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Why Is $(SiO)_4$ Calculated To Be Tetrahedral, Whereas $(CO)_4$ Is Square Planar? A Molecular Orbital Analysis

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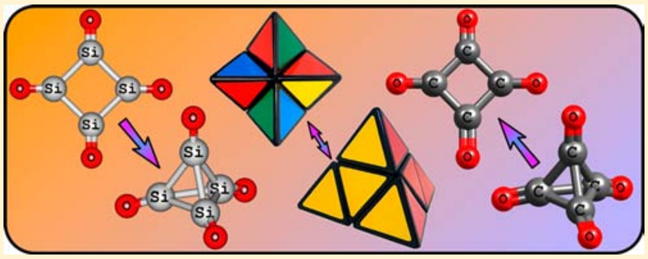
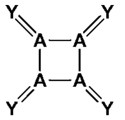
Supporting Information

ABSTRACT: Qualitative molecular orbital (MO) theory predicts that square-planar tetrasilacyclobutanetetraone **D_{4h}-$(SiO)_4$** should, like **D_{4h}-$(CO)_4$**, have a triplet ground state, and the results of the (U)CCSD(T)-F12b/cc-pVTZ-F12//(U)-B3LYP/6-311+G(2df) calculations, reported here, confirm this expectation. Calculations at the same level of theory find that square-planar tetrasilacyclobutanetetrathione **D_{4h}-$(SiS)_4$** also has a triplet ground state. However, these ab initio calculations predict that $(SiO)_4$ and $(SiS)_4$ both have a singlet state of much lower energy, with a tetrahedral (T_d) equilibrium geometry and six, electron-deficient, Si−Si bonds. In contrast, the lowest singlet state of $(CO)_4$ and of $(CS)_4$ is calculated to prefer a D_{4h} to a T_d geometry. An analysis, based on the second-order Jahn−Teller effect, rationalizes the influence of the electronegativity difference between A and Y in $(AY)_4$ on the energy difference between a D_{4h} and T_d geometry. This analysis predicts that $(BF)_4$ and $(BCl)_4$, which are isoelectronic with, respectively, $(CO)_4$ and $(CS)_4$, should both prefer a T_d to a D_{4h} equilibrium geometry. These qualitative predictions have been confirmed by our calculations, and $(BCl)_4$ is known experimentally to have a T_d equilibrium geometry.



INTRODUCTION

Calculations have predicted,[1] and experiments have confirmed[2] that square-planar cyclobutanetetraone [**D_{4h}-$(CO)_4$**] has a triplet ground state. The reason for this very surprising finding is that the frontier orbitals, a_{2u} and b_{2g} (Figure 1), of this molecule are nearly degenerate in energy.[1d] These two MOs are occupied by a total of two electrons in **D_{4h}-$(CO)_4$**; and, because these MOs are nondisjoint, Hund's rule[3] predicts that square-planar $(CO)_4$ should have a triplet ground state.



D_{4h}-$(CO)_4$, A = C, Y = O
D_{4h}-$(CS)_4$, A = C, Y = S
D_{4h}-$(SiO)_4$, A = Si, Y = O
D_{4h}-$(SiS)_4$, A = Si, Y = S

The a_{2u} and b_{2g} MOs of **D_{4h}-$(CO)_4$** are both formed from the in-phase combinations of the degenerate pairs of π^* MOs of four molecules of CO.[4] In **D_{4h}-$(CO)_4$**, the degeneracy of the a_{2u} and b_{2g} combinations of the π^* MOs of four molecules of CO is lifted because in square-planar $(CO)_4$ the bonding interactions between the 2p AOs on the carbons come from π overlaps in the a_{2u} MO and σ overlaps in the b_{2g} MO. Therefore, one would have anticipated that the b_{2g} σ MO of **D_{4h}-$(CO)_4$** would be significantly lower in energy than the a_{2u} π MO, but this is not the case.

The reason is that in the four-membered ring of **D_{4h}-$(CO)_4$**, the cross-ring, 1,3 interactions between the carbons work in the opposite direction from the 1,2-interactions between nearest-neighbor carbons. As shown in Figure 1, the 1,3 interactions between the 2p AOs on carbon are bonding in the a_{2u} π MO but antibonding in the b_{2g} σ MO. Apparently, the 1,3-interactions in **D_{4h}-$(CO)_4$** are, accidentally, of just the right size to cancel the greater strength of the 1,2−C-C σ bonding in the b_{2g} MO, compared to the 1,2−C-C π bonding in the a_{2u} MO.[4,5] Consequently, the a_{2u} and b_{2g} MOs of **D_{4h}-$(CO)_4$** are

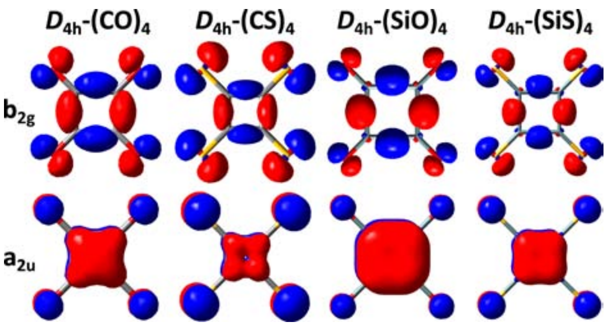


Figure 1. Frontier orbitals of square-planar $(CO)_4$, $(CS)_4$, $(SiO)_4$, and $(SiS)_4$.

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accidentally degenerate in energy,[1d] leading to the experimental finding that, as predicted,[1] square-planar (CO)$_4$ has a triplet ground state.[2]

Unlike the case in **D_{4h}-(CO)$_4$**, calculations predict[6a] and experiments confirm[7] that **D_{4h}-(CS)$_4$** has a singlet ground state. The calculations find that in square-planar (CS)$_4$, the a_{2u} and b_{2g} MOs are not degenerate and that the b_{2g} MO is 12 kcal/mol lower in energy than the a_{2u} MO. Apparently, in **D_{4h}-(CS)$_4$** the strength of the 1,3 cross-ring interactions between the carbons is insufficient to overcome the greater strength of the 1,2 σ bonding interactions in b_{2g}, compared to the 1,2-π bonding interactions in a_{2u}.

A simple rationalization of why the energy difference between the a_{2u} and b_{2g} frontier orbitals is much larger in **D_{4h}-(CS)$_4$** than in **D_{4h}-(CO)$_4$** comes from visual comparison of these MOs, which are shown in Figure 1. The coefficients on carbon are much smaller in these two frontier orbitals in square-planar (CS)$_4$ than in square-planar (CO)$_4$. Consequently, the 1,3 cross-ring interactions between the carbons are also smaller in **D_{4h}-(CS)$_4$** than in **D_{4h}-(CO)$_4$**. Since these interactions selectively stabilize the a_{2u} relative to the b_{2g} MO, their smaller size in square-planar (CS)$_4$ than in square-planar (CO)$_4$ can account for the higher energy of the a_{2u}, relative to the b_{2g} MO, in **D_{4h}-(CS)$_4$** than in **D_{4h}-(CO)$_4$**.[6]

The reason for the smaller coefficients on carbon in the a_{2u} and b_{2g} MOs of **D_{4h}-(CS)$_4$** than of **D_{4h}-(CO)$_4$** is easy to understand. These frontier orbitals are derived from the π^* orbitals of, respectively, CS and CO. In the bonding π MOs of these two molecules, the lower electronegativity of S versus O means that the electron density on C is much greater in **D_{4h}-(CS)$_4$** than in **D_{4h}-(CO)$_4$**. However, in the antibonding π^* MOs, the lower electronegativity of S versus O means that the electron density on C is much smaller in square-planar (CS)$_4$ than in square-planar (CO)$_4$.

The same considerations of the effect of electronegativity on the coefficients in antibonding MOs that rationalize the difference between the frontier orbitals of **D_{4h}-(CO)$_4$** and **D_{4h}-(CS)$_4$** can be applied to the a_{2u} and b_{2g} frontier MOs of **D_{4h}-(SiO)$_4$** and **D_{4h}-(SiS)$_4$**. Si is less electronegative than C; hence, the coefficients on Si in the frontier MOs of **D_{4h}-(SiO)$_4$** and **D_{4h}-(SiS)$_4$** should be larger than those on C in the frontier MOs of, respectively, **D_{4h}-(CO)$_4$** and **D_{4h}-(CS)$_4$**. Therefore, going from square-planar (CO)$_4$ and (CS)$_4$ to square-planar (SiO)$_4$ and (SiS)$_4$, greater cross-ring bonding should selectively stabilize the a_{2u}, relative to the b_{2g} MO. Depending on the size of the stabilization of a_{2u}, relative to b_{2g}, it is possible that not only **D_{4h}-(SiO)$_4$** but also **D_{4h}-(SiS)$_4$** might have a triplet ground state.

In order to investigate the nature of the ground state of **D_{4h}-(SiO)$_4$** and **D_{4h}-(SiS)$_4$**, we have carried out DFT and ab initio calculations. Our calculations predict that, as in square-planar (CO)$_4$, the ground state of square-planar (SiO)$_4$ and square-planar (SiS)$_4$ is, in fact, the triplet. In addition, our calculations find that, unlike the case in **D_{4h}-(CO)$_4$**, in **D_{4h}-(SiO)$_4$** the singlet state in which the a_{2u} MO is doubly occupied is lower in energy than the singlet state in which the b_{2g} MO is doubly occupied.

However, to our surprise, the calculations also predict that, with the a_{2u} MO doubly occupied, the D_{4h} geometries of both (SiO)$_4$ and (SiS)$_4$ are not energy minima. Instead, they are transition structures, connecting a pair of equivalent T_d energy minima (respectively, **T_d-(SiO)$_4$** and **T_d-(SiS)$_4$** in Figure 2). Furthermore, our calculations show that the bonding in **T_d-(SiO)$_4$** and **T_d-(SiS)$_4$** consists of four Si−Y (Y = O or S) double bonds and six, electron-deficient, Si−Si bonds.

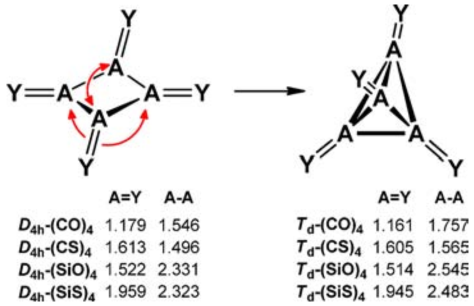

Figure 2. Rearrangement of the D_{4h} geometries of the 10 π singlet states of (AY)$_4$ to the T_d geometries. The A—A and A═Y bond lengths in both geometries are given in Å for each (AY)$_4$ molecule.

Our calculations also find that although the rearrangement from D_{4h} to T_d is energetically very favorable for (SiO)$_4$ and (SiS)$_4$, this type of rearrangement is energetically unfavorable for (CO)$_4$ and for (CS)$_4$. In order to understand the reason for this difference between the energies of **D_{4h}-(CO)$_4$ → T_d-(CO)$_4$** and **D_{4h}-(CS)$_4$ → T_d-(CS)$_4$** on one hand and **D_{4h}-(SiO)$_4$ → T_d-(SiO)$_4$** and **D_{4h}-(SiS)$_4$ → T_d-(SiS)$_4$** on the other, we have also performed calculations on (BF)$_4$ and (BCl)$_4$. These boron compounds are isoelectronic with, respectively, (CO)$_4$ and (CS)$_4$. We have also carried out calculations on (PN)$_4$, which is isoelectronic with (SiO)$_4$. Herein, we report the results of our calculations on these molecules at square-planar and tetrahedral geometries.

■ COMPUTATIONAL METHODS

Geometries were optimized and vibrational analyses were performed with the B3LYP functional,[8] using the 6-311+G(2df) basis set.[9] For calculations on triplets, unrestricted, UB3LYP calculations were carried out. Gaussian09[10] was used to perform these DFT calculations. The (U)B3LYP/6-311+G(2df) optimized geometries are available as Supporting Information.[11]

Single-point energies were obtained with (U)CCSD(T)-F12b calculations,[12] using the cc-pVTZ-F12 basis set.[13] These single-point calculations were performed with Molpro 2010.[14]

The high symmetry of all eight molecules in Figure 2 made it possible for us to consider reoptimizing the (U)B3LYP/6-311+G(2df) geometries of these molecules at the (U)CCSD(T)-F12b/cc-pVDZ-F12 level of theory. However, such geometry reoptimizations of the two lowest singlet states of **D_{4h}-(SiO)$_4$** had a negligible effect on their energies, and reoptimization of the geometry of the lowest singlet state of **T_d-(SiO)$_4$** lowered the (U)CCSD(T)-F12b/cc-pVTZ-F12 energy by only 0.2 kcal/mol. Therefore, we did not perform any further (U)CCSD(T)-F12b/cc-pVDZ-F12 geometry optimizations.

■ RESULTS AND DISCUSSION

Before discussing the square-planar and tetrahedral geometries of (SiO)$_4$, it is worth noting that both of these isomers are much higher in energy than the global energy minimum, which consists of a puckered eight-membered ring of D_{2d} symmetry with alternating Si and O atoms.[15] We calculate that this D_{2d} structure, which contains only Si−O bonds and no Si−Si bonds, is 142.3 kcal/mol lower in energy than **T_d-(SiO)$_4$**. However, this paper is concerned with the **T_d** local energy minimum and not with the D_{2d} global energy minimum.

Calculations at D$_{4h}$ Geometries. In order to compare the relative energies of the low-lying electronic states of **D_{4h}-(SiO)$_4$**

and **D_{4h}-(SiS)$_4$** with those of **D_{4h}-(CO)$_4$** and **D_{4h}-(CS)$_4$** at the same level of theory, the previous (U)CCSD(T)/6-311+G-(2df) single-point calculations on square-planar $(CO)_4$[4,6] and $(CS)_4$[6] were repeated at the (U)CCSD(T)-F12b/cc-pVTZ-F12 level of theory. The energies of the singlet states with 8*π* electrons ($|...b_{2g}{}^{2}a_{2u}{}^{0}>$) and 10*π* electrons ($|...b_{2g}{}^{0}a_{2u}{}^{2}>$), relative to the triplet states with 9*π* electrons ($|...b_{2g}{}^{\alpha}a_{2u}{}^{\alpha}>$), are compared in Table 1 at the optimized D_{4h} geometry of each electronic state of $(CO)_4$, $(CS)_4$, $(SiO)_4$, and $(SiS)_4$.

The results in Table 1 show that, although **D_{4h}-(CO)$_4$** and **D_{4h}-(SiO)$_4$** are both computed to have triplet ground states, there is a difference between them. The 10*π* singlet is calculated to be 2.6 kcal/mol higher in energy than the 8*π* singlet in square-planar $(CO)_4$ but 1.4 kcal/mol lower in energy than the 8*π* singlet in square-planar $(SiO)_4$.

Table 1. (U)CCSD(T)-F12b/cc-pVTZ-F12//(U)B3LYP/6-311+G(2df) Energies (kcal/mol) of the 8*π* ($|...b_{2g}{}^{2}a_{2u}{}^{0}>$) and 10*π* ($|...b_{2g}{}^{0}a_{2u}{}^{2}>$) Singlet States of D_{4h}-(CO)$_4$, D_{4h}-(CS)$_4$, D_{4h}-(SiO)$_4$, and D_{4h}-(SiS)$_4$, Relative to the Energy of the 9*π* Triplet ($|...b_{2g}{}^{\alpha}a_{2u}{}^{\alpha}>$)

molecule	9*π* triplet	8*π* singlet	10*π* singlet
$(CO)_4$	0	3.3[a]	5.9
$(CS)_4$	0	−9.3[b]	11.2
$(SiO)_4$	0[c]	6.4	5.0[d]
$(SiS)_4$	0	2.5	4.4[d]

[a] Experimentally, 1.5 kcal/mol.[2] [b] Experimentally, −7.2 kcal/mol.[7] [c] Unstable geometry; an almost planar stable D_{2d} geometry is 0.1 kcal/mol lower than the D_{4h} geometry for triplet $(SiO)_4$. [d] Unstable D_{4h} geometry; leads to a T_d geometry.

The 4.0 kcal/mol selective stabilization of the 10*π* singlet state, relative to the 8*π* singlet state, in going from **D_{4h}-(CO)$_4$** to **D_{4h}-(SiO)$_4$** is attributable to the larger coefficients on the atoms of the four-membered ring in the b_{2g} and a_{2u} frontier orbitals of the latter molecule. This difference in coefficients is clearly visible in Figure 1, and, as discussed in the introduction, this difference is attributable to the effect of the lower electronegativity of Si, compared to C, on the size of the coefficients in both the b_{2g} and a_{2u} MOs.

This difference between the frontier orbitals of **D_{4h}-(CO)$_4$** and **D_{4h}-(SiO)$_4$** makes the cross-ring interactions in the b_{2g} and a_{2u} MOs larger in planar $(SiO)_4$ than in planar $(CO)_4$. The larger cross-ring interactions in these two MOs in **D_{4h}-(SiO)$_4$**, compared to **D_{4h}-(CO)$_4$**, stabilize the 10*π* configuration of planar $(SiO)_4$, in which the a_{2u} MO is doubly occupied and the b_{2g} MO is empty, relative to the 8*π* configuration, in which the b_{2g} *σ* MO is doubly occupied and the a_{2u} *π*, MO is empty. This accounts for the reversal in the relative energies of the 10*π* and 8*π* states on going from **D_{4h}-(CO)$_4$** to **D_{4h}-(SiO)$_4$**.

Rearrangements of (SiO)$_4$ and (SiS)$_4$ from D_{4h} to T_d Geometries. The relative energies of the 8*π* and 10*π* states of $(SiO)_4$ and $(SiS)_4$ at their optimized D_{4h} geometries turn out to be of little importance, because the D_{4h} geometry of the 10*π* singlet state of each molecule has an imaginary frequency for a b_{2u} vibration that distorts the square-planar geometry toward the T_d geometry of a regular tetrahedron. In contrast, the 8*π* singlet states of **D_{4h}-(SiO)$_4$** and **D_{4h}-(SiS)$_4$** and all of the low-lying electronic states of **D_{4h}-(CO)$_4$** and **D_{4h}-(CS)$_4$** have no imaginary frequencies and are true energy minima.

The imaginary b_{2u} frequencies for the 10*π* singlet states of square-planar $(SiO)_4$ and $(SiS)_4$ indicate that the planar geometries of these states are transition structures that connect two, nonplanar, equilibrium geometries. The b_{2u} folding distortion leads to a perfectly tetrahedral equilibrium geometry for both molecules. As shown in Table 2, this geometry change lowers the energy of the 10*π* singlet state by 43.3 kcal/mol for **D_{4h}-(SiO)$_4$** → **T_d-(SiO)$_4$** and by 28.2 kcal/mol for **D_{4h}-(SiS)$_4$** → **T_d-(SiS)$_4$**. In contrast, **D_{4h}-(CO)$_4$** → **T_d-(CO)$_4$** and **D_{4h}-(CS)$_4$** → **T_d-(CS)$_4$** are both calculated to be energetically unfavorable by, respectively, 18.7 and 37.1 kcal/mol. We will discuss the reasons for this difference between the silicon and carbon compounds in a subsequent section.

Table 2. (U)CCSD(T)-F12b/cc-pVTZ-F12//(U)B3LYP/6-311+G(2df) Energy Change (Δ*E*, kcal/mol) on Going from the D_{4h} to the T_d Geometry of (CO)$_4$, (CS)$_4$, (SiO)$_4$, and (SiS)$_4$, Starting from the 10*π* Singlet State of Each D_{4h}-(AY)$_4$ Molecule

molecule	Δ*E*
$(CO)_4$	18.7
$(CS)_4$	37.1
$(SiO)_4$	−43.3
$(SiS)_4$	−28.2

The b_{2u} vibration, which has an imaginary frequency in the 10*π* singlet state of both square-planar $(SiO)_4$ and square-planar $(SiS)_4$, allows the a_{2u} *π* MO, which is doubly occupied in the singlet state,[16] to mix with the empty b_{1g} *σ* MO of the four-membered ring. The a_{2u} and b_{1g} MOs of **D_{4h}-(SiO)$_4$** and the t_2 MO of **T_d-(SiO)$_4$** to which the mixing of a_{2u} with b_{1g} gives rise are shown in Figure 3.[17] The mixing of the filled a_{2u} MO with the empty b_{1g} MO under the influence of a b_{2u} geometry distortion can be viewed as a pseudo or second-order Jahn–Teller effect.[18,19]

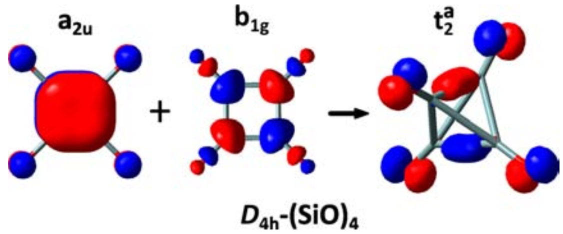

Figure 3. Second-order Jahn–Teller mixing[18,19] of the a_{2u} HOMO of the 10*π* singlet state with the virtual b_{1g} MO upon a b_{2u} distortion of **D_{4h}-(SiO)$_4$**. This vibrational mode ultimately leads to a T_d equilibrium geometry. At this geometry the MO that results from the mixing of a_{2u} with b_{1g} becomes $t_2{}^a$, one of the triply degenerate HOMOs of **T_d-(SiO)**.[17]

As shown in Figure 3 (and in more detail in Figure S1 of the Supporting Information[11]), the mixing of the a_{2u} HOMO of the 10*π* singlet state of **D_{4h}-(SiO)$_4$** with the virtual b_{1g} orbital results in the silicon atoms hybridizing, so that the pure 3p-*π* AOs on silicon in the D_{4h} geometry are replaced by 3s-3p hybrid AOs. The hybrid AOs point in opposite directions on adjacent silicon atoms but in the same direction on silicon atoms that are across the four-membered ring from each other. It is these hybrid AOs that form the out-of-phase combination of Si–Si bonds in the $t_2{}^a$ MO of **T_d-(SiO)$_4$**.

Figure 3 shows that the unfilled, b_{1g} MO of **D_{4h}-(SiO)$_4$** is 1,2 antibonding but 1,3-bonding. Consequently, as the b_{2u} distortion toward a T_d geometry proceeds, and the size of the

1,3−Si-Si bonding interactions increase, the energy of the b_{1g} MO decreases. This energy lowering of the empty b_{1g} MO enhances its mixing with the occupied a_{2u} MO as the size of the b_{2u} distortion increases.

MOs t_2^b and t_2^c of T_d-(SiO)$_4$. The t_2^a MO of T_d-(SiO)$_4$, shown in Figure 3, is one of the triply degenerate, t_2 MOs. The two other t_2 HOMOs of T_d-(SiO)$_4$, t_2^b and t_2^c, come from the mixing of a degenerate pair of filled, e_u, σ orbitals of the ring of D_{4h}-(SiO)$_4$ with the unfilled, e_g, Si−O, π^* MOs. The mixing between each of the pair of e_u, σ orbitals with one of the pair of e_g, Si−O, π^* MOs is shown in Figure 4. This second-order Jahn−Teller mixing again occurs under the influence of the b_{2u} geometry distortion that transforms square-planar (SiO)$_4$ into tetrahedral (SiO)$_4$.

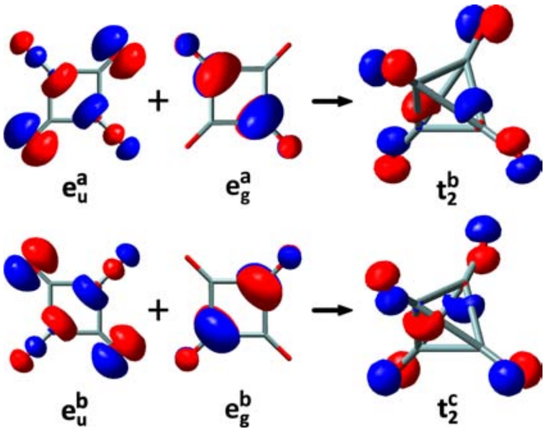

Figure 4. Mixing of the doubly degenerate pair of occupied, e_u, σ orbitals of D_{4h}-(SiO)$_4$ with the doubly degenerate pair of unoccupied, e_g, π^* MOs to form the t_2^b and t_2^c orbitals of T_d-(SiO)$_4$ under the influence of a b_{2u} vibration.

Although symmetry mandates that the t_2^b and t_2^c MOs of T_d-(SiO)$_4$ be degenerate with the t_2^a MO, t_2^b and t_2^c in Figure 4 look very different from t_2^a in Figure 3. However, since t_2^b and t_2^c are degenerate MOs, it is possible to form two equivalent MOs from them by taking the sum and difference of t_2^b and t_2^c. The resulting MOs, $t_2^{b'} = t_2^c - t_2^b$ and $t_2^{c'} = t_2^b + t_2^c$ are shown in Figure 5.

Figure 5 reveals the reason that t_2^a, $t_2^{b'}$, and $t_2^{c'}$ are a triply degenerate set of MOs. Each of these three MOs represents an out-of-phase combination of two of the six Si−Si bonds in T_d-(SiO)$_4$. However, in one sense, t_2^a is unique. Since, as shown in Figure 3, it is formed by mixing of the a_{2u} and b_{1g} MOs in D_{4h}-(SiO)$_4$, t_2^a is the out-of phase combination of the two *new* Si−Si σ bonds in T_d-(SiO)$_4$.

It is, of course, also possible to form linear combinations of the degenerate pairs of e_u and e_g MOs of D_{4h}-(SiO)$_4$ in Figure 4, and these combinations are also shown in Figure 5. Figure 5 reveals that $t_2^{b'}$, and $t_2^{c'}$ are really the out-of-phase, e_u, combinations of the pairs of Si−Si σ bonds that already exist in D_{4h}-(SiO)$_4$ but with additional antibonding interactions between pairs of silicons across the four-membered ring from each other.

Whereas, the new Si−Si cross-ring interactions lower the energy of the t_2^a MO of T_d-(SiO)$_4$, relative to that of the a_{2u} MO of D_{4h}-(SiO)$_4$, the additional cross-ring interactions destabilize the $t_2^{b'}$ and $t_2^{c'}$ MOs of T_d-(SiO)$_4$, relative to the $e_u^{a'}$ and $e_u^{b'}$ MOs of D_{4h}-(SiO)$_4$. The reason for this destabilization is even more evident in the equivalent set of unprimed, degenerate MOs in Figure 4 because it is obvious that the e_u MOs in Figure 4 are strongly antibonding between the silicon atoms that are situated across the four-membered ring from each other. Therefore, the energies of the e_u MOs rise, as the size of the cross-ring interactions in (SiO)$_4$ increases.

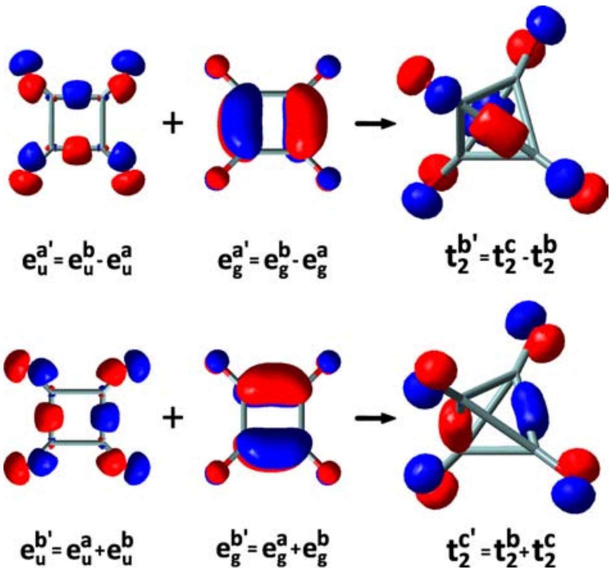

Figure 5. Another possible pair, $t_2^{b'}$ and $t_2^{c'}$, of the degenerate t_2 MOs that are formed from mixing of the occupied $e_u{}'$ and virtual $e_g{}'$ orbitals of D_{4h}-(SiO)$_4$. These $t_2{}'$, $e_u{}'$, and $e_g{}'$ MOs can be formed by taking the sums and differences of the unprimed t_2, e_u, and e_g MOs of T_d-(SiO)$_4$ in Figure 4.

The mixing of the e_u σ MOs with the unoccupied, e_g π MOs ameliorates some of the destabilizing effect of cross-ring bonding on the t_2^b and t_2^c MOs of T_d-(SiO)$_4$. As shown in Figure 4, the mixing of e_u with e_g reorients the resulting t_2^b and t_2^c MOs, so that they do not lie directly along the newly formed Si−Si bonds but are, instead, directed along the four original Si−Si bonds. Nevertheless, Figure 4 clearly shows that increasing the cross-ring interactions between the e_u combinations of σ bonds result in the t_2^b and t_2^c MOs of T_d-(SiO)$_4$ being higher in energy than the pair of e_u MOs in D_{4h}-(SiO)$_4$.

These qualitative conclusions about how the energies of the a_{2u} and e_u MOs of D_{4h}-(SiO)$_4$ change on forming the t_2 MOs of T_d-(SiO)$_4$ can easily be assessed from the actual changes in the B3LYP/6-311+G(2df) orbital energies. The energy of the a_{2u} orbital is calculated to decrease by −39.5 kcal/mol, whereas the energy of the pair of e_u MOs is calculated to increase by a total of $2 \times 10.0 = 20.0$ kcal/mol.[20]

If one were to believe that the sum of the changes in the energies of the three pairs of electrons that occupy the t_2 MOs in D_{4h}-(SiO)$_4$ would give a semiquantitative estimate of the energy change for square-planar → tetrahedral-(SiO)$_4$, one would predict the cyclization to be favorable by $2(-39.5 + 20.0) = -39.0$ kcal/mol. Probably fortuitously, this naïve estimate is close to the (U)CCSD(T)-F12b/cc-pVTZ-F12 value in Table 2 of −43.3 kcal/mol for D_{4h}-(SiO)$_4$ → T_d-(SiO)$_4$.

Bonding in T_d-(SiO)$_4$ and in Other T_d-(AY)$_4$ Molecules. The A—Y bond lengths in Figure 2 indicate that the total amount of A—Y π bonding does not change significantly on going from a square-planar to a tetrahedral geometry in any of the $(AY)_4$ molecules in this figure. Therefore, all four T_d-$(AY)_4$ molecules in Figure 2 must have a double bond between each A atom (A = C or Si) and the Y atom attached to it (Y = O or S).

If a total of two valence electrons is used by each A atom in forming a bond to the Y atom attached to it, then each A atom has only two valence electrons to contribute to forming the six A−A bonds in each T_d-$(AY)_4$ molecule. Consequently, the A−A bonds in the tetrahedral $(AY)_4$ molecules must each consist of $2 \times 4/6 = 4/3$ electrons, rather than the pair of electrons in each of the A−A σ bonds in the planar $(AY)_4$ molecules. The electron deficient nature of the A−A bonds in the T_d molecules explains why, as shown in Figure 2, these bonds are, respectively, 0.16 and 0.21 Å longer in T_d-$(SiS)_4$ and T_d-$(SiO)_4$ than in their D_{4h} counterparts.

The nature of the lowest unoccupied (LU)MOs of the T_d-$(AY)_4$ molecules is also indicative of the electron-deficient bonding in the A—A bonds of the A_4 tetrahedra. The pair of degenerate, e LUMOs in T_d-$(SiO)_4$ are shown in Figure 6. They are Si−Si bonding but Si−O antibonding orbitals.

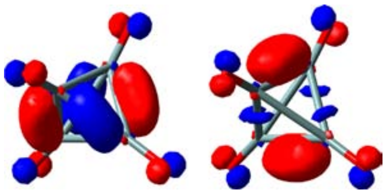

Figure 6. Pair of degenerate, e LUMOs of T_d-$(SiO)_4$.

Addition of two electrons to each of these LUMOs is required to provide the four electrons that are missing from the six, electron-deficient Si−Si bonds in T_d-$(SiO)_4$. In fact, on addition of four electrons and four protons to tetrahedral $(SiO)_4$ to form $(SiOH)_4$, the Si−O bonds lengthen by 0.143 Å, but the Si−Si bonds shorten by 0.194 Å.

Exciting two electrons into the pair of degenerate LUMOs from a degenerate pair of C−O, π-bonding MOs, to form an excited quintet state of T_d-$(SiO)_4$, requires 193.7 kcal/mol. The effect of this excitation is to lengthen the Si−O bonds by 0.083 Å and to shorten the Si−Si bonds by 0.098 Å. These changes in bond lengths are qualitatively similar but only a little over half the size of the changes that occur upon adding four electrons to the LUMOs and four protons to the resulting tetra-anion to form tetrahedral $(SiOH)_4$.

Do the Energy Changes for the $a_{2u} \rightarrow t_2^a$ MOs Control the Favorability of the Rearrangement of D_{4h}- to T_d-$(AY)_4$? What accounts for the calculated energetic favorability of the rearrangements of the square-planar silicon compounds, D_{4h}-$(SiO)_4$ and D_{4h}-$(SiS)_4$, to their tetrahedral isomers and for the contrasting energetic unfavorability of the rearrangement of the square-planar carbon compounds, D_{4h}-$(CO)_4$ and D_{4h}-$(CS)_4$, to their tetrahedral isomers?[21] As shown in Table 2, the differences in ΔE between A = Si and A = C for rearrangement of square-planar to tetrahedral $(AY)_4$ are huge, amounting to 62.0 kcal/mol for Y = O and 55.4 kcal/mol for Y = S.

A fruitful way to begin to analyze this difference between $(AY)_4$ molecules with A = Si and A = C is in terms of the second-order Jahn−Teller (SOJT) effect[18] that results in the formation of the t_2 MOs of T_d-$(AY)_4$ by mixing of the a_{2u} and b_{1g} MOs (see Figure 3) and the e_u and e_g MOs (Figures 4 and 5) of D_{4h}-$(AY)_4$.[19] As already discussed, this mixing occurs under the influence of the b_{2u} distortion that takes the square-planar geometry of D_{4h}-$(AY)_4$ to the tetrahedral geometry of T_d-$(AY)_4$. For example, the energy lowering due to mixing of the a_{2u} with the b_{1g} MO is given by the formula[18,19]

$$\Delta E_{\text{mix}} \approx \frac{[\int \psi(a_{2u})H'(b_{2u})\psi(b_{1g})d\tau]^2}{\varepsilon(a_{2u}) - \varepsilon(b_{1g})} \tag{1}$$

where $\int \psi(a_{2u})H'(b_{2u})\psi(b_{1g})d\tau$ gives the energy of mixing of these two MOs upon a b_{2u} geometry distortion, and $\varepsilon(a_{2u}) - \varepsilon(b_{1g})$ is the energy required to excite an electron from the a_{2u} to the b_{1g} MO.

Figure 7 shows the a_{2u} and the b_{1g} MOs of D_{4h}-$(CO)_4$ and the t_2^a MO of T_d-$(CO)_4$ formed from their mixing. Comparison of Figure 7 with Figure 3 immediately reveals a possible reason why a b_{2u} distortion might be much more favorable for D_{4h}-$(SiO)_4$ than for D_{4h}-$(CO)_4$. This comparison shows that the lower electronegativity of Si, compared to C, results in the π^*, a_{2u} MO having much larger coefficients on the ring atoms for A = Si than for A = C. Consequently, the square of the term $\int \psi(a_{2u})H'(b_{2u})\psi(b_{1g})d\tau$, which gives the mixing energy of the a_{2u} and b_{1g} MOs, might be expected to be much larger in D_{4h}-$(SiO)_4$ than in D_{4h}-$(CO)_4$.

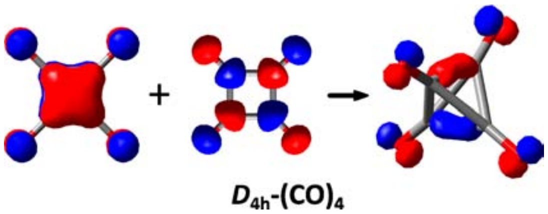

Figure 7. Second-order Jahn−Teller mixing[18,19] of the a_{2u} with the virtual b_{1g} MO of D_{4h}-$(CO)_4$, leading to the t_2^a MO of T_d-$(CO)_4$.

Our calculations also find that the excitation energy from the a_{2u} to the b_{1g} MOs is much smaller in D_{4h}-$(SiO)_4$ than in D_{4h}-$(CO)_4$. We approximated this orbital energy difference by the energy required to excite one electron from the a_{2u} MO in the 10π, $|...\psi(a_{2u})^2\rangle$, singlet state to the b_{1g} MO in the 9π, $|...\psi(a_{2u})\psi(b_{1g})(\alpha\beta - \beta\alpha)/\sqrt{2}\rangle$, singlet state. Our TD-B3LYP/6-311+g(2df) calculations found this energy difference to be only 72.0 kcal/mol in D_{4h}-$(SiO)_4$, compared to 187.4 kcal/mol in D_{4h}-$(CO)_4$.

Why is the $a_{2u} \rightarrow b_{1g}$ excitation energy calculated to be so much smaller in D_{4h}-$(SiO)_4$ than in D_{4h}-$(CO)_4$? The principle reason is that b_{1g} is a σ antibonding MO; and trigonal silicon atoms, such as those in the four-membered ring of $(SiO)_4$, are known to have very low-lying σ^* MOs.[22] Because the spatial extents of 3s AOs are significantly smaller than those of 3p AOs, the 3s−3s overlaps between silicon AOs in D_{4h}-$(SiO)_4$ are significantly smaller than the 2s−2s and 2p−2p overlaps in D_{4h}-$(CO)_4$.[23] The small size of the 3s−3s overlaps means that they contribute less to antibonding interactions in D_{4h}-$(SiO)_4$ than the 2s−2s and 2p−2p overlaps contribute in D_{4h}-$(CO)_4$.

The Si ring atoms in $(SiS)_4$ make the $a_{2u} \rightarrow b_{1g}$ excitation energy low in D_{4h}-$(SiS)_4$ too. This excitation energy is calculated to be 77.0 kcal/mol, only 5.0 kcal/mol higher than that in D_{4h}-$(SiO)_4$. Nevertheless, Table 2 shows that the transformation from a square-planar to tetrahedral geometry is less favorable by 15 kcal/mol in $(SiS)_4$ than in $(SiO)_4$.

The reason for this large difference in rearrangement energies obviously cannot be the very small difference of 5.0 kcal/mol between the a_{2u} → b_{1g} excitation energies in $\boldsymbol{D_{4h}}$**-(SiS)$_4$** and $\boldsymbol{D_{4h}}$**-(SiO)$_4$** in the denominator of eq 1. Instead, we attribute this difference to the smaller coefficients of the Si ring atoms in the a_{2u} frontier MO of square-planar $(SiS)_4$, compared to square-planar $(SiO)_4$ in the numerator of eq 1.

The greater electronegativity of O relative to S makes the coefficients on Si in the Si−Y π-bonding a_{2u} MO larger for Y = S than for Y = O, but the reverse is true in the Si−Y π-antibonding, a_{2u}, frontier MOs. The larger size of the coefficients on the ring atoms in the a_{2u}, frontier MO on substitution of Y = O for Y = S, not only in D_{4h} $(SiY)_4$ but also in D_{4h} $(CY)_4$, can be clearly seen by comparison of the a_{2u} frontier MOs of $(SiO)_4$ and $(SiS)_4$ and of $(CO)_4$ and $(CS)_4$ in Figure 1.

The larger size of the coefficients of the ring atoms in the a_{2u} frontier MOs of $(AY)_4$ for Y = O than for Y = S correlates with the larger size of the orbital energy decrease for a_{2u} → t_2^a for Y = O than for Y = S. The changes in the B3LYP MO energies[20b] for a_{2u} → t_2^a are −39.5 kcal/mol for $(SiO)_4$ versus −26.4 kcal/mol for $(SiS)_4$ and −47.7 kcal/mol for $(CO)_4$ versus −20.1 kcal/mol for $(CS)_4$. The larger size of the a_{2u} → t_2^a orbital energy decrease for $(AO)_4$ than for $(AS)_4$ correlates with the greater energetic favorability of D_{4h} → T_d for $(SiO)_4$ than for $(SiS)_4$, shown in Table 2, and with the smaller energetic unfavorability of D_{4h} → T_d for $(CO)_4$ than for $(CS)_4$, also shown in Table 2.

Similarly, the greater electronegativity of C relative to Si makes the coefficients on Si in the Si−Y π-antibonding a_{2u} MO of $\boldsymbol{D_{4h}}$**-(SiY)$_4$** larger than those for C in the C−Y π-antibonding a_{2u} MO of $\boldsymbol{D_{4h}}$**-(CY)$_4$**. The larger size of the coefficients on the Si ring atoms in these MOs, for both Y = O and Y = S, can be clearly seen in Figure 1 by comparison of the a_{2u} frontier MOs of $\boldsymbol{D_{4h}}$**-(SiO)$_4$** versus $\boldsymbol{D_{4h}}$**-(CO)$_4$** and of $\boldsymbol{D_{4h}}$**-(SiS)$_4$** versus $\boldsymbol{D_{4h}}$**-(CS)$_4$**.

Although the relative sizes of the coefficients on the ring atoms in the a_{2u} frontier MOs play an important role in the size of the numerator of eq 1, the differences between the $H'(b_{2u})$ terms are also likely to play a role if comparisons are made between forming a pair of new Si−Si bonds in $(SiO)_4$ and $(SiS)_4$ and a pair of new C−C bonds in $(CO)_4$ and $(CS)_4$. The greater lengths of Si−Si bonds, compared to C−C bonds should be reflected in the difference between the perturbed Hamiltonians, $H'(b_{2u})$, for forming these bonds. This difference between $H'(b_{2u})^{Si-Si}$ and $H'(b_{2u})^{C-C}$ could, at least in principle, offset the differences between the coefficients in the a_{2u} frontier MOs of $\boldsymbol{D_{4h}}$**-(SiO)$_4$** and $\boldsymbol{D_{4h}}$**-(CO)$_4$** and between $\boldsymbol{D_{4h}}$**-(SiS)$_4$** and $\boldsymbol{D_{4h}}$**-(CS)$_4$**.

Based on the changes in the B3LYP MO energies,[20b] in forming the t_2^a MO of the tetrahedral geometry from the a_{2u} MO of the planar geometry, the absolute value of the energy decrease is actually larger in $(CO)_4$ than in $(SiO)_4$. The orbital energy decrease is −47.7 kcal/mol in $(CO)_4$, which is 8.2 kcal/mol larger than the −39.5 kcal/mol in $(SiO)_4$. Consequently, it is not possible to argue that the reason why D_{4h} → T_d is energetically favorable for $(SiO)_4$, but not for $(CO)_4$, is that the size of the orbital energy decrease for a_{2u} → t_2^a is greater in $(SiO)_4$ than in $(CO)_4$.

On forming the t_2^a MO of the tetrahedral geometry from the a_{2u} MO of the planar geometry, the magnitude of the orbital energy decrease of −20.1 kcal/mol in $(CS)_4$ is at least smaller than that of −26.4 kcal/mol in $(SiS)_4$. However, the difference of 6.3 kcal/mol between these orbital energy decreases is an order of magnitude smaller than the difference between the total energies in Table 2 for D_{4h} → T_d in $(CS)_4$ and $(SiS)_4$.

Do the Energy Changes for the e_u → t_2 MOs Control the Favorability of the Rearrangement of D_{4h}- to T_d-$(AY)_4$? The energy changes for the a_{2u} → t_2^a MOs are not the only changes in orbital energies that occur in the formation of the t_2 MOs in the rearrangement of $\boldsymbol{D_{4h}}$- to $\boldsymbol{T_d}$**-(AY)$_4$**. The orbital energy changes in forming the t_2^b and t_2^c MOs from the e_u MOs of the D_{4h} geometries must also play a role in determining the energetic favorability of this reaction.

As already discussed, the geometry change from D_{4h} to T_d is destabilizing for the e_u MOs because they are strongly antibonding between the non-nearest-neighbor atoms across the four-membered rings. In fact, as already noted, the B3LYP energies of the e_u MOs of $\boldsymbol{D_{4h}}$**-(SiO)$_4$** increase by a total of 2 × 10.0 = 20.0 kcal/mol in forming the t_2^b and t_2^c MOs of $\boldsymbol{T_d}$**-(SiO)$_4$**. However, the increase in the B3LYP energies of the e_u MOs of $\boldsymbol{D_{4h}}$**-(CO)$_4$** is much larger, amounting to 2 × 22.6 = 45.2 kcal/mol.[20b]

Using the changes in the B3LYP orbital energies for forming the three, doubly occupied, t_2 MOs of $\boldsymbol{T_d}$**-(SiO)$_4$**, the total energy decrease is ΔE_T = 2 × (−39.5 + 20.0) = −39.0 kcal/mol. In $(CO)_4$, the much larger rise in the energies of the e_u MOs almost cancels the slightly larger energy decrease in the energy of the a_{2u} MO, making the total energy change ΔE_T = 2 × (−47.7 + 45.2) = −5.3 kcal/mol. Thus, as shown schematically in Figure 8, when the energy changes on forming all three of the t_2 MOs of the T_d geometries are taken into account, the net changes in the sums of orbital energies rationalize, at least qualitatively, why the formation of $\boldsymbol{T_d}$**-(SiO)$_4$** from $\boldsymbol{D_{4h}}$**-(SiO)$_4$** is much more energetically favorable than the formation of $\boldsymbol{T_d}$**-(CO)$_4$** from $\boldsymbol{D_{4h}}$**-(CO)$_4$**.[24]

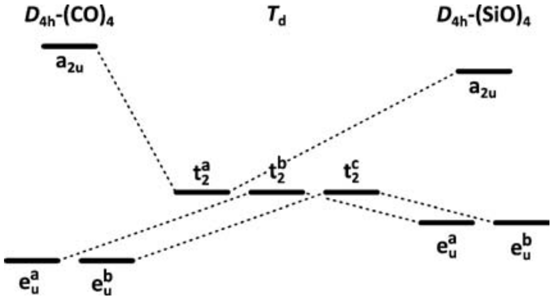

Figure 8. Schematic depiction of the changes in the energies of the a_{2u} and e_u MOs of $\boldsymbol{D_{4h}}$**-(CO)$_4$** and $\boldsymbol{D_{4h}}$**-(SiO)$_4$** on forming the t_2 MOs of the tetrahedral molecules. The t_2 MOs of $\boldsymbol{T_d}$**-(CO)$_4$** and $\boldsymbol{T_d}$**-(SiO)$_4$** actually do, accidentally, have the same B3LYP orbital energies.

Why is the energy increase for e_u → t_2 so much larger in $(CO)_4$ than in $(SiO)_4$? The e_u MOs in $\boldsymbol{D_{4h}}$**-(CO)$_4$** are shown in Figure 9. They can be compared with those in Figure 4 for $\boldsymbol{D_{4h}}$**-(SiO)$_4$**. The e_u MOs in these two molecules look very similar;

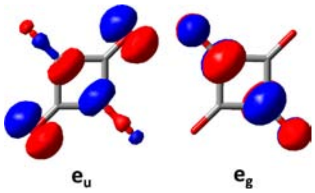

Figure 9. One member of the occupied e_u and virtual e_g orbitals of $\boldsymbol{D_{4h}}$**-(CO)$_4$**.

therefore, a large difference between the coefficients at the ring atoms in these orbitals does not provide an answer to the question of why the increase in the energy for $e_u \rightarrow t_2$ is so much higher in $(CO)_4$ than in $(SiO)_4$.[25]

It could be argued that the energy increase is much larger in $(CO)_4$ than in $(SiO)_4$ because the C−C bond lengths in **T_d-$(CO)_4$** of 1.757 Å are much shorter than the Si−Si bond lengths of 2.545 Å in **T_d-$(SiO)_4$**. This is of course true, but, by the same argument, the decrease in the energy of the a_{2u} MO is slightly larger in $(CO)_4$ than in $(SiO)_4$ because the C−C bond lengths in **T_d-$(CO)_4$** are much shorter than the Si−Si bond lengths in **T_d-$(SiO)_4$**.

If the orbital energy changes for **D_{4h}-$(CO)_4$ → T_d-$(CO)_4$** were recomputed at C−C bond lengths of 2.545 Å in **T_d-$(CO)_4$**, the same lengths as those of the Si−Si bonds in **T_d-$(SiO)_4$**, the energy changes in the a_{2u} and e_u MOs of $(CO)_4$ would both be much smaller, but the overall energy changes would still provide less net stabilization for $D_{4h} \rightarrow T_d$ in $(CO)_4$ than in $(SiO)_4$. However, the rationalization of the greater stabilization of $(SiO)_4$ would change from focusing on the smaller destabilization of $e_g \rightarrow t_2$ in $(SiO)_4$ to the greater stabilization of $a_{2u} \rightarrow t_2$ in $(SiO)_4$.

Rather than formulate an explanation of the greater stabilization of $(SiO)_4$, relative to $(CO)_4$, on the basis of an imagined universe in which C−C and Si−Si bond lengths are the same, we offer a different type of explanation of the smaller energy increase for $e_g \rightarrow t_2$ in $(SiO)_4$ than in $(CO)_4$. Our explanation is based on a comparison of the e_u and e_g $(SiO)_4$ MOs, shown in Figures 4, with the e_u and e_g $(CO)_4$ MOs shown in Figure 9.

Although it is true that the e_u MOs in **D_{4h}-$(SiO)_4$** and in **D_{4h}-$(CO)_4$** appear to be quite similar, the e_g π MOs with which the e_u σ MOs mix are different. The e_g π MOs of $(AO)_4$ (A = Si or C) are A−O antibonding, as is the case with the a_{2u} π MOs. In both the a_{2u} and e_g antibonding π MOs, the larger electronegativity difference between Si and O than between C and O makes the coefficients on the ring atoms much larger in **D_{4h}-$(SiO)_4$** than in **D_{4h}-$(CO)_4$**.

Consequently, the e_u π MOs can mix more strongly with the e_g σ MOs in **D_{4h}-$(SiO)_4$** than in **D_{4h}-$(CO)_4$** when these molecules are transformed from D_{4h} to T_d symmetry. As already discussed, this mixing ameliorates the antibonding interactions that destabilize the e_u MOs as the cross-ring distances decrease on going from a D_{4h} to a T_d geometry. Thus, the larger coefficients in the e_g π MOs of **D_{4h}-$(SiO)_4$** than of **D_{4h}-$(CO)_4$** provide a rationale for why the energies of the e_u MOs increase less in $(SiO)_4$ than in $(CO)_4$ on going from a D_{4h} to a T_d geometry.

How To Design $(AY)_4$ Molecules that Will Prefer T_d Geometries. If larger coefficients on the ring atoms in both the a_{2u} and e_u A−Y π antibonding MOs do, in fact, favor rearrangement of an $(AY)_4$ molecule from a D_{4h} to a T_d geometry, then it should be possible to design other molecules which, like $(SiO)_4$, will prefer a T_d to a D_{4h} geometry. Increasing the electronegativity difference between A and Y should increase the coefficients on the ring atoms in both the a_{2u} and e_u A−Y π antibonding MOs and thus transform an $(AY)_4$ molecule like $(CO)_4$, which prefers a D_{4h} equilibrium geometry, into a molecule like $(SiO)_4$, which prefers a T_d equilibrium geometry.

Such a transformation of $(CO)_4$ is easy to imagine by moving a proton from the nucleus of carbon to the nucleus of oxygen. This imagined nuclear reaction would transform $(CO)_4$ into the isoelectronic $(BF)_4$ molecule. The electronegativity difference between B and F is certainly much larger than that between C and O. Therefore, $(BF)_4$ is predicted to be much more likely than $(CO)_4$ to prefer a T_d to a D_{4h} geometry.

Shown in Figure 10 are the a_{2u} and one of the e_g MOs of $(BF)_4$. They can be compared with the a_{2u} and e_g MOs of the isoelectronic $(CO)_4$ molecule, which are shown in, respectively, Figures 7 and 9. Decreasing the electronegativity of the ring atoms, A, in $(AY)_4$ by substituting B for C and increasing the electronegavity of the exocyclic Y atoms by substituting F for O has the anticipated effect of increasing the coefficients of the AOs on the ring atoms in both of these A−Y π antibonding MOs.

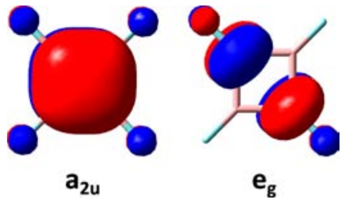

Figure 10. Representation of a_{2u} and one of the e_g MOs of square-planar $(BF)_4$.

As expected, the effect of the larger coefficients on the ring atoms in the a_{2u} and e_g MOs of $(BF)_4$, compared to $(CO)_4$, is to favor the rearrangement from a square-planar to a tetrahedral geometry in $(BF)_4$. Table 3 shows that, in stark contrast to the case in the isoelectronic $(CO)_4$ molecule, the transformation of $(BF)_4$ from a square-planar to a tetrahedral geometry is calculated to be energetically favorable by −56.9 kcal/mol.[26]

Table 3. CCSD(T)-F12/cc-pVTZ-F12//B3LYP/6-311+G(2df,p) Energy Change (ΔE, kcal/mol) on Going from the D_{4h} to the T_d Geometry of $(BF)_4$, $(BCl)_4$, and $(BH)_4$, Starting from the Singlet State with the a_{2u} MO Doubly Occupied

molecule	ΔE
$(BF)_4$[a]	−56.9
$(BCl)_4$[b]	−63.0
$(BH)_4$[c]	−98.4

[a]The lowest electronic state in the square-planar molecule is the triplet, which is 5.9 kcal/mol lower in energy than the singlet state in which the a_{2u} MO is doubly occupied. [b]The lowest electronic state in the square-planar molecule is the triplet. The singlet states in which the a_{2u} and b_{2g} MOs are doubly occupied are, respectively, 7.2 and 3.1 kcal/mol higher in energy than the triplet. [c]The lowest electronic state in the square-planar molecule is the singlet in which the b_{2g} MO is doubly occupied. The triplet and the singlet state in which the a_{2u} MO is doubly occupied are higher in energy by, respectively, 6.8 and 9.5 kcal/mol.

Although Cl is less electronegative than F, Cl is actually a slightly worse π donor than F. Therefore, the a_{2u} π^* MO should be slightly more localized on the ring atoms in $(BCl)_4$ than in $(BF)_4$. Consequently, the transformation from a square-planar to a tetrahedral geometry is expected to be energetically more favorable in $(BCl)_4$ than in $(BF)_4$, and the computational results in Table 3 confirm this prediction.[26]

Fortunately, unlike $(SiO)_4$ and $(BF)_4$, $(BCl)_4$ is a known molecule.[27] Consistent with our qualitative arguments and with the computational results in Table 3, $(BCl)_4$ is known to have a tetrahedral geometry.[28,29]

With no π-donor substituents attached to boron in square-planar $(BH)_4$, the empty a_{2u} and e_u π MOs are completely localized on the ring atoms. Therefore, removing two electrons from the b_{2g} σ orbital of the four-membered ring and placing them in the a_{2u} π MO should make the transformation from square-planar to tetrahedral even more favorable in $(BH)_4$ than in $(BCl)_4$, and the results in Table 3 confirm this prediction.[26,30]

Since increasing the electronegativity of Y and decreasing the electronegativity of A makes $(CO)_4$ into $(BF)_4$, an isoelectronic $(AY)_4$ molecule that is unstable toward a distortion from D_{4h} to T_d symmetry, then decreasing the electronegativity of Y and increasing the electronegativity of A should have the opposite effect in $(SiO)_4$. Therefore, it seems possible that, unlike $(SiO)_4$, the isoelectronic $(PN)_4$ molecule might be stable toward a distortion from D_{4h} to T_d symmetry.

In order to test this hypothesis, we optimized the geometry of $\boldsymbol{D_{4h}}$**-(PN)$_4$** and did a vibrational analysis, to see if the b_{2u} distortion from a square-planar toward a tetrahedral geometry would be found to have a real, rather than an imaginary frequency. Surprisingly, the b_{2u} frequency was found to be 543i cm^{-1}, more than twice the size of the imaginary frequency of $\boldsymbol{D_{4h}}$**-(SiO)$_4$**. However, following the b_{2u} distortion of $\boldsymbol{D_{4h}}$**-(PN)$_4$** did not lead to $\boldsymbol{T_d}$**-(PN)$_4$** but, instead, to four molecules of PN.[31]

Fragmentation of $(AY)_4$ → 4 AY. The fragmentation of the D_{4h} geometry of any $(AY)_4$ molecule is an orbital-symmetry forbidden reaction[32] because this reaction requires a crossing between a filled b_{2g} or a_{2u} frontier MO and an empty b_{1g} MO.[4] However, as has already been discussed, upon a b_{2u} distortion, a_{2u} and b_{1g} mix. Consequently, although the reaction $\boldsymbol{D_{4h}}$**-(AY)$_4$** → 4 AY is forbidden by orbital symmetry, the reaction $\boldsymbol{T_d}$**-(AY)$_4$** → 4 AY is allowed.[32]

Table 4 shows the reason that T_d geometries of $(AY)_4$ molecules can be optimized for A = C and Si and Y = O and S and for A = B and Y = F, Cl, and H is that, for six of these seven $(AY)_4$ molecules, fragmentation is calculated to be endothermic. The increase in A–Y π bonding that occurs on fragmentation does not compensate for breaking the six A–A bonds in $\boldsymbol{T_d}$**-(AY)$_4$**, even though these bonds are electron deficient and contain a total of only eight electrons.

Table 4. Calculated Energy Changes (ΔE) for T_d-$(AY)_4$ → 4AY and the Energy Barriers ($\Delta E^\ddagger$) Computed for These Reactions at the CCSD(T)-F12b/cc-pVTZ-F12//B3LYP/6-311+g(2df,p) Level of Theory, with the B3LYP/6-311+g(2df,p) Energies in Parentheses

AY	ΔE (kcal/mol)	$\Delta E^\ddagger$(kcal/mol)
CO	−68.6 (−57.9)	−0.9[a] (1.7)
CS	71.2 (84.8)	98.4 (110.5)
SiO	16.2 (1.4)	24.1 (14.5)
SiS	47.7 (29.7)	46.4[b] (34.5)
BF	169.7 (177.5)	177.2 (186.9)
BCl	238.7 (243.1)	242.8 (250.5)
BH	336.7 (343.1)	344.3 (352.9)

[a] $\Delta E^\ddagger$ is negative because the CCSD(T)-F12b energy was computed at the B3LYP geometry of the transition structure. [b] $\Delta E^\ddagger$ is less than ΔE because the CCSD(T)-F12 energy was computed at the B3LYP geometry of the transition structure.

Only for $\boldsymbol{T_d}$**-(CO)$_4$** is the fragmentation reaction calculated to be energetically favorable. The fact that this very exothermic reaction is computed to have a small (1.7 kcal/mol) B3LYP/6-311+g(2df) energy barrier is what allows the geometry of $\boldsymbol{T_d}$**-(CO)$_4$** to be optimized at this level of theory.

SUMMARY AND CONCLUSIONS

Our calculations find that the rearrangement from a square-planar to a tetrahedral equilibrium geometry is energetically favorable and barrierless for the 10π singlet state of $(SiO)_4$ but not for the 10π singlet state of $(CO)_4$. Substitution of sulfur for oxygen is calculated to make the rearrangement of $\boldsymbol{D_{4h}}$**-(SiS)$_4$** less energetically favorable than that of $\boldsymbol{D_{4h}}$**-(SiO)$_4$**, and the rearrangement of $\boldsymbol{D_{4h}}$**-(CS)$_4$** is calculated to be even more energetically unfavorable than that of $\boldsymbol{D_{4h}}$**-(CO)$_4$**.

The energetic favorability/unfavorability of the D_{4h} → T_d rearrangement of $(AY)_4$ can be understood in terms of the second-order Jahn–Teller effect[18] and the mixing of the filled a_{2u} and e_u orbitals of the D_{4h} geometry with, respectively, the empty b_{1g} and e_g MOs under the influence of a b_{2u} vibration.[19] The extent to which the filled a_{2u} and empty e_g π MOs are localized on the ring atoms, so that they can mix strongly with, respectively, the empty b_{1g} and filled e_u σ MOs of the planar, four-membered ring in forming the triply degenerate t_2 MOs of the T_d geometry, appears to be a crucial factor in determining the energetic favorability of the D_{4h} to T_d rearrangement.[33]

The increase in the localization of the a_{2u} and e_g π MOs on the ring atoms with an increasing difference between the electronegativities of A and Y in $\boldsymbol{D_{4h}}$**-(AY)$_4$** helps to explain why $(SiO)_4$ rearranges from a square-planar to a tetrahedral geometry but $(CO)_4$ does not. Decreasing localization of these two π MOs on the ring atoms with a decreasing difference between the electronegativities of A and Y in $\boldsymbol{D_{4h}}$**-(AY)$_4$** rationalizes why substitution of S for O reduces the preference for a T_d geometry in $(SiS)_4$ from that in $(SiO)_4$ and enhances the preference for a D_{4h} geometry in $(CS)_4$, relative to $(CO)_4$. The much greater difference between the electronegativities of B and F, compared to C and O, explains why $(BF)_4$ is calculated to have a tetrahedral equilibrium geometry;[26] whereas, the equilibrium geometry of the isoelectronic $(CO)_4$ is square-planar.

Since F is a better π donor than Cl, the a_{2u} frontier MO is more localized at the ring atoms in $\boldsymbol{D_{4h}}$**-(BCl)$_4$** than in $\boldsymbol{D_{4h}}$**-(BF)$_4$**. This is the reason why the preference for a tetrahedral equilibrium geometry is computed to be higher in $(BCl)_4$ than in $(BF)_4$. Experimentally, $(BCl)_4$ is known to have a T_d equilibrium geometry.[28]

In $(BH)_4$, the a_{2u} orbital is completely localized at the ring atoms. This explains why the preference for a tetrahedral over a square-planar equilibrium geometry is computed to be much larger in $(BH)_4$ than in $(BF)_4$ or $(BCl)_4$.[30]

Finally, substitution of P for Si and N for O in $(SiO)_4$ would be expected to reduce the preference for a tetrahedral equilibrium geometry in $(PN)_4$, compared to the isoelectronic $(SiO)_4$. We were, unfortunately, unable to test this prediction because, upon a b_{2u} distortion from D_{4h} symmetry, $(PN)_4$ is calculated to fragment to four molecules of PN.[31]

An interesting feature of the bonding in the tetrahedral geometries of the $(AY)_4$ molecules for A = C and Si and Y = O and S, is indicated by the A–Y bond lengths, which are computed to be close to those in the square-planar geometries. This finding indicates that the amount of A–Y π bonding is nearly the same in both D_{4h} and T_d geometries, implying that the six A–A bonds in $\boldsymbol{T_d}$-**(AY)$_4$** are electron deficient, each involving only 4/3 of an electron. The electron deficient nature of the A–A bonds in $\boldsymbol{T_d}$-**(AY)$_4$** explains why these bonds are calculated to be substantially longer than the A–A bonds in $\boldsymbol{D_{4h}}$-**(AY)$_4$**.

The recognition that the MOs of $\boldsymbol{T_d}$-**(SiO)$_4$** have much in common with the MOs of $(BF)_4$ and of $(BH)_4$ suggests that the electron-deficient bonding in other *closo*-boranes, $(BH)_n$, might be mimicked by the bonding in other *closo*-polysilanones $(SiO)_n$. We are in the process of testing the merits of this suggestion with additional calculations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed depictions of the effects of mixing of the a_{2u} and e_u MOs of $(SiO)_4$, tables comparing B3LYP-Kohn–Sham and HF orbital energies and total energies, discussions of the changes in the orbital energies of $(BF)_4$, $(BCl)_4$ and $(BH)_4$ and of models for the changes in the strain energies in $(SiO)_4$ and $(CO)_4$ on $D_{4h} \rightarrow T_d$, (U)CCSD(T)-F12b/cc-pVTZ-F12 and (U)B3LYP/6-311+G(2df,p) energies and (U)B3LYP/6-311+G(2df,p) optimized geometries for all the molecules in this manuscript, MO correlation diagrams for $D_{4h} \rightarrow T_d$ in $(SiO)_4$, $(CO)_4$, and the e_u and t_2 MOs of $(SiS)_4$ and $(CS)_4$. (14 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) The doubly occupied, A–Y bonding a_{2u}, π MO of square-planar $(AY)_4$ is, of course, also mixed with the b_{1g} σ* MO by a b_{2u} geometry distortion.

(17) The corresponding MOs of $\boldsymbol{T_d}$-**(SiS)$_4$** are available in Table S2 of the Supporting Information.[11]

(18) See, inter alia (a) Öpik, U.; Pryce, M. H. L. *Proc. R. Soc. London* **1957**, *A238*, 425. (b) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164. (c) Pearson, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 4947. (d) Pearson, R. G. *J. Mol. Struct.* **1983**, *103*, 25. For a recent review see (e) Bersuker, I. B. *Chem. Rev.* **2013**, *113*, 1351.

(19) When the second-order Jahn–Teller (SOJT) effect is used to describe the effect on vibrational frequencies of mixing low-lying excited states into the ground state wave function upon molecular distortions, the resulting decreases in frequencies are often said to be due to "vibronic coupling" between the states that are mixed. However, the mixing of the ground state with an excited state that differs from it by a one-electron excitation is largely due to mixing between the MO from which the electron is removed and the MO into which the electron is excited. Therefore, the SOJT effect/vibronic coupling can be qualitatively described in terms of mixing between MOs, rather than between electronic states, provided that the differences between the energies of the ground and singlet excited states are used for the energy differences between the MOs that are mixed.[18]

(20) The changes in the Hartree–Fock (HF)/6-311+g(2df,p) energies of the a_{2u} and e_g MOs are, respectively, −69.0 kcal/mol and 2 × 15.7 = 31.4 kcal/mol. (b) Complete tables of the changes in the HF and B3LYP energies of the a_{2u} and eg MOs for all the $(AY)_4$

molecules that are discussed in this paper are given in Tables S1 and S2 of the Supporting Information.[11] As expected (Stowasser, R.; Hoffmann, R. *J. Am. Chem. Soc.*, **1999**, 121, 3414), the changes in the HF orbital energies are related, approximately linearly, to the changes in the B3LYP orbital energies, with the HF MO energy changes being about 50% larger than the B3LYP MO energy changes. Thus, the qualitative conclusions drawn from either set of orbital energy changes are the same. We have somewhat arbitrarily chosen to cite the changes in the B3LYP orbital energies in the text, but only because, as shown Tables S1 and S2, the changes in the B3LYP total energies for $D_{4h} \rightarrow T_d$ are much closer than the changes in the HF total energies to the CCSD(T) values in Table 2

(21) As discussed on page S4 of the Supporting Information, a lower increase in strain energy in $(SiO)_4$ than in $(CO)_4$ on going from a square-planar to a tetrahedral geometry does not appear to provide a viable explanation for the very large energy difference between this rearrangement of these two molecules.

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(25) Although the highest occupied e_u MOs in $\boldsymbol{D_{4h}}$-$\mathbf{(CO)_4}$ and $\boldsymbol{D_{4h}}$-$\mathbf{(SiO)_4}$ are very similar, they are very different from the highest occupied e_u MOs in $\boldsymbol{D_{4h}}$-$\mathbf{(CS)_4}$ and $\boldsymbol{D_{4h}}$-$\mathbf{(SiS)_4}$. As shown in Figure S4 of the Supporting Information, the highest energy e_u MOs in the latter two molecules are largely comprised of 3p AOs on sulfur, and the coefficients on the ring atoms are very small. Consequently, the decrease in distances across the four-membered ring that occur upon the transformation from a square-planar to a tetrahedral geometry causes only small energy increases of, respectively, 5.6 and 5.2 kcal/mol in the e_u MOs of $\boldsymbol{D_{4h}}$-$\mathbf{(CS)_4}$ and $\boldsymbol{D_{4h}}$-$\mathbf{(SiS)_4}$.

(26) Previous calculations, reported in Swanton, D. J.; Ahlrichs, R. *Theor. Chim. Acta* **1989**, *75*, 163 , of the energies for the $D_{4h} \rightarrow T_d$ isomerizations of $(BF)_4$, $(BCl)_4$, and $(BH)_4$, starting with the D_{4h} singlet state in which the b_{2g} MO is doubly occupied and the a_{2u} MO is empty, gave results that are qualitatively similar to those in Table 3.

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(31) We calculate ΔE for the fragmentation of $\boldsymbol{D_{4h}}$-$\mathbf{(PN)_4}$ to four PN molecules to be −111.7 kcal/mol.

(32) For a review of reactions that are forbidden or allowed by orbital symmetry, see Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed.* **1969**, *8*, 781.

(33) The degree to which the a_{2u} π and b_{2g} σ MOs are localized at the ring atoms, A, in $\boldsymbol{D_{4h}}$-$\mathbf{(AY)_4}$ also determines the relative energies of these two MOs and, hence, the energy of the triplet, relative to the lowest energy closed-shell singlet.[6]