Ab Initio Quantum Mechanical Investigation of $H_2(A_{n+1}X_{2n})H_2$ (A=C or Si, X=O or S, n = 1-2)]; Energetics, Molecular Structures, and Vibrational Frequencies

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The geometrical parameters, vibrational frequencies, and relative energies of $H_2(A_{n+1}X_{2n})H_2$ (A=C or Si, X=O or S, n = 1-2) oligomers have been investigated using high level *ab initio* quantum mechanical techniques with large basis sets. The equilibrium geometries have been optimized at the self-consistent field (SCF), the coupled cluster with single and double excitation (CCSD), and the CCSD with connected triple excitations [CCSD(T)] levels of theory. The highest level of theory employed in this study is cc-pVTZ CCSD(T). Harmonic vibrational frequencies and IR intensities are also determined at the SCF level of theory with various basis sets and confirm that all the optimized geometries are true minima. Also zero-point vibrational energies have been considered to predict the dimerization and the relative energies.

Key Words : Cyclodisiloxane, Cyclodioxetane, Cyclodithietane, *Ab initio*

Introduction

The theoretical studies for the spectroscopic properties and their relative stabilities of 1,2-dioxetane (**1**) and 1,3-dioxetane (**2**) have been extensively performed during last two decades even though the experimental observations for them have been limited because of their thermodynamic instability.[1-4] The molecular structure and spectroscopic property for 1,3-dioxetane were first investigated by Skancke in 1980.[1] Their result and several other theoretical studies showed that the 1,3-isomer is thermodynamically more stable than 1,2-isomer.[2] The relative stability and geometrical specificity of 1,3-isomer have caused to extend the interest of theoretical investigator to the relative isomers replaced C to Si and/or O to S.
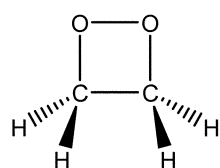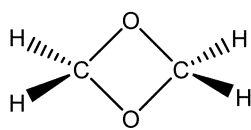
**(1)** 1,2-dioxetane   **(2)** 1,3-dioxetane
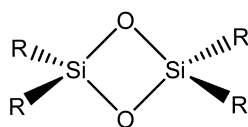
(3) 1,3-cyclodisiloxane

In 1984 and 1986, some substituted 1,3-cyclodisiloxanes (**3**) with bulky groups (R=Mes, *t*-Bu, etc.) at the silicon atom were isolated by West and coworkers and their structures were determined using X-ray diffraction techniques.[5,6] In the four-membered ring structure of substitued 1,3-cyclodisiloxanes, the Si⋯Si distance (2.31 Å) measured by the X-ray

diffraction turned out to be shorter than the normal Si-Si single bond length (2.34 Å). This experimental result has inspired many theoretical investigations and a couple of theoretical studies have well characterized about the nature of this nonbonded Si⋯Si short distance. In 1987, Grev and Schaefer[7] described this bonding between silicons as "unsupported π-bond" and after few years, Liang and Allen[8] explained using "σ-bridged-π bonding" model. More recently (2000), Ma and Inagaki proposed "cyclic (n, d, d) interaction" model, which is that the cyclic delocalization of the non-bonding lone pair electrons through two vacant d-type polarization functions of silicon atoms is responsible for the short Si⋯Si distance.[9]

Several simple disiloxanes (R=CH₃, OCH₃) were identified in the gas phase using the mass-spectrometry during the vacuum pyrolysis of 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane and its derivative.[10,11] Also some disiloxanes have been identified experimentally.[12] However the parent 1,3-cyclodisiloxane (R=H) has not been yet observed experimentally. Instead many theoretical studies have been reported. In 1985, The theoretical results for the structure, vibrational frequencies, and dimerization energy of (H₂SiO)₂ were reported by Kudo and Nagase.[13] They predicted that 1,3-cyclodisiloxane has a planar four membered ring structure and is fairly stable thermodynamically through the result at the MP2/6-31G*//HF/6-31G* level of theory. They also compared these results with those calculated for the similar cyclic dimers (H₂SiS)₂ and (H₂CO)₂ at the same level of theory. Also, molecular structures and spectroscopic properties for some simple cyclodisiloxane derivatives (R=OH, CH₃, OCH₃, *etc.*) are investigated using low level theoretical methods.[14,15]

In 1996, Gordon and coworkers reported optimized geometries at the Hartree-Fock level of theory for several conformations of larger cyclic siloxanes (H₂SiO)n, n = 3-5, which have six, eight, and ten membered rings, respectively.[16] For the consecutive four-membered ring structures,

$H_2C_{n+1}X_{2n}H_2(X=O$ or S, $n = 2$-$4)$, DFT calculations were performed by Frapper and Saillard in 2000.[17] They focused on the relative energies of CX_2-based oligomer with respect to free CX_2 to examine the possibility of the polymerization of CX_2. In more recently, Bromley *et al.* reported the calculated harmonic vibrational frequencies of four-membered rings containing two silicon and two oxygen atoms in fully connected $(SiO_2)_{12}$ clusters.[18]
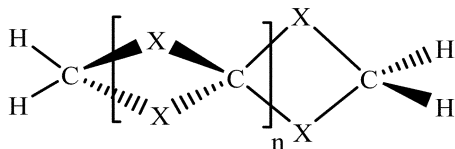
In this study, the molecular structures and relative energies for $H_2(C_{n+1}O_{2n})H_2$, $n = 1$-2 are investigated using high level *ab initio* quantum mechanical techniques with large basis sets. The highest level of theory employed is cc-pVTZ CCSD(T). The harmonic vibrational frequencies and IR intensities are also determined at the SCF level of theory with various basis sets. In addition the thermodynamic stability and molecular spectroscopic properties for small oligomers substituted by silicon(Si) instead of C and by sulfur(S) instead of O are investigated and the relative energies between the CO_2-based (or SiO_2 or CS_2) oligomers and free CO_2 are compared.

Theoretical Approach

The basis sets employed in this study are double zeta (DZ), correlation-consistent polarized valence double zeta (cc-pVDZ) sets and correlation-consistent polarized valence triple zeta (cc-pVTZ) sets for hydrogen (H), carbon (C), silicon (Si), oxygen (O), and sulfur (S). The DZ basis set consists of the standard Huzinaga[19] and Dunning[20] (9s5p/4s2p) contracted gaussian functions for C and O, the (11s7p/6s4p)[21] set for S and Si, and the (4s/2s) set for H. The cc-pVDZ basis set consists of an (4s1p/2s1p) set for H, (9s4p1d/3s2p1d) set for C and O, and the (12s8p1d/4s3p1d) set for S and Si with orbital exponents $\alpha_d(C) = 0.55$, $\alpha_d(O) = 1.185$, $\alpha_d(Si) = 0.275$, $\alpha_d(S) = 0.479$, and $\alpha_p(H) = 0.727$. The cc-pVTZ basis consists of the Dunning (5s2p1d/3s2p1d) contracted gaussian function contraction including the two sets of polarized p and a d functions with orbital exponents $\alpha_p = 1.407$, 0.388, $\alpha_d = 1.057$ for H, (10s5p2d1f/4s3p2d1f) set including the two sets of polarized d and a f functions with orbital exponents $\alpha_d = 1.097$, 0.318, $\alpha_f = 0.761$ for C and $\alpha_d = 2.314$, 0.645, $\alpha_f = 1.428$ for O, and the (15s9p2d1f/4s3p2d1f) set with orbital exponents $\alpha_d = 0.159$, 0.481, $\alpha_f = 0.336$, for Si and $\alpha_d = 0.269$, 0.819, $\alpha_f = 0.557$ for S.

The structures for the ground states of monomers, dimmers ($n = 1$) and other oligomers ($n = 2$) of $H_2(A_{n+1}X_{2n})H_2$ (A=C or Si, X=O or S) were fully optimized at the self-consistent field (SCF) level of theory using analytic techniques[22] with all basis sets described above. The SCF equilibrium geometries were subsequently used to optimize

structures at the single and double excitation coupled cluster (CCSD) level by employing analytic gradient methods.[23] The CCSD geometries of the ground state were finally used to obtain geometries optimized at the CCSD(T) levels, which are the single and double excitation coupled cluster method with the effects of connected triple excitation included perturbatively.[24] Harmonic vibrational frequencies and infrared (IR) for $H_2(A_{n+1}X_{2n})H_2$ (A=C or Si, X=O or S, n = 1-2) were evaluated using analytic second energy derivatives[25] at the SCF level with above three basis sets. All computations described above were carried out with the PSI-2[26] and PSI-3 suits of computer programs developed by Schaefer's group.

Results and Discussion

Structures.

1,3-Cyclodisiloxane[(H₂SiO)₂], dioxetane[(H₂CO)₂], and dithietane[(H₂CS)₂]: The cc-pVTZ CCSD(T) optimized geometries of the 1,3-cyclodisiloxane are shown in Figure 1. The geometrical parameters at the many different levels are listed in Table 1. The 1,3-cyclodisiloxane shows the shape of
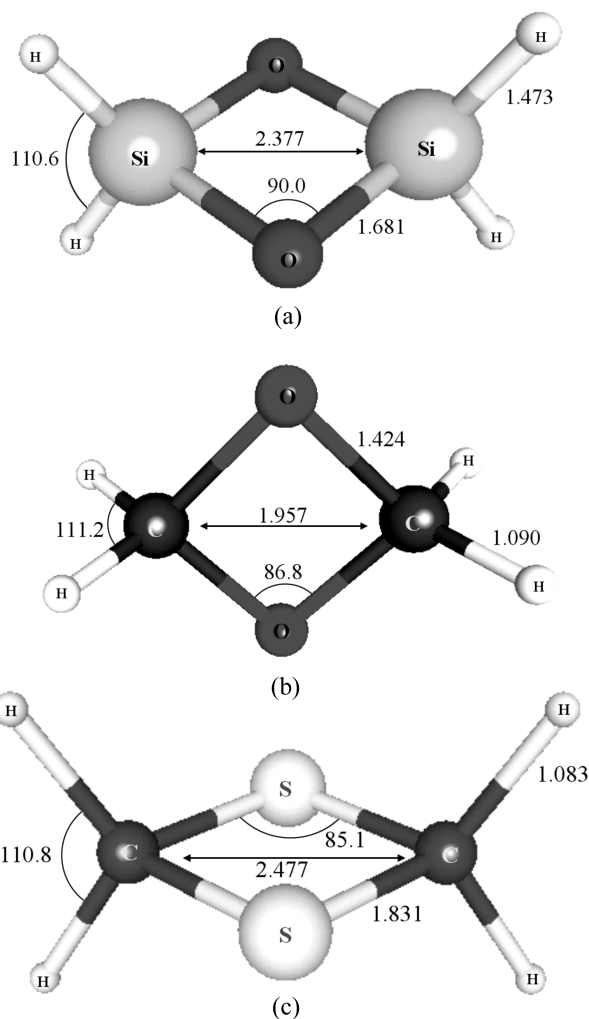
Figure 1. Optimized structures at the cc-pVTZ CCSD(T) level of theory: (a) $Si_2O_2H_4$; (b) $C_2O_2H_4$; (c) $C_2S_2H_4$.

**Table 1**. Optimized geometrical parameters of Si_2O_2H, C_2O_2H and $C_2S_2H_4$ at various levels of theory

	SCF			CCSD			CCSD(T)		
	DZ	cc-pVDZ	cc-pVTZ	DZ	cc-pVDZ	cc-pVTZ	DZ	cc-pVDZ	cc-pVTZ
					$Si_2O_2H_4$					
R(Si-O)	1.741	1.697	1.660	1.780	1.718	1.676	1.784	1.723	1.681
R(Si-H)	1.468	1.476	1.470	1.492	1.482	1.471	1.494	1.484	1.473
R(Si⋯Si)	2.595	2.443	2.373	2.632	2.447	2.375	2.634	2.448	2.377
R(O⋯O)	2.320	2.356	2.321	2.397	2.411	2.365	2.407	2.425	2.378
∠ H-Si-H	112.7	111.4	110.5	112.6	111.2	110.8	112.5	111.1	110.6
∠ Si-O-Si	96.4	92.1	91.3	95.3	90.8	90.2	95.2	90.5	90.0
					$C_2O_2H_4$					
R(C-O)	1.455	1.403	1.402	1.505	1.426	1.418	1.511	1.430	1.424
R(C-H)	1.076	1.092	1.084	1.102	1.108	1.088	1.104	1.109	1.090
R(C⋯C)	2.047	1.943	1.940	2.103	1.961	1.951	2.110	1.965	1.957
R(O⋯O)	2.070	2.026	2.025	2.155	2.070	2.058	2.165	2.079	2.070
∠ H-C-H	112.8	110.5	110.8	113.5	110.3	111.1	113.6	110.3	111.2
∠ C-O-C	89.4	87.6	87.6	88.6	86.9	86.9	88.5	86.8	86.8
					$C_2S_2H_4$					
R(C-S)	1.886	1.831	1.822	1.933	1.844	1.825	1.940	1.850	1.831
R(C-H)	1.073	1.087	1.077	1.098	1.101	1.081	1.100	1.103	1.083
R(C⋯C)	2.528	2.476	2.476	2.576	2.479	2.471	2.585	2.484	2.477
R(S⋯S)	2.800	2.699	2.675	2.883	2.732	2.688	2.895	2.742	2.698
∠ H-C-H	111.9	110.2	110.3	112.7	110.0	110.6	112.9	110.1	110.8
∠ C-S-C	84.2	85.1	85.6	83.6	84.4	85.2	83.5	84.3	85.1

a plane lozenge (D_{2h} symmetry) that is formed with four Si-O bonds having the same length. The increasing of the basis set from cc-pVDZ to cc-pVTZ shortens all bond distances significantly, while bond angles are relatively stable with respect to both electron correlation and basis set size effects. At the highest level of theory employed in this study, the Si⋯Si distance is predicted to be 2.377 Å, which is almost the same with Si-Si single bond length (2.38 Å). The X-ray structure of substituted 1,3-cyclodisiloxane by mesityl (2,4,6-trimethylphenyl, Mes) showed also very short nonbonded Si⋯Si distance (2.31 Å).[6] For this relatively short Si⋯Si distance, Grev and Schaefer proposed the "dibridged-π-complex" model where the π bonding between the silicon atoms is not supported by σ-bonding.[7] Liang and Allen explained that the shortening of the Si⋯Si distance is a consequence of more favorable σ-bridged-π bonding.[8] They employed the weak π-bonding effect concept between lone pairs on the oxygen atom and the electrons that constitute σ bonding of Si-H at the perfectly plane structure in spite of four-membered ring compound. Recently, Ma and Inagaki proposed "cyclic (n, d, d) interaction" model, which is that the cyclic delocalization of the non-bonding lone pair electrons through two vacant d-type polarization functions of silicon atoms is responsible for the short Si⋯Si distance.[9] In our knowledgement, there has not been reported for the experimental study of the parent 1,3-cyclodisiloxane.

The optimized geometries of the 1,3-dioxetane and 1,3-dithietane at the cc-pVTZ CCSD(T) level of theory are also shown in Figure 1 and the geometrical parameters at the many different levels are listed in Table 1. Their optimized

structures also have D_{2h} symmetry including planar four-membered ring. The predicted C⋯C distances of 1.957 and 2.477 Å in 1,3-dioxetane and 1,3-dithietane, respectively, are much longer than the normal C-C single bond length. Based on our result, the planar ring structure in 1,3-dioxetane or 1,3-dithietane can be explained by "σ-bridged-π bonding" model. However, for the short Si⋯Si distance in cyclodisiloxane, we support the "cyclic (n, d, d) interaction" model which is that that the cyclic delocalization of the non-bonding lone pair electrons through two vacant d-type polarization functions of silicon atoms is responsible. The C-O-C and C-S-C bond angles are predicted to be highly strained to 86.8 and 85.1°, respectively. The C-O and C-S bond distances of 1.424 and 1.831 Å 1,3-dioxetane and 1,3-dithietane, respectively, are comparable to the typical C-O and C-S single bond lengths of ca. 1.43 and 1.81 Å.

$H_4Si_3O_4$, $H_4C_3O_4$ and $H_4C_3S_4$: As shown in Figure 2(a), the structure of $H_4Si_3O_4$ is formed with two four-membered rings, which have C_{2v} symmetry along a Si⋯Si⋯Si molecular axis. The predicted geometrical parameters at various levels of theory are listed in Table 2. The highest level of theory employed for this oligomer is cc-pVTZ CCSD. Geometrical parameters of $H_4Si_3O_4$ are predicted to be 2.361 Å for Si⋯Si distance, 2.354 Å for O⋯O, 1.680 Å for outer Si-O bond, 1.654 Å for inner Si-O, 1.468 Å for Si-H, 111.7° for H-Si-H bond angle, and 90.2° for Si-O-Si angle. The bond distances are significantly decreased with increasing the basis set sizes from cc-pVDZ to cc-pVTZ which means that the effect of the polarization function should be very important. The electron correlation effect from CCSD to

(a)

(b)

(c)
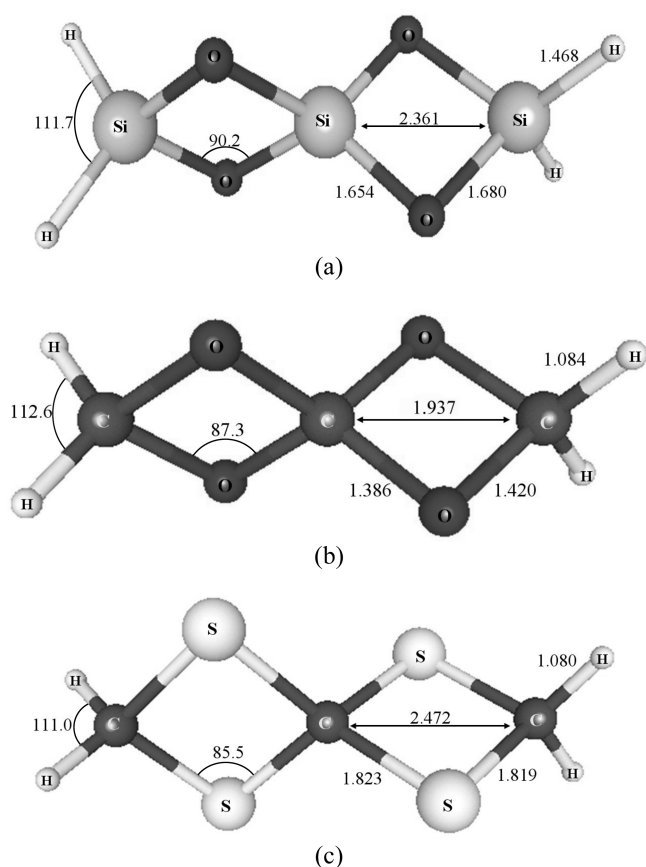
Figure 2. Optimized structures at the cc-pVTZ CCSD level of theory: (a) $Si_3O_4H_4$; (b) $C_3O_4H_4$; (c) $C_3S_4H_4$.

CCSD(T) is relatively less important.

The average Si-O bond distance predicted in this study of 1.667 Å is not too different with Si-O bond (1.676 Å) distance in the 1,3-cyclodisiloxane at the same level of theory. The Si⋯Si and O⋯O distances of 2.361 Å and 2.354 Å, respectively, are predicted to be a little decreased than those (2.375 and 2.365 Å) in the 1,3-cyclodisiloxane. This result implies that the electron delocalization effect around rings or dibridged-π effect might be increased due to adding a four-membered ring. To our knowledge, there have been no theoretical and experimental results to be compared for the geometrical parameters of these compounds. On the other hand, Gordon *et al.* reported the calculated geometrical parameters for larger (six-, eight- and ten-membered) rings of $(H_2SiO)_n$, n = 3-5, and their predicted Si-O bond distance also decreases as ring size increases.[16]

As shown in Figure 2(b), the structure of $C_3O_4H_4$ takes the shape of the two lozenges which is similar to $Si_3O_4H_4$. One planar four-membered ring is at right angle to another four-membered ring. The geometrical parameters at various levels of theory are also listed in Table 2. In general bond distances decrease with increasing basis set size at CCSD and CCSD(T) levels, while bond angles are not varied significantly. Based on Table 1, the basis set effects of cc-pVTZ are relatively more important than the correlation effect between CCSD and CCSD(T). In comparison with the 1,3-dioxetane, the C⋯C distance of 1.937 Å in the $C_3O_4H_4$ is a little shorter than 1.951 Å in 1,3-dioxetane at the same level (cc-pVTZ CCSD) of theory because of the short

Table 2. Optimized geometrical parameters of $Si_3O_4H_4$, $C_3O_4H_4$ and $C_3S_4H_4$ at various levels of theory

	SCF			CCSD			CCSD(T)	
	DZ	cc-pVDZ	cc-pVTZ	DZ	cc-pVDZ	cc-pVTZ	DZ	cc-pVDZ
				$Si_3O_4H_4$				
R(Si-O)[a]	1.750	1.703	1.665	1.790	1.724	1.680	1.795	1.729
R(Si-O)[b]	1.705	1.669	1.638	1.745	1.692	1.654	1.750	1.697
R(Si-H)	1.464	1.472	1.467	1.487	1.479	1.468	1.490	1.481
R(Si⋯Si)	2.575	2.425	2.340	2.611	2.431	2.361	2.614	2.432
R(O⋯O)	2.303	2.344	2.310	2.383	2.399	2.354	2.395	2.413
∠ H-Si-H	114.6	112.6	111.4	114.7	112.4	111.7	114.6	112.3
∠ Si-O-Si	96.4	91.9	91.2	95.2	90.7	90.2	95.0	90.4
				$C_3O_4H_4$				
R(C-O)[a]	1.459	1.406	1.404	1.509	1.428	1.420	1.515	1.433
R(C-O)[b]	1.412	1.371	1.370	1.459	1.395	1.386	1.465	1.401
R(C-H)	1.073	1.088	1.080	1.099	1.103	1.084	1.100	1.104
R(C⋯C)	2.023	1.928	1.926	2.079	1.949	1.937	2.087	1.954
R(O⋯O)	2.036	1.999	1.997	2.117	2.043	2.030	2.127	2.052
∠ H-C-H	114.4	111.9	112.1	115.4	111.9	112.6	115.6	112.0
∠ C-O-C	89.6	87.9	90.0	88.9	87.3	87.3	88.9	87.2
				$C_3S_4H_4$				
R(C-S)[a]	1.880	1.825	1.816	1.927	1.838	1.819	1.935	1.844
R(C-S)[b]	1.877	1.832	1.821	1.914	1.846	1.823	1.922	1.852
R(C-H)	1.072	1.087	1.077	1.098	1.101	1.080	1.099	1.102
R(C⋯C)	2.523	2.481	2.480	2.562	2.484	2.472	2.570	2.490
R(S⋯S)	2.783	2.686	2.660	2.862	2.721	2.674	2.875	2.732
∠ H-C-H	112.3	110.6	110.7	113.3	110.4	111.0	113.5	110.5
∠ C-S-C	84.4	85.4	86.0	83.7	84.8	85.5	83.6	84.7

[a]Outer A-X bond distance in four-membered ring (refer figure 2). [b]Inner A-X bond distance in four-membered ring (refer figure 2)

inner C-O bond length of 1.386 Å. The outer C-O bond distance of 1.420 Å is almost same with C-O bond length (1.418 Å) in 1,3-dioxetane. The molecular shape of $H_4C_3S_4$ presented in Figure 2(c) is also similar to other compounds and geometrical parameters at various levels of theory are listed in Table 2. The outer and inner C-S bond distances at the cc-pVTZ CCSD level of theory are predicted to be 1.819 and 1.823 Å, respectively. This result which is longer inner C-S bond distance does not coincide with the result for $H_4Si_3O_4$ and $C_3O_4H_4$. This can be explained by the steric hindrance of four large size sulfur atoms connected by sp^3 hybrid of center carbon. These relatively large sulfur atoms in comparison with oxygen could elongate inner C-S bond distances.

Harmonic Vibrational Frequencies. The calculated harmonic vibrational frequencies, infrared (IR) intensities and zero-point vibrational energies (ZPVE) of the 1,3-cyclodisiloxne, dioxetane and dithietane are listed in Table 3. All vibrational frequencies are real, which means that all optimized structures are local minima. They involve seven

a_1, four b_1 and five b_2 modes in C_{2v} symmetry. To our knowledge, no experimental observations have been reported for any vibrational feature of 1,3-cyclodisiloxne, dioxetane and dithietane. In theory, Kudo and Nagase reported the calculated harmonic vibrational frequencies of 1,3-cyclo-disiloxne and dioxetane without detailed assignments for each peak. The SCF harmonic vibrational frequencies are in general 10% larger than the experimental values.[27,28] The infrared intensities of vibrational frequencies are presented in parenthesis at the cc-pVTZ SCF level of theory.

For 1,3-cyclodisiloxne, six strong and one weak peaks are expected. After 10% off for each frequency, two strong peaks around 2230 cm⁻¹ are assigned to the Si-H stretching, three strong peaks around 720, 950 and 970 cm⁻¹ to SiH₂ bending, one strong peak around 830 cm⁻¹ to Si-O symmetric stretching, and one weak peak around 720 cm⁻¹ to Si-H bending mode. The ring torsional peak (around 225 cm⁻¹) could not be observed because of its weak intensity. For 1,3-dioxetane, four strong and four weak peaks are expected. Two strong peaks around 2900 cm⁻¹ are assigned

Table 3. Harmonic vibrational frequencies (in cm⁻¹), infrared intensities (in km/mol), and zero-point vibrational energies (ZPVE, in kcal/mol) of 1,3-cyclodisiloxane, dioxetane, dithietane at the SCF level of theory

Assignments	sym C_{2v}	SCF			Assignments	sym C_{2v}	SCF			Assignments	sym C_{2v}	SCF		
		DZ	cc-pVDZ	cc-pVTZ			DZ	cc-pVDZ	cc-pVTZ			DZ	cc-pVDZ	cc-pVTZ
SiH sym str	a_1	2375	2378	2375(0)	CH sym str	a_1	3315	3202	3180(0)	CH sym str	a_1	3328	3244	3230(76)
SiH sym str	a_1	2364	2366	2363(243)	CH sym str	a_1	3303	3186	3166(226)	CH sym str	a_1	3327	3244	3230(0)
SiH₂ bend - scissor	a_1	1096	1096	1111(0)	CH₂ bend - scissor	a_1	1707	1696	1717(0)	CH₂ bend - scissor	a_1	1629	1594	1620(0)
SiH₂ bend - scissor	a_1	1061	1063	1079(325)	CH₂ bend - scissor	a_1	1679	1659	1681(17)	CH₂ bend - scissor	a_1	1619	1583	1610(3)
Si-O sym str	a_1	863	912	958(0)	C-O sym str	a_1	1151	1232	1234(0)	C-S sym str	a_1	779	841	851(0)
Si-O sym str	a_1	851	888	925(534)	C-O sym str	a_1	1112	1212	1210(322)	C-S sym str	a_1	690	764	775(9)
Si-O-Si bend	a_1	582	589	612(0)	C-O-C bend	a_1	950	995	981(0)	C-S-C bend	a_1	499	496	494(0)
SiH₂ bend - wag	b_1	1001	1045	1059(490)	CH₂ bend - wag	b_1	1531	1579	1586(32)	CH₂ bend - wag	b_1	1368	1335	1349(2)
SiH₂ bend - wag	b_1	908	934	953(0)	CH₂ bend - wag	b_1	1440	1455	1475(0)	CH₂ bend - wag	b_1	1324	1285	1305(0)
SiH₂ bend - rock	b_1	672	775	804(12)	CH₂ bend - rock	b_1	1037	1113	1098(0)	CH₂ bend - rock	b_1	748	807	813(0)
Si-O asym str	b_1	671	685	721(0)	C-O asym str	b_1	952	1079	1076(144)	C-S asym str	b_1	681	756	762(3)
SiH₂ bend - twist	a_2	634	660	675(0)	CH₂ bend - twist	a_2	1200	1225	1239(0)	CH₂ bend - twist	a_2	1168	1138	1151(0)
SiH₂ bend - twist	a_2	627	647	661(0)	CH₂ bend - twist	a_2	1172	1195	1221(0)	CH₂ bend - twist	a_2	1138	1095	1109(0)
SiH asym str	b_2	2372	2369	2360(362)	CH asym str	b_2	3394	3251	3221(145)	CH asym str	b_2	3423	3314	3287(11)
SiH asym str	b_2	2366	2365	2356(0)	CH asym str	b_2	3386	3245	3217(0)	CH asym str	b_2	3421	3312	3286(0)
SiH₂ bend - rock	b_2	785	790	804(253)	CH₂ bend - rock	b_2	1243	1277	1290(29)	CH₂ bend - rock	b_2	954	951	970(4)
Si-O asym str	b_2	701	719	730(0)	C-O asym str	b_2	1177	1210	1221(0)	C-S asym str	b_2	933	949	970(0)
ring torsion	b_2	245	241	250(2)	ring torsion	b_2	225	214	207(19)	ring torsion	b_2	121	102	100(9)
ZPVE		28.8	29.3	29.7			42.9	42.9	42.9			38.8	38.3	38.5

Zero-point vibrational energies are 12.01, 12.30, 12.44 kcal/mol for H₂SiO, 18.22, 18.05, 18.00 kcal/mol for H₂CO and 16.84, 16.58, 16.56 kcal/mol H₂CS from going to DZ, cc-pVDZ, and cc-pVTZ basis set at the SCF level of theory.

Table 4. Harmonic vibrational frequencies (in cm^{-1}), infrared intensities (in km/mol), and zero-point vibrational energies (ZPVE, in kcal/mol) of $Si_3O_4H_4$, $C_3O_4H_4$, and $C_3S_4H_4$ at the SCF level of theory

sym (C_{2v})	$Si_3O_4H_4$ SCF			sym (C_{2v})	$C_3O_4H_4$ SCF			sym (C_{2v})	$C_3S_4H_4$ SCF		
	DZ	cc-pVDZ	cc-pVTZ		DZ	cc-pVDZ	cc-pVTZ		DZ	cc-pVDZ	cc-pVTZ
a_1	2395	2391(0)	2385(0)	a_1	3351	3242(0)	3218(0)	a_1	3333	3250(0)	3236(0)
a_1	2393	2388(210)	2378(157)	a_1	3350	3240(148)	3216(162)	a_1	3332	3250(65)	3235(66)
a_1	1088	1105(28)	1129(72)	a_1	1690	1687(20)	1708(10)	a_1	1624	1589(0)	1615(0)
a_1	1071	1077(0)	1095(0)	a_1	1684	1671(0)	1696(0)	a_1	1624	1588(6)	1614(5)
a_1	1022	1037(867)	1064(775)	a_1	1455	1499(685)	1488(622)	a_1	937	994(133)	1005(116)
a_1	859	907(0)	953(0)	a_1	1146	1241(0)	1243(0)	a_1	735	807(0)	819(0)
a_1	845	884(788)	929(804)	a_1	1114	1214(565)	1211(612)	a_1	705	788(35)	801(31)
a_1	831	869(0)	908(0)	a_1	1055	1140(0)	1130(0)	a_1	522	538(0)	540(0)
a_1	674	682(35)	709(35)	a_1	1033	1093(94)	1081(85)	a_1	518	510(2)	508(3)
a_1	382	388(0)	404(0)	a_1	607	636(0)	635(0)	a_1	320	339(0)	342(0)
b_1	2403	2390(145)	2377(157)	b_1	3447	3311(44)	3278(39)	b_1	3430	3322(3)	3296(3)
b_1	967	1023(396)	1042(393)	b_1	1489	1545(85)	1554(58)	b_1	1340	1302(0)	1318(0)
b_1	766	836(61)	866(52)	b_1	1229	1275(135)	1285(105)	b_1	956	961(2)	980(1)
b_1	721	756(92)	770(83)	b_1	1119	1218(62)	1224(86)	b_1	787	857(5)	861(3)
b_1	702	719(9)	756(18)	b_1	994	1078(7)	1067(6)	b_1	722	786(2)	793(1)
b_1	382	389(10)	407(5)	b_1	557	610(0)	610(0)	b_1	272	279(0)	281(0)
b_1	123	125(2)	138(1)	b_1	180	190(12)	190(12)	b_1	95	96(3)	97(4)
a_2	628	653(0)	668(0)	a_2	1189	1213(0)	1229(0)	a_2	1158	1122(0)	1135(0)
a_2	626	652(0)	667(0)	a_2	1187	1213(0)	1229(0)	a_2	1155	1117(0)	1131(0)
a_2	193	201(0)	211(0)	a_2	325	352(0)	352(0)	a_2	162	154(0)	152(0)
b_2	2403	2390(145)	2382(222)	b_2	3447	3312(44)	3278(39)	b_2	3430	3322(3)	3296(3)
b_2	967	1023(396)	1042(393)	b_2	1491	1545(85)	1554(58)	b_2	1340	1302(0)	1318(0)
b_2	766	836(61)	866(52)	b_2	1228	1275(135)	1285(105)	b_2	956	961(2)	980(1)
b_2	721	756(92)	770(83)	b_2	1122	1218(62)	1224(86)	b_2	787	857(5)	861(3)
b_2	702	719(9)	756(18)	b_2	1000	1078(7)	1067(6)	b_2	722	786(2)	793(1)
b_2	382	389(10)	406(5)	b_2	556	610(0)	610(0)	b_2	272	279(0)	285(0)
b_2	123	125(2)	138(1)	b_2	181	190(12)	190(12)	b_2	95	96(3)	98(4)
ZPVE	35.9	36.8	37.5	ZPVE	53.2	54.2	54.1	ZPVE	44.8	44.7	44.9

Zero-point vibrational energies are 3.91, 4.67, 4.88 kcal/mol for SiO_2, 7.46, 8.03, 8.04 kcal/mol for CO_2 and 4.23, 4.58, 4.59 kcal/mol CS_2 from going to DZ, cc-pVDZ, and cc-pVTZ basis set at the SCF level of theory.

to the C-H stretching, two other strong peaks around 970 and 1100 cm^{-1} to C-O stretching, three weak peaks around 1170, 1430, and 1520 cm^{-1} to CH_2 bending, and one weak peak around 190 cm^{-1} to ring torsional mode. For 1,3-dithietane, all peak intensities are relatively weak. One strong and seven weak peaks are expected. Relatively two strong peaks around 2900 cm^{-1} are assigned to the C-H stretching, two weak peaks around 690 and 700 cm^{-1} to C-S stretching, two weak peaks around 880, 1210 and 1450 cm^{-1} to CH_2 bending, and one weak peak around 90 cm^{-1} to ring torsional mode.

In Table 4, the calculated vibrational frequencies, infrared intensities, and zero-point vibrational energies of $H_4Si_3O_4$, $H_4C_3O_4$, and $H_4C_3S_4$ are presented. As stated elsewhere, since vibrational frequencies are all real numbers, they are thermodynamically stable in their minimum energy structures under ideal state (0 K). They involve ten a_1, three a_2, seven b_1 and seven b_2 symmetric modes. To date, no experimental and theoretical studies have been reported for the vibrational frequency of these compounds. After 10% off

for each frequency, Si-H stretching modes in $Si_3O_4H_4$ appear around 2160 cm^{-1}, C-H stretching modes in $H_4C_3O_4$ and $C_3S_4H_4$ around 2900 cm^{-1}. Also zero-point vibrational frequencies listed in Table 4 have been considered to evaluate the dimerization and relative energies at room temperature described next section.

Energetics. Predicted dimerization energies of $H_2(A_2X_2)H_2$ (A=C or Si, and X=O or S) and relative energies with respect to free AX_2 for $H_2(A_3X_4)H_2$ (A=C or Si, and X=O or S) oligomers are listed in Table 5. Although the relative energies at the CISD level of theory are calculated, the results are excluded from Table 5 because of size consistency problem. The dimerization energy (ΔE) of $H_2(A_2X_2)H_2$ is calculated using the energy difference between dimer and the sum of monomers (H_2AX). Relative energies per AX_2 can be obtained by the energy difference of $H_2(A_3X_4)H_2$ from the sum of $H_2(A_2X_2)H_2$ and AX_2. The scaled SCF zero-point vibrational energy (ZPVE) correction has been considered to predict the relative energies more

Table 5. Absolute energies (in hartree), dimerization and relative energies (in kcal/mol) for monomers and oligomers at various levels of theory

Basis set/Method	Monomer	Dimer ($H_4A_2X_2$)	Dimerization energies	AX_2	$H_4A_3X_3$	Relative energies[a]
	H_2SiO	$(H_2SiO)_2$	ΔE	SiO_2	Si_3O_4H	ΔE
DZ/SCF	−364.843559	−729.871123	−115.5(−111.2)	−438.524157	−1168.575398	−113.0(−110.1)
cc-pVDZ/SCF	−364.925953	−730.044938	−121.1(−116.9)	−438.629362	−1168.864423	−119.3(−116.8)
cc-pVTZ/SCF	−364.981701	−730.164114	−125.9(−121.6)	−438.720705	−1169.085592	−126.0(−123.1)
DZ/CCSD	−365.126074	−730.393424	−88.7(−84.4)	−438.940044	−1169.476286	−89.6(−86.7)
cc-pVDZ/CCSD	−365.240545	−730.652954	−107.8(−103.6)	−439.107078	−1169.931629	−107.7(−105.2)
cc-pVTZ/CCSD	−365.423310	−731.039072	−121.0(−116.7)	−439.377052	−1170.607883	−120.3(−117.4)
DZ/CCSD(T)	−365.134448	−730.403735	−84.6(−80.3)	−438.959025	−1169.496682	−84.0(−81.1)
cc-pVDZ/CCSD(T)	−365.251291	−730.668691	−104.2(−99.9)	−439.127076	−1169.961381	−103.9(−101.4)
cc-pVTZ/CCSD(T)	−365.440602	−731.051747	−107.0(−102.7)	−439.407950	−	−
	H_2CO	$(H_2CO)_2$	ΔE	CO_2	$C_3O_4H_4$	ΔE
DZ/SCF	−113.830712	−227.654591	4.3(10.1)	−187.553392	−415.158725	30.9(33.5)
cc-pVDZ/SCF	−113.877223	−227.747108	4.6(10.7)	−187.652896	−415.350964	30.8(33.7)
cc-pVTZ/SCF	−113.913225	−227.819899	4.1(10.3)	−187.709909	−415.481292	30.4(33.6)
DZ/CCSD	−114.081016	−228.140489	13.5(19.3)	−187.923974	−416.009363	34.6(37.2)
cc-pVDZ/CCSD	−114.213089	−228.419452	4.2(10.3)	−188.135826	−416.514076	25.9(28.8)
cc-pVTZ/CCSD	−114.345666	−228.693785	−1.5(4.7)	−188.339445	−416.999754	21.0(24.2)
DZ/CCSD(T)	−114.086956	−228.151384	14.1(19.9)	−187.940729	−416.032986	37.1(39.7)
cc-pVDZ/CCSD(T)	−114.223273	−228.438297	5.2(11.3)	−188.154402	−416.549974	26.8(29.7)
cc-pVTZ/CCSD(T)	−114.362499	−228.726551	−1.0(5.21)	−188.368323	−417.060879	21.3(24.5)
	H_2CS	$(H_2CS)_2$	ΔE	CS_2	$C_3S_4H_4$	ΔE
DZ/SCF	−436.458837	−872.945585	−17.5(−12.9)	−832.789874	−1705.706606	18.1(19.7)
cc-pVDZ/SCF	−436.529203	−873.095764	−23.9(−18.8)	−832.926009	−1705.999624	13.9(15.5)
cc-pVTZ/SCF	−436.557062	−873.155428	−25.9(−21.1)	−832.967078	−1706.102667	12.4(13.2)
DZ/CCSD	−436.711403	−873.440867	−11.3(−6.7)	−833.167053	−1706.584271	14.8(16.4)
cc-pVDZ/CCSD	−436.830139	−873.699282	−24.5(−19.9)	−833.345357	−1707.029690	9.4(11.0)
cc-pVTZ/CCSD	−436.965456	−873.982241	−32.2(−27.4)	−833.554178	−1707.532001	2.8(3.6)
DZ/CCSD(T)	−436.717453	−873.451537	−10.4(−5.8)	−833.183428	−1706.607051	17.5(19.1)
cc-pVDZ/CCSD(T)	−436.841697	−873.720337	−23.2(−18.6)	−833.369071	−707.071268	11.4(13.0)
cc-pVTZ/CCSD(T)	−436.984734	−873.019674	−31.5(−26.7)	−833.590861	−	−

The values in parentheses are including scaled zero-point vibration energies (by 0.9). [a]Relative energies per AX_2 repeat unit of the oligomers with respect to the free AX_2 monomer. [$\Delta E = E(H_4A_3X_3) - \{E(H_4A_2X_2) + E(AX_2)\}$]

precisely and presented in parentheses of Table 5. The dimerization and relative energies are sensitive to the size of basis functions, but the correlation effects from CCSD to CCSD(T) with cc-pVTZ basis set are not too serious as shown in the result for $H_2(C_{n+1}O_{2n})H_2$.

The dimerization energies of $(H_2SiO)_2$, $(H_2CO)_2$, and $(H_2CS)_2$ are predicted to be −102.7, 5.21, and −26.7 kcal/mol including ZPVE correction at the cc-pVTZ CCSD(T) level of theory. This high exothermic result (−102.7 kcal/mol) for $(H_2SiO)_2$ implies that four single bonds in four-membered ring are more strong than two double bonds of two H₂Si=O. The exothermicity in the H₂C=S dimerization decreases significantly, indicating the much stronger C=S π bond than π bond in H₂Si=O and the formation of weaker C-S single bonds compared with Si-O single bonds. In contrast, the dimerization of H₂C=O is predicted to be rather endothermic by 5.21 kcal/mol, which implies that the cleavage of two C=O double bonds in monomers to form four C-O single bonds in dimer needs more energy. However

this small endothermicity for the dimerization of H₂C=O might be overcome by polymerization.

We also calculated the relative energies per AX_2 repeat unit of $H_2(A_3X_4)H_2$ with respect to the free AX_2 monomer. The geometry optimizations for $H_2(C_3S_4)H_2$ and $H_2(Si_3O_4)H_2$ at the cc-pVTZ CCSD(T) level of theory are not possible due to the size of the system and program limitations. The relative energy of $Si_3O_4H_4$ per SiO_2 is predicted to be −117.4 kcal/mol including ZPVE correction at the cc-pVTZ CCSD level of theory. This result means that the SiO_2 moiety in $Si_3O_4H_4$ is more stable thermodynamically than the free SiO_2 monomer by 117.4 kcal/mol. The relative energy per CO_2 repeat unit of $C_3O_4H_4$ is predicted to be higher than that of free CO_2 by 24.5 kcal/mol. And the relative energy per CS_2 in $C_3S_4H_4$ is calculated to be higher than the energy of the free CS_2 monomer by only 3.6 kcal/mol. These results are much smaller than the previous theoretical (DFT) predictions of 40.1 and 20.6 kcal/mol for CO_2 and CS_2, respectively, by Frapper and Saillard in 2000.[17]

Conclusion

The molecular structures and relative energies for $H_2(A_{n+1}X_{2n})H_2$, (A=C or Si, X=O or S) oligomers (n = 1-2) are investigated using high level *ab initio* quantum mechanical techniques with large basis sets. The highest level of theory employed is cc-pVTZ CCSD(T). The harmonic vibrational frequencies and IR intensities are also determined at the SCF level of theory with various basis sets. The zero-point vibrational energies are considered to predict the dimerization energy of $H_2(A_2X_2)H_2$ and relative energies per AX_2 repeat unit of $H_2(A_3X_4)H_2$ with respect to the free AX_2 monomer. At all levels of theory, the dimerization energies increase dramatically in the order $(H_2CO)_2 < (H_2CS)_2 < (H_2SiO)_2$. The dimerization energy of $(H_2SiO)_2$ is predicted to be highly exothermic reaction, which means that 1,3-cyclodisiloxane is thermodynamically very stable and can be polymerized in high possibility via cyclic Si-O single bonds. The relative energies per AX_2 repeat unit of $H_2(A_3X_4)H_2$ with respect to the free AX_2 monomer are predicted to increase in the order $H_2(C_3S_4)H_2 < H_2(C_3O_4)H_2 < H_2(Si_3O_4)H_2$. $H_2(C_3O_4)H_2$ and $H_2(C_3S_4)H_2$ are less stable than the free CX_2 by 24.2 and 3.6 kcal/mol (per CX_2 unit), for X=O and S, respectively. However, we may conclude that the ring strains in the four-membered ring of $H_2(C_3O_4)H_2$ and $H_2(C_3S_4)H_2$ are not too high to be characterized in experiment.

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