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Structural Isomers of Dihalosilanones. Theoretical Determination of Their Geometries, Spectroscopic Constants, and Potential Energy Surfaces

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The geometries and spectroscopic constants of the dihalosilanones, F_2SiO, Cl_2SiO, Br_2SiO, and I_2SiO, and their *cis*- and *trans*-XSiOX isomers were calculated by high-level computations. The potential energy surfaces of the isomerization reactions were investigated and the transition-state structures determined, together with the isomerization and activation energies and enthalpies. It was shown that, in contrast to silanone and the hydroxysilylenes, the dihalosilanones are much more stable than their other structural isomers. Thus, even at several thousand kelvin temperatures, a common condition inside a metal halide lamp, the presence of appreciable amounts of the *cis*- and *trans*-BrSiOBr and ISiOI isomers is unlikely.

Introduction

Silanone, H_2SiO, and its two isomers, *cis*- and *trans*-hydroxysilylene, *cis*-HSiOH, and *trans*-HSiOH, have been studied extensively by computations (see refs 1−7 and references therein). There has been some controversy about which of the isomers is the most stable, but the latest high-level computations suggest that silanone, H_2SiO, is the global minimum, being about 0.5 kcal/mol more stable than *cis*-HSiOH, which, in turn, is only about 0.05 kcal/mol[6] or 0.04(3) kcal/mol[7] more stable than the trans isomer. All three of them were observed experimentally by matrix isolation infrared spectroscopy[8,9] and high-resolution rotational spectroscopy.[10,11]

Halogen derivatives of H_2SiO have also been experimentally observed by matrix isolation infrared spectroscopy, F_2SiO[12] and Cl_2SiO.[13,14] The possible formation of the bromine and iodine analogues have also come up in connection with studying the corrosion in metal halide lamps. It has been shown by mass spectrometry[15,16] and computations[16] that Br_2SiO and I_2SiO molecules are formed due to chemical transport reactions in metal halide lamps. Computational studies of difluorosilanone[17] and the X_2SiO (X = F, Cl, Br) molecules[18] were published earlier. No computational studies have yet appeared on I_2SiO.

The structural isomers and relative stabilities of the dihalosilanones have not been studied and we decided to perform such a study and compare its results with the well-known silanone and hydroxysilylene structures. We have also calculated the transition structures between the different isomers of dihalosilanones.

Computational Details

All computations were performed with the Gaussian03[19] program package. Full geometry optimizations were carried out for the X_2SiO and XSiOX molecules, for the latter with different starting dihedral angles, covering the cis and trans positions as well as intermediate gauche conformations about the central SiO bond. All these optimizations ended up with either the cis or the trans isomer; therefore, further calculations on the XSiOX isomers were only done for the *cis*-XSiOX and *trans*-XSiOX molecules.

The different molecules in the series contain halogen atoms of very different sizes; therefore, we had to find a basis set combination that is good enough for the lightest molecules but at the same time is still affordable for those with the heaviest atoms. On the basis of a large number of preliminary computations, and also on our experience with the computations of the Br_2SiO and I_2SiO systems and their fragments,[16] we decided to use the B3LYP density functional method. Martin[6] also found that the B3LYP method performed very well in his calculations of silanone and its isomers. For the smaller atoms, the 6-311G(d,p) type basis sets were chosen. For the large bromine and iodine atoms, we calculated the geometry of the X_2SiO molecules with both the 6-311G(d,p) all-electron basis set and with a Stuttgart-type quasirelativistic effective core potential (ECP). The results for the bromine derivative were the same with the two approaches, so we decided to use the all-electron basis set. For I_2SiO, however, there was a large difference in the bond lengths; the all-electron basis calculation yielded much longer bonds than the ECP calculation (ECP: $r_{Si-I} = 2.426$ Å; all-electron basis: $r_{Si-I} = 2.446$ Å). This could be an indication of the importance of relativistic effects for molecules containing iodine, since the quasirelativistic ECP includes the major relativistic effects. Therefore, for the iodine derivatives, the multielectron adjusted quasirelativistic effective core potential of the Stuttgart group, covering 46 electrons ([Kr]$4d^{10}$)[20] with an associated valence electron basis of the type (14s10p2d1f)/[3s3p2d1f],[21] was used. Table 1 gives the geometrical parameters of all dihalosilanones and their *cis*-XSiOX and *trans*-XSiOX isomers together with those of silanone. Figure 1 shows the minimum energy geometries together with the transition-state structures.

To make sure that our conclusions about the geometries and relative energies are correct, we performed a series of calculations with various methods and basis sets on the lighter halogen derivatives and on the well-known silanone as well as on their isomers. The results are shown in Table 2, together with relevant data from the literature. First, we checked the suitability of our

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TABLE 1: Calculated Geometrical Parameters of Different Isomers of Silanone and Dihalosilanones, X_2SiO (X = H, F, Cl, Br, I) at the B3LYP/6-311G(d,p) Level of Theory (Bond Lengths in Å, Angles in Degrees)[a,b]

	r(Si−O)	r(Si−X1)	r(O−X2)	α(X1−Si−O)	α(Si−O−X2)	∠D[c]
			X_2SiO[d]			
H_2SiO	1.528[e]	1.483		124.3		
F_2SiO	1.510	1.586		127.9		
Cl_2SiO	1.517	2.030		125.7		
Br_2SiO	1.520	2.199		125.0		
I_2SiO	1.524	2.426		124.2		
			cis-XSiOX			
cis-HSiOH	1.666	1.552	0.962	98.0	120.5	0.0
cis-FSiOF	1.693	1.618	1.448	103.1	118.5	0.0
cis-ClSiOCl	1.661	2.107	1.750	106.0	133.0	0.0
cis-BrSiOBr	1.646	2.287	1.898	107.6	136.6	0.0
cis-ISiOI	1.638	2.532	2.035	107.9	141.0	0.0
			trans-XSiOX			
trans-HSiOH	1.674	1.532	0.963	94.8	114.4	180.0
trans-FSiOF	1.724	1.626	1.444	92.5	105.1	180.0
trans-ClSiOCl	1.703	2.104	1.737	94.3	116.1	180.0
trans-BrSiOBr	1.690	2.285	1.876	94.7	117.2	180.0
trans-ISiOI	1.676	2.526	2.021	96.2	121.2	180.0

[a] For numbering of the halogen atoms, see Figure 1. For iodine basis set, see text. [b] For comparison with CCSD(T) computational results as well as with literature data, see Table 2. [c] Dihedral angle ∠X1−Si−O−X2. [d] C_{2v} symmetry. [e] The experimental SiO bond length is 1.515(2) Å.[11]

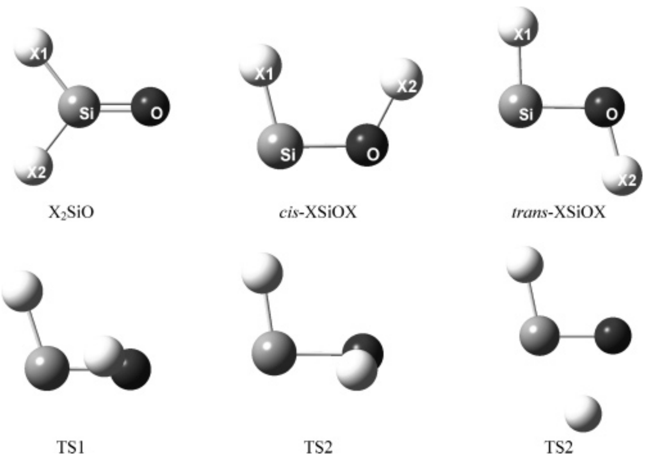

Figure 1. Molecular models of X_2SiO, *cis*-XSiOX, and *trans*-XSiOX molecules and the transition-state structures between them. The numbering of the halogen atoms is indicated on X_2SiO. The transition-state structures refer to the following relationship: TS1: from X_2SiO to *cis*-XSiOX; TS2 from *cis*- to *trans*-XSiOX; TS3: from X_2SiO to *trans*-XSiOX.

basis sets with calculating the structure of H_2SiO with the same 6-311G(d,p) basis set. Then, we computed the structures of both H_2SiO and F_2SiO with larger bases to check the reliability of our relative energies as well as the trends in the changes of geometrical parameters. The geometry of H_2SiO at the larger, 6-311G(3df,3pd) level (Si−O = 1.517 Å) compares very well with the experimental geometry of the molecule (Si−O = 1.515(2) Å)[11] and the trends in geometrical changes between H_2SiO and F_2SiO were the same as obtained with the somewhat smaller basis sets. Next, we checked how reliable the DFT method works for these systems compared with other approaches by performing ab initio calculations at the CCSD(T)/cc-pVTZ level for the X_2SiO molecules and their isomers for X = H, F, and Cl. The results of these calculations are also given in Table 2. The resulting geometries compare remarkably well with the results of the B3LYP/6-311G(d,p) level computations. This is also true for the energies; all the trends in the relative energies are the same, and their absolute values do not differ more than a few percent for the fluorine and chlorine derivatives. For H_2SiO, the CCSD(T)/cc-pVTZ calculation yields a 3.3 and 3.5 kcal/mol energy difference between H_2SiO and *cis*- and *trans*-hydroxisilylene, respectively, which is actually worse than our DFT results compared with the high-level earlier studies. Thus, we believe that our observations based on the particular level of computation used in the bulk of our investigation are reliable.

Frequency calculations were performed for all structures at the B3LYP/6-311G(d,p) computational level. The frequencies of all minimum structures are given in Table 3. Natural population analysis (NBO) was also carried out for the dihalosilanone molecules; the partial charges are given in Table 4. The dipole moments and rotational constants of all minimum structures are collected in Table 5. Finally, single-point energy calculations were performed using the above ECP with an extended (14s10p3d2f1g)/[4s4p3d2f1g] basis set combination for the iodine atom and using the aug-cc-pVQZ all-electron bases of Dunning et al.[22] for all the other atoms. The choice of the aug-cc-pVQZ basis sets was based on our extensive trial calculations on the Br_2SiO and I_2SiO systems and their fragments and on comparing the computed thermodynamic functions with those available from experiment.[16] The energies of all minimum structures are listed in Table 6.

Transition-state structures were also computed for all isomerization reactions. Their geometries were optimized using synchronous transit-guided quasi-Newton (STQ2 and STQ3) methods as implemented in Gaussian03;[23] they are given in Table 7. Their transition-state nature was verified by frequency calculations. The isomerization energies, enthalpies, and free energies, ΔE_0, $\Delta H°$, and $\Delta G°$, are given in Table 8. Finally, the activation energies and enthalpies for both forward and reverse rearrangements are given in Table 9.

Results and Discussion

Comparison of the geometrical changes in the dihalosilanone series (see Table 1) shows that the length of the Si═O bond decreases by almost 0.02 Å when the hydrogens in H_2SiO are substituted by fluorines. Further substitution with heavier halogens gradually lengthens the Si═O bond and, eventually, in I_2SiO it reaches about the same length as that in H_2SiO. A similar trend is observed among the corresponding carbon molecules. The C═O bond in F_2CO[24] is shorter by about 0.03 Å than in H_2CO.[25] Further substituting fluorine in F_2CO to chlorine the C═O bond length increases by a small amount[26]

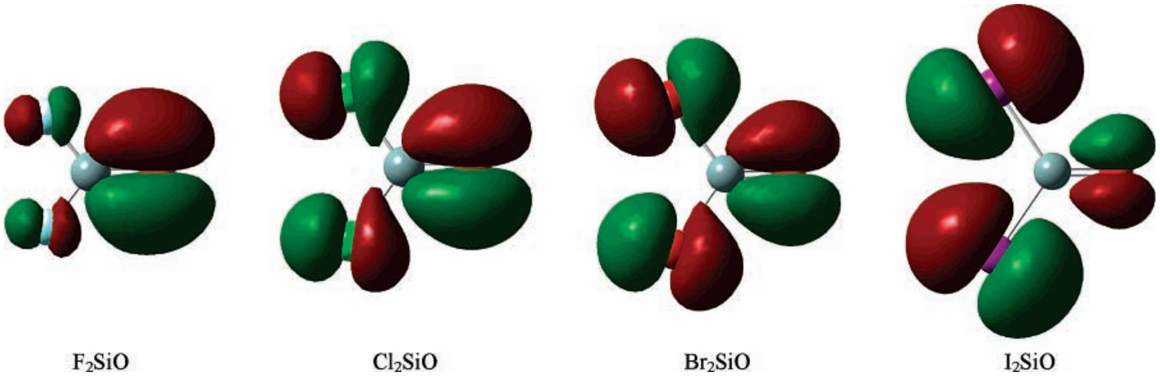
F_2SiO Cl_2SiO Br_2SiO I_2SiO

Figure 2. The HOMO of X_2SiO (X = F, Cl, Br, I) molecules.

TABLE 2: Comparison of Calculated Geometrical Parameters of Different Isomers of Silanone and Dihalosilanones, X_2SiO (X = H, F, Cl, Br) (Bond Lengths in Å; Angles in Degrees)

	method	r(Si−O)	r(Si−X1)	r(O−X2)	α(X1−Si−O)	α(Si−O−X2)	<D[a]	ref
				X_2SiO[b]				
H_2SiO	B3LYP/6-311G(3df,3pd)	1.517	1.482		124.2			this work
	CCSD(T)/cc-pVTZ	1.532	1.482		124.4			this work
	CCSD(T)/MT core VTZ	1.514	1.473		124.3			ref 6
	CCSD(T)/AVQZ+1	1.523	1.478		124.2			ref 17
F_2SiO	B3LYP/6-311(3df)	1.502	1.571		127.7			this work
	CCSD(T)/cc-pVTZ	1.515	1.573		127.9			this work
	B3LYP/6-311+G(2d)	1.506	1.575		127.7			ref 18
	MP2/6-311+G(2d)	1.515	1.572		127.7			ref 18
	CCSD(T)/AVQZ+1	1.507	1.563		127.7			ref 17
Cl_2SiO	CCSD(T))/cc-pVTZ	1.521	2.022		125.9			this work
	B3LYP/6-311+G(2d)	1.511	2.028		125.8			ref 18
	B3LYP/TZVPP	1.525	2.034		125.6			ref 14
Br_2SiO	B3LYP/6-311+G(2d)	1.513	2.204		125.1			ref 18
				cis-XSiOX				
cis-HSiOH	CCSD(T)/cc-pVTZ	1.664	1.542	0.960	98.0	116.6	0.0	this work
cis-FSiOF	CCSD(T)/cc-pVTZ	1.693	1.603	1.444	103.1	115.7	0.0	this work
cis-ClSiOCl	CCSD(T)/cc-pVTZ	1.669	2.086	1.707	105.2	128.7	0.0	this work
				trans-XSiOX				
trans-HSiOH	CCSD(T)/cc-pVTZ	1.669	1.525	0.961	94.7	112.6	180.0	this work
trans-FSiOF	CCSD(T)/cc-pVTZ	1.713	1.610	1.450	93.4	103.1	180.0	this work
trans-ClSiOCl	CCSD(T)/cc-pVTZ	1.695	2.085	1.714	95.0	112.2	180.0	this work

[a] Dihedral angle ∠X1−Si−O−X2. [b] C_{2v} symmetry.

and for the bromine analogue actually a very small decrease is observed,[27] which, however, may be just the result of different bond length representations.

Figure 2 shows the HOMO of the X_2SiO molecules, which corresponds to the Si═O double bond. The shape of the MO shows that the double-bond character of the Si═O bond decreases from the fluorine toward the iodine derivative. As the data of Table 4 show, the highly electronegative fluorine draws away electron density from silicon, which has the largest positive partial charge in F_2SiO.

The bond angle X−Si−X in the X_2SiO series decreases considerably, by about 7°, upon substitution of H by F. This is, again, in accordance with the larger electronegativity of fluorine.[28] Further substitution of fluorine by the heavier halogens gradually increases this angle as the electronegativity of the ligands decreases and their size increases. Eventually, I_2SiO has about the same bond angle as H_2SiO. The trend, again, is similar in the X_2CO series.

The SiO stretching frequency in F_2SiO is 1329 cm^{-1} at the B3LYP/6-311G(d,p) level (Table 3). The same frequency, also in a harmonic approximation, was calculated to be 1332 cm^{-1} by Breidung and Thiel,[17] which, after anharmonic corrections, gave a value of 1314 cm^{-1}, in good agreement with the experimentally observed value of 1309.4 cm^{-1}.[12] The SiO stretching frequency in Cl_2SiO is 1262 cm^{-1}, which agrees very well with the 1258 cm^{-1} value calculated in ref 14. The experimental value measured in an argon-matrix infrared experiment[13] is 1240 cm^{-1}, somewhat lower. Considering the whole X_2SiO (X = F, Cl, Br, I) series of molecules, the SiO stretching frequency gradually decreases upon substitution by the larger halogens, in agreement with the lengthening of the SiO bond. The experimental SiO stretching frequency in H_2SiO is 1202 cm^{-1},[9] which is well reproduced in the high-level computation of Martin. Our computed value of 1217 cm^{-1} is somewhat higher but considering the much lower level of computation is acceptable. Again, we would like to stress that our aim with this study was the halogen derivatives and we calculated the H_2SiO molecule and its isomers only for comparative purposes.

The silicon−oxygen bond markedly lengthens when going from a dihalosilanone to its cis or trans isomer (Table 1). The largest changes occur in the fluorine derivatives and the amount of change gradually decreases toward the heavier halogens. The difference in the SiO bond lengths in F_2SiO and *cis*-FSiOF is 0.183 Å, while the difference between I_2SiO and *cis*-ISiOI is only 0.114 Å. For H_2SiO this difference is 0.138 Å. The Si−O bond is always longer in the *trans*- than in the *cis*-XSiOX molecule, by about 0.03−0.04 Å, in each respective pair. For the HSiOH molecules, on the other hand, this difference is only 0.008 Å and is similarly small at the CCSD(T)/cc-pVTZ

TABLE 3: Vibrational Frequencies (in cm^{-1}) for X_2SiO (X = H, F, Cl, Br, I) Molecules and Their *cis*-XSiOX and *trans*-XSiOX Isomers at the B3LYP/6-311G(d,p) Level of Theory[a]

X_2SiO	A_1	B_1	B_2
H_2SiO	2223 1217 1023	712	2238 706
F_2SiO	1329 (1309.4) 809 (835) 341	349 (344.3)	972 (996.0) 321 (332.6)
Cl_2SiO	1262 (1239.9) 479 (501.1) 205	276	609 (637.5) 264 (269.0)
Br_2SiO	1244 347 130	252	504 228
I_2SiO	1229 276 90	228	438 200

XSiOX	*cis*-XSiOX		*trans*-XSiOX	
	A′	A″	A′	A″
HSiOH	3848 1913 965 850 713	657	3851 2008 948 843 800	695
FSiOF	887 842 698 408 171	197	949 843 742 326 211	162
ClSiOCl	831 512 487 328 114	184	830 601 498 228 147	119
BrSiOBr	848 434 387 269 69	178	820 525 401 155 110	98
ISiOI	880 396 334 231 50	161	841 481 349 121 83	75

[a] For iodine basis set, see text. Experimental argon-matrix frequencies of F_2SiO[12] and Cl_2SiO[13] are in parenthesis.

TABLE 4: Partial Charges from NBO Analysis for X_2SiO (X = H, F, Cl, Br, I) Molecules (*q* in e)

X_2SiO	*q*(Si)	*q*(O)	*q*(X)
H	1.45730	−1.02315	−0.21707
F	2.25410	−1.05498	−0.59956
Cl	1.64544	−1.01315	−0.31614
Br	1.49935	−1.01303	−0.24316
I	1.28273	−1.05160	−0.11556

computational level. The Si−X bonds are also longer in the cis and trans isomers compared with the X_2SiO molecules, in an increasing manner from the fluorine toward the iodine derivatives. The same observation can be made if we compare silanone with *cis*- and *trans*-hydroxysilylene. The higher stability of the four-valence state versus the two-valence state, including the destabilizing effect of lone-pair repulsions on silicon in the cis and trans isomers, may explain the observed geometrical variations.

TABLE 5: Computed Dipole Moments and Rotational Constants at the B3LYP/aug-cc-pVQZ Level[a] for X_2SiO (X = H, F, Cl, Br, I) Molecules and Their Isomers

	μ (Debye)	rotational constants (MHz)		
		A	B	C
SiO	3.2270	0	21489	21489
H_2SiO	3.7948	166788	18383	16558
cis-HSiOH	1.4532	171426	16129	14742
trans-HSiOH	1.1537	174108	16083	14723
F_2SiO	2.2528	8486	7169	3886
cis-FSiOF	1.9719	12021	4841	3451
trans-FSiOF	1.6265	24118	3511	3065
Cl_2SiO	3.0959	4828	2657	1714
cis-ClSiOCl	0.8531	6263	2064	1552
trans-ClSiOCl	1.4217	17919	1383	1284
Br_2SiO	3.3144	3694	987	779
cis-BrSiOBr	0.4820	4373	838	703
trans-BrSiOBr	2.0209	16009	561	542
I_2SiO	3.6633	3129	495	427
cis-ISiOI	0.7665	3522	451	400
trans-ISiOI	2.3673	13043	294	287

[a] For iodine basis set, see text.

TABLE 6: Computed Energies (*E*), Zero-Point Energy Corrections (ZPE), and Relative Energies at the B3LYP/aug-cc-pVQZ Level[a] for X_2SiO Molecules and Their *cis*- and *trans*-XSiOX Isomers

	E Hartree	ZPE Hartree	ΔE kcal/mol	ΔE_0[b] kcal/mol
H_2SiO	−365.981359	0.018497	0	0
cis-HSiOH	−365.984000	0.020381	1.7	0.5
trans-HSiOH	−365.984162	0.020831	1.8	0.3
F_2SiO	−564.701482	0.009389	0	0
cis-FSiOF	−564.518909	0.007300	114.6	113.6
trans-FSiOF	−564.517625	0.007367	115.4	114.5
Cl_2SiO	−1285.37104	0.007049	0	0
cis-ClSiOCl	−1285.26840	0.005591	64.4	63.7
trans-ClSiOCl	−1285.26483	0.005519	66.6	65.9
Br_2SiO	−5513.35231	0.006163	0	0
cis-BrSiOBr	−5513.26994	0.004978	51.7	51.1
trans-BrSiOBr	−5513.26286	0.004805	56.1	55.5
I_2SiO	−387.721951	0.005608	0	0
cis-ISiOI	−387.663848	0.004672	36.5	36.0
trans-ISiOI	−387.657970	0.003506	40.1	39.5

[a] For iodine basis set, see text. [b] ZPE-corrected electronic energy.

Silanone is a highly polar molecule with a dipole moment of 3.79 D (at the B3LYP/aug-cc-pVQZ level). The previously computed dipole moment is 3.82 D at the TZ2P(f,d) CCSD level.[3] The dipole moments of the halogen derivatives (see Table 5) that have negative charges on all three terminal atoms are still rather large and point in the same direction as that of H_2SiO (i.e., along the molecular axis and opposite to the SiO bond). It is largest in the iodine derivative, 3.66 D, and decreases toward the fluorine derivative, in which it is 2.25 D. The reason is simply the much longer Si−X bonds compared to the Si−H bond.

The most interesting feature of this series of molecules is the relative stability of the X_2SiO structures and their isomers (see Table 6 and Figure 3), and this is where they basically differ from silanone and its isomers. While silanone is more stable than its isomers by barely about 0.5 kcal/mol, the dihalosilanones are markedly more stable than their isomers. The relative stability is largest for F_2SiO, and it gradually decreases toward I_2SiO, but even for that molecule it is rather large. The isomerization energies between the X_2SiO and *cis*-XSiOX isomers are 113, 64, 51, and 36 kcal/mol for the F, Cl, Br, and I derivatives, respectively. Thus, halogen substitution

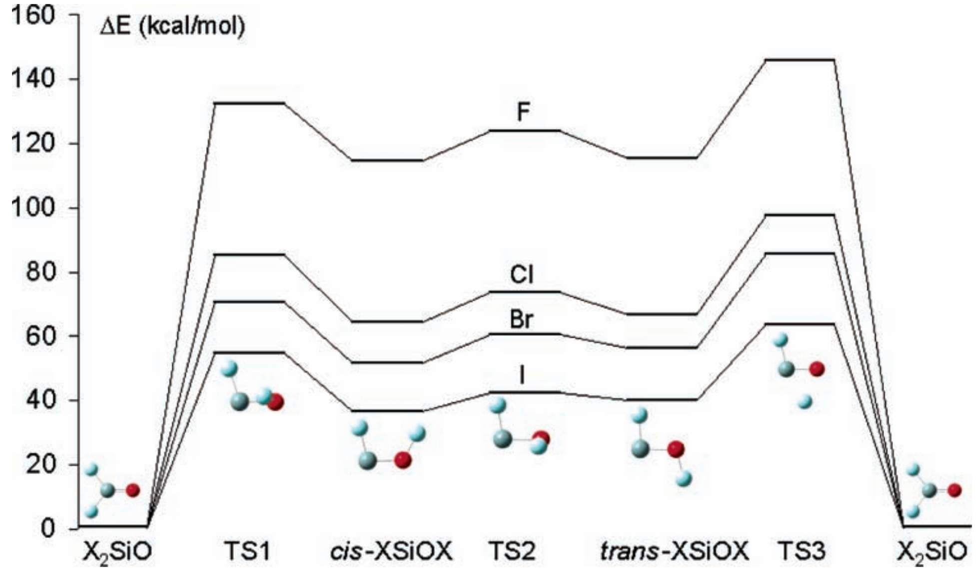

Figure 3. Energy differences between the different isomers and their transition states.

TABLE 7: Computed Geometrical Parameters of the Transition-State Structures for the Isomerization of X_2SiO to *cis*-XSiOX, to *trans*-XSiOX, and to X_2SiO Molecules at the B3LYP/6-311G(d,p) Level of Theory

	r(Si−O)	r(Si−X1)	r(O−X2)	α(X1−Si−O)	α(Si−O−X2)	∠D[a]
			TS1[b]			
F	1.675	1.620	1.735	108.6	69.3	82.8
Cl	1.624	2.102	2.079	114.9	77.3	92.2
Br	1.613	2.285	2.207	117.9	79.4	95.7
I	1.599	2.526	2.382	120.6	80.6	103.2
			TS2[c]			
F	1.775	1.623	1.477	99.0	88.3	101.6
Cl	1.687	2.120	1.716	101.7	130.2	105.5
Br	1.666	2.305	1.848	102.5	137.5	112.8
I	1.626	2.560	1.989	106.5	179.8	90.1
			TS3[d]			
F	1.636	1.631	1.872	101.7	69.2	180.0
Cl	1.635	2.447	2.190	122.2	78.0	180.0
Br	1.633	2.610	2.315	122.3	80.7	180.0
I	1.627	2.838	2.485	60.6	84.5	180.0

[a] Dihedral angle. [b] TS1: transition state from X_2SiO to *cis*-XSiOX. [c] TS2: transition state from *cis*-XSiOX to *trans*-XSiOX. [d] TS3: transition state from *trans*-XSiOX to X_2SiO.

TABLE 8: Isomerization Energies (ΔE_0), Standard Enthalpies, and Gibbs Free Energies at the B3LYP/aug-cc-pVQZ Level[a] for X_2SiO Molecules and Their *cis*- and *trans*-XSiOX Isomers

isomerization energies	ΔE_0[b] kcal/mol	$\Delta H°$[c] kcal/mol	$\Delta G°$ kcal/mol
F_2SiO → *cis*-FSiOF	113.3	113.5	112.4
F_2SiO → *trans*-FSiOF	114.1	114.4	113.3
cis-FSiOF → *trans*-FSiOF	0.8	0.9	0.9
Cl_2SiO → *cis*-ClSiOCl	63.5	63.7	62.7
Cl_2SiO → *trans*-ClSiOCl	65.7	66.0	64.9
cis-ClSiOCl → *trans*-ClSiOCl	2.2	2.3	2.2
Br_2SiO → *cis*-BrSiOBr	50.9	51.1	50.1
Br_2SiO → *trans*-BrSiOBr	55.3	55.5	54.4
cis-BrSiOBr → *trans*-BrSiOBr	4.3	4.4	4.3
I_2SiO → *cis*-ISiOI	35.9	36.0	35.1
I_2SiO → *trans*-ISiOI	39.4	39.6	38.5
cis-ISiOI → *trans*-ISiOI	3.5	3.7	3.4

[a] For iodine basis set, see text. [b] ZPE-corrected electronic energy. [c] The standard state is 1 atm at 298.15 K.

appears to considerably stabilize silanone compared with its other isomers. The activation energies for this reaction are 130, 84, 69, and 54 kcal/mol for the four different halogen derivatives, respectively. We also compared the energies of the different isomers at the CCSD(T)/cc-pVTZ level of computation to make sure that our density functional calculations are correct. The relative energies of the X_2SiO and *cis*-XSiOX isomers for the fluorine derivative are 115 versus 117 and for the chlorine derivative 64 versus 67 kcal/mol for the B3LYP versus CCSD(T) computation. Thus, we feel confident about our B3LYP results and may conclude that the dihalosilanones are both thermodynamically and kinetically much more stable than their structural isomers. Thus, even at several thousand kelvin temperatures, a common condition inside a metal halide lamp, the presence of appreciable amounts of the *cis*- and *trans*-BrSiOBr and ISiOI isomers is unlikely.

The energy differences between the cis and trans isomers are 0.9, 2.2, 4.3, and 3.5 kcal/mol for the F, Cl, Br, and I derivatives, respectively, with the cis isomer being more stable than the trans in all cases. At the CCSD(T) level, this difference is 0.4 and −1.0 kcal/mol for the F and Cl derivatives, respectively; that is, for the chlorine derivatives the trans isomer is predicted to be slightly more stable. The barrier height between the cis and trans forms is less than 10 kcal/mol in each case as shown in Table 9 and Figure 3. This is considerably smaller than the barrier toward the X_2SiO forms. Interestingly, the energy differences and barrier heights between the cis and trans forms of the halogen derivatives are not that different from the ones between *cis*- and *trans*-HSiOH. It is the relative stability of the X_2SiO form that makes a difference.

Figure 1 shows the geometries of all three isomers as well as the transition-state geometries for the fluorine derivatives. The structures of the other halogen derivatives are similar; only the bond angles increase gradually from the fluorine toward the iodine derivative. TS1 is the transition state between X_2SiO and the cis isomer. It seems that this isomerization proceeds through a transition state, in which one of the halogen atoms rotates out of the molecular plane of X_2SiO. TS2 is the transition state between the cis and trans isomers and, again, this structure is also nonplanar. Ma and Schaefer calculated[3] the transition structure for the same type of cis-to-trans transition for the silanone isomers and found the same type of structure, as did Kudo and Nagase for the trans-to-cis isomerization.[2] At the same time, while both TS1 and TS2 have nonplanar geometries, the third transition structure, TS3, the structure between the X_2SiO

TABLE 9: Activation Energies (ΔE_0) and Enthalpies ($\Delta H°$) at the B3LYP/aug-cc-pVQZ Level[a] for X_2SiO Molecules and Their *cis*- and *trans*-XSiOX Isomers

activation energies	ΔE_0[b] kcal/mol	ΔH^0[c] kcal/mol
F_2SiO → TS1 → *cis*-FSiOF	130.2	130.3
cis-FSiOF → TS1 → F_2SiO	16.9	16.8
F_2SiO → TS3 → *trans*-FSiOF	143.4	143.7
trans-FSiOF → TS3 → F_2SiO	29.3	29.3
cis-FSiOF → TS2 → *trans*-FSiOF	8.8	8.5
trans-FSiOF → TS2 → *cis*-FSiOF	8.0	7.7
Cl_2SiO → TS1 → *cis*-ClSiOCl	83.6	83.6
cis-ClSiOCl → TS1 → Cl_2SiO	20.1	20.0
Cl_2SiO → TS3 → *trans*-ClSiOCl	95.9	96.0
trans-ClSiOCl → TS3 → Cl_2SiO	30.2	30.0
cis-ClSiOCl → TS2 → *trans*-ClSiOCl	9.0	8.7
trans-ClSiOCl → TS2 → *cis*-ClSiOCl	6.8	6.5
Br_2SiO → TS1 → *cis*-BrSiOBr	69.4	69.4
cis-BrSiOBr → TS1 → Br_2SiO	18.5	18.3
Br_2SiO → TS3 → *trans*-BrSiOBr	84.5	84.5
trans-BrSiOBr → TS3 → Br_2SiO	29.2	28.9
cis-BrSiOBr → TS2 → *trans*-BrSiOBr	8.4	8.2
trans-BrSiOBr → TS2 → *cis*-BrSiOBr	4.1	3.7
I_2SiO → TS1 → *cis*-ISiOI	53.6	53.5
cis-ISiOI → TS1 → I_2SiO	17.7	17.5
I_2SiO → TS3 → *trans*-ISiOI	62.1	62.1
trans-ISiOI → TS3 → I_2SiO	22.7	22.5
cis-ISiOI → TS2 → *trans*-ISiOI	5.6	5.3
trans-ISiOI → TS2 → *cis*-ISiOI	2.0	1.6

[a] For iodine basis set, see text. [b] ZPE-corrected electronic energy. [c] The standard state is 1 atm at 298.15 K.

molecule and the trans isomer, is planar and involves the shift of the X4 halogen atom toward silicon in the molecular plane.

Summary

The molecular structure, vibrational frequencies, rotational constants, and dipole moments of all dihalosilanones, X_2SiO ($X = F, Cl, Br, I$), and their *cis*- and *trans*-XSiOX isomers were calculated by high-level computations. The potential energy surfaces of the isomerization reactions were investigated and the transition-state structures determined, together with the isomerization and activation energies, enthalpies, and free energies. The dihalosilanones, X_2SiO, are considerably more stable than their *cis*- and *trans*-XSiOX isomers. The relative stability is largest for F_2SiO with a 113 kcal/mol energy difference and it is smallest for I_2SiO with a 36 kcal/mol energy difference (for the cis isomer). The energy difference between the cis and trans isomers is only a few kcal/mol. This is in contrast to silanone, H_2SiO, and its isomers, where silanone is only about 0.5 kcal/mol more stable than the other isomers. Fluorine substitution of silanone strongly stabilizes the $Si{=}O$ double bond, which is about 0.02 Å shorter in F_2SiO than in H_2SiO. Further substitution with the heavier halogens lengthens the $Si{=}O$ bond.

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