervalent atom (Chart 1).[14]

For the pentacoordinated species, the (ap, eq) isomers with the electronegative ring atom in the equatorial position are more stable than those with the electronegative ring atom in the apical position because of the stabilization by the delocalization of the lone pairs on the electronegative atom to the equatorial X−F bonds. The relative stabilities of the tetracoordinated species are reversed because the repulsion is significant between the lone pair on the hypervalent atom and the apical bond.

Finally, the new bond-model method for analyzing the electronic structures of molecules and the electron-pair bond model for hypervalent molecules were shown to be useful for understanding and predicting the properties of hypervalent molecules.

Supporting Information Available: Tables for the selected structural parameters, figures, and Cartesian matrices of compounds **1**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Schmidt orthogonalization of atomic basis functions on each atom gives a set of orthonormal atomic orbitals, a_1, a_2, ..., a_i, a_j, ..., a_n. A pair of the orthogonal orbitals, a_i and a_j, on the atom is transformed (hybridized) by a 2 × 2 orthogonal matrix into a'_i and a'_j to give a new set of orthonormal atomic orbitals (a_1, a_2, ..., a'_i, a'_j, ..., a_n):

$$\begin{bmatrix} a'_i \\ a'_j \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} a_i \\ a_j \end{bmatrix} \qquad \text{(r1)}$$

The successive rehybridization by the 2 × 2 orthogonal matrix was carried out to give the maximum P value or the minimum P^* value. Each lone pair orbital is represented by a hybrid orbital. The remaining hybrid orbitals are vacant orbitals.

(19) The geometries and total energies were obtained by the ab initio molecular orbital calculations at the MP2/6-311+G** level of theory using the Gaussian 98 program.[20] All geometries examined here were optimized by the gradient methods and checked by the frequency calculations using analytical second derivatives. The relative and strain energies were corrected with the zero-point energies. The geometries and the wave functions for the analysis of the bond interactions were obtained by the RHF/6-31G* calculations.

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(22) The apical ring bonds are longer than the equatorial ring bonds and deviate more from the ideal positions of the trigonal bipyramid than the equatorial ring bonds (see Supporting Information). These features result from the relatively weak apical ring bonds or the high p-characters of the hybrid orbitals on the hypervalent atom X for the bonds.

(23) (a) The structures of $\mathrm{FH_2\overline{Si{-}CH_2{-}C}H_2}$ and $\mathrm{FH_2\overline{Si{-}X{-}C}H_2}$ (X = NH, O) were previously investigated by the ab initio molecular orbital calculations.[23b] The structures have the similar features as **1a** and as **5a** and **6a**. (b) Skancke, P. N. *J. Phys. Chem.* **1994**, *98*, 3154. Schlegel, H. B.; Skancke, P. N. *J. Am. Chem. Soc.* **1993**, *115*, 10916.

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