

## Ab Initio and Natural Bond Orbital (NBO) Study on the Strain Energy of Chlorocyclotrisilane and Chlorocyclopropane

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### Abstract

A comparative study between hexachlorocyclotrisilane (1) and hexachlorocyclopropane (2) by ab initio method and natural bond orbital (NBO) analysis was carried out using 6-31G\*\* basis set, implemented in GAUSSIAN 03 program. The s and p character of Si-Cl and Si-Si bonds obtained for the compounds were then used to examine the rehybridization effect from the strain energy. A higher strain energy in the former can be satisfactorily attributed to the weaker rehybridization capability of silicon relative to carbon in response to the angle strain such that Si-Cl bond strengthening is less effective. Strained  $\text{XCl}_4$  and  $\text{X}_2\text{Cl}_2$  ( $\text{X} = \text{C}, \text{Si}$ ) were used as models to show the rehybridization effect on the geometry and bond orbital energy.

**Keywords:** Natural bond orbital analysis, Rehybridization, Chlorocyclotrisilane, Strain energy

### 1. Introduction

Strain energy (SE) is one of the most important concepts involved in chemistry of the cyclic compounds. During the past three decades both synthesis and theoretical studies of the three membered rings containing Si atoms have received a great interest [1-6]. Among the most interesting results one can refer to the theoretical studies is that several authors especially San Yan Chu and coworkers predicted the strain energy (SE) of cyclotrisilane to be about 10 kcal mol<sup>-1</sup> larger than that of cyclopropane [1-7]. Most discussions of this SE difference were based on the notion of more serious SiSi bond weakening in cyclotrisilane. San-Yan Chu and coworkers considering the two contributions from natural bond orbital (NBO) analysis, one from the interior of the three-membered ring, concerning the XX ( $\text{X} = \text{Si}, \text{C}$ ) bonding contribution, and the other from the exterior of the ring, concerning the XCl bonding contribution, showed that the energy separation between the

two compounds comes from coupling of the two types of bonding by the rehybridization effect at X centers. They also showed the weakening of CC bonds in cyclopropane were compensated substantially by strengthening of CH bonds from the angle strain. This compensation effect is less effective in cyclotrisilane and results in its larger SE.

In this paper, we focused on the effect of the two contributions from NBO analysis of hexachlorocyclotrisilane (1) and hexachlorocyclopropane (2): one from the interior of the three-membered ring, concerning the XX ( $\text{X} = \text{Si}, \text{C}$ ) bonding contribution, and the other from the exterior of the ring, concerning the XCl bonding contribution. The energy separation in this case will be due to the coupling of the two types of bonding by the rehybridization effect at X centers. For instance, the weakening of CC bonds in hexachlorocyclopropane is compensated for substantially by the strengthening of CCl bonds from the angle strain. In this paper we show that such a compensatory effect is less effective in 1, and results in its larger SE.

To show the rehybridization effect, we firstly used a few simple model systems rehybridization effect, such as strained tetra chloromethane and hexa chloromethane and their

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silicon analogs. In the strained tetra chloromethane, one CClCl angle is bent to  $60^\circ$ , with all the other parameters fully optimized to simulate the local angle strain situation at a carbon center in hexa chlorocyclopropane. We also looked into the strengthening effect of the two free CCl bonds. In the case of strained hexa chloroethane system, all six ClCCl angles were fixed at  $90^\circ$  to simulate the angle strain in bridgehead-coupled system. We have also examined bridgehead CC bond strengthening from rehybridization. Finally, the NBO energies of CC and CCl bonds in hexa chlorocyclopropane were compared with those in the acyclic compound of chloropropane and their difference used for a qualitative estimation of SE.

## 2. Theoretical method

Ab initio LCAO-MO SCF calculations were performed with the 6-31G\*\* basis set using the GAUSSIAN03 program [8-9]. The results show the difference in the bonding capability between carbon and silicon under the strained conditions. Geometries obtained from this calculation were then used to perform NBO analysis by the NBO 3.1 program as implemented in Gaussian03. We found out the s and p character analysis from the NBO [10,11] to be useful for examining the rehybridization effect from the strain. The NBO energy is also informative for the bonding situation at a specific localized orbital.

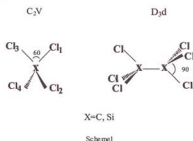
## 3. Results and discussion

### 3.1. Strained $\text{XC}_4$ and $\text{X}_2\text{C}_2$

We firstly note that the CCl bond in **2** has larger bond dissociation energy than that of octachloropropane chain. The difference between these two values can be attributed to the rehybridization effect from the strain. There is a decrease in s

character for the carbon hybrid orbitals along the CC bonds in the ring. This may be a consequence of the conservation of total s character for the carbon center under strain. From a structural point of view, it has been also observed that there is a compensatory effect among all the bond lengths around a strained carbon center [8]. According to our computational results, this is generally valid for a carbon center under a moderate strain. Further, we expect such compensation to be less effective for a second-row atom such as Si, where the hybridization between s and p orbitals is less effective. The 3s orbital is known to be more contracted relative to the 3p orbital.

Table 1 shows the calculated results for strained  $\text{CCl}_4$  systems with  $\angle\text{Cl}_1\text{XCl}_1 = 60^\circ$  in comparison with those of normal  $\text{XCl}_4$  ( $\text{T}_d$ ) systems. Table 2 shows the results for strained  $\text{X}_2\text{C}_2$  with all six  $\angle\text{Cl}_1\text{XCl}_1 = 90^\circ$  in comparison with those for free  $\text{X}_2\text{C}_2$ . Their geometries are defined in Scheme 1.



In Table 1, the magnitude of the bond length of the  $\text{XCl}_1$  bond is the same as the bond length for the  $\text{XCl}_2$  bond. Also, the conservation of s character for the central atom X holds well, since changes in s character ( $\Delta s$ ) for the hybrid orbital along  $\text{XCl}_1$  and  $\text{XCl}_2$  are nearly equal in magnitude but opposite in sign. However, the magnitude of  $\text{XCl}_1$  bond

strengthening is only about one tenth of that for the  $\text{XCl}_2$  bond weakening, as indicated by changes in NBO energy. In general,  $\text{CCl}_4$  shows similar but weaker effects than  $\text{SiCl}_4$ .

Table 2 shows some similar rehybridization behavior from a milder strain for  $\text{C}_2\text{Cl}_4$  and  $\text{Si}_2\text{Cl}_6$ . One notable difference in this case is that the SiSi bond length shortening is 0.128 Å compared with 0.039 Å for that of the CC bond. If one considers the value of the change in relative bond length,  $\Delta R/R$ , then the ratio of the two values is about 12 for SiSi vs. CC. this strained XCl bond is used to simulate the strained XX bond in the real system. [12,13], much shorter than the normal CC single bond distance of 1.54 Å.

In contrast, we expect the model to be less realistic for a silicon system with a bigger difference in electronegativity between Si and Cl relative to that between C and Cl. Nevertheless, the result here is qualitatively consistent with X-ray structures and ab initio calculations of cubycubane and persilacubycubane. For example, the X-ray structures give a bridgehead-CC bond distance of 1.458 Å [12,13], much shorter than the normal CC single bond distance of 1.54 Å. In contrast, the corresponding SiSi bond distance is 2.343 Å from Nagase's calculation [14], not much different from the value of 2.35 Å for a normal single SiSi bond. The results indicate some important differences in rehybridization capability between C and Si. We are now ready to examine the results for the three-membered ring system (Scheme2).

Table 1.

The Calculated SCF results for strained  $\text{CCl}_4$  and  $\text{SiCl}_4$ , each with  $\text{C}_{2v}$  and  $\text{T}_d$  structure. The bond length ( $R_{\text{XCl}}$ ) in Å, s character of the X hybrid orbital along the XCl bond ( $s_{\text{XCl}}$ ), natural bond orbital energy ( $\epsilon_{\text{XCl}}$ ), total electronic energy E in hartree, and  $\Delta Y$  ( $\Delta Y = Y(60^\circ) - Y(109.47^\circ)$ ) for each quantity are given. The energy difference is in  $\text{KJmol}^{-1}$ , s=c

Y	$\text{CCl}_4$			$\text{SiCl}_4$		
	$\text{C}_{2v}$	$\text{T}_d$	$\Delta Y$	$\text{C}_{2v}$	$\text{T}_d$	$\Delta Y$
$\angle \text{Cl}_3\text{XCl}$	$60^\circ$	$109.47^\circ$	$-49.47^\circ$	$60^\circ$	$109.47^\circ$	$-49.74^\circ$
$R_{\text{XCl}}$	1.766	1.766	0.000	2.000	2.027	-0.027
$R_{\text{XCC}}$	1.767	1.766	0.001	2.160	2.027	0.133
$s_{\text{XCl}}$	0.250	0.250	0.000	0.279	0.250	0.029
$s_{\text{XCC}}$	0.249	0.250	-0.001	0.219	0.250	-0.031
$\epsilon_{\text{XCl}}$	-0.987	-0.988	0.627	-0.871	-0.961	56.44
$\epsilon_{\text{XCC}}$	-0.976	-0.987	6.898	-0.788	-0.961	108.496
E	-1875.687	-1875.744	149.653	-	-2127.046	622.243
				2126.809		

Table 2. The Calculated SCF results for strained  $C_2Cl_6$  and  $Si_2Cl_6$ , each with  $D_{3d}$  structures. The bond length ( $R_{XCl}$ ) in Å, s character of the X hybrid orbital along the XCl bond ( $s_{XCl}$ ), natural bond orbital energy ( $\epsilon_{XCl}$ ), total electronic energy E in hartree, and  $\Delta Y$  ( $\Delta Y = Y(90^\circ) - Y(11.22^\circ)$ ) for each quantity are given. The energy difference is in  $KJ\ mol^{-1}$ .

Y	$C_2Cl_6$			$Si_2Cl_6$		
	$D_{3d}$	$D_{3d}$	$\Delta Y$	$D_{3d}$	$D_{3d}$	$\Delta Y$
$\angle CIXCl$	$90^\circ$	$111.22^\circ$	$-21.22^\circ$	$90^\circ$	$111.22^\circ$	$-20.36^\circ$
$R_{XCl}$	2.688	1.759	0.929	2.099	2.040	0.059
$R_{XX}$	1.500	1.539	0.039	2.219	2.347	0.128
$S_{XCl}$	0.209	0.230	-0.021	0.234	0.236	0.002
$S_{XX}$	0.346	0.307	0.039	0.322	0.291	0.031
$\epsilon_{XCl}$	-0.972	-0.979	4.390	-0.930	-0.967	23.204
$\epsilon_{XX}$	-1.055	-1.016	-24.458	-0.730	-0.662	-42.646
E	-2832.518	-2832.551	86.641	-3335.007	-3335.037	78.765

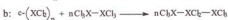
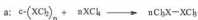
### 3.2. Strain energy in the three-membered ring

The calculated SE values are shown in Table 3. The Strain energy that are generally used for cycloalkanes are divided by comparison the experiment heat of formation with that of hypothetical strain-free isomer [15], using the definitions of isodesmic and homodesmotic reactions [16,17]. In general, the SE of chlorocycloalkane is greater than that of chlorocyclosilane. The three-membered ring is the only exception. This can serve as motivation for the present

study. We include  $C_2Cl_4$  and  $Si_2Cl_4$  as "two-membered ring" systems purposely scale of comparing them. If the banana-bonds picture is used for double-bond systems, they can indeed be considered as the smallest ring systems. Although the difference between the two definitions of SE is significant, both show consistently that SE values of c- $(CCl_2)_n$  are less than those of c- $(SiCl_2)_n$  for  $n = 2, 3$ , but the order is reversed for  $n = 4$ .

Table 3. Strain energy in  $KJmol^{-1}$  from isodesmic and homodesmotic reactions, for cycloalkane and cyclosilane with  $n=2$  to  $n=4$ .

n	Isodesmic reaction <sup>a</sup>		Homodesmotic reaction <sup>b</sup>	
	HF		HF	
	X = C	X = Si	X = C	X = Si
2	2002.7	2528.1	2041	2528.1
3	2670.3	3371.2	2690.8	3653.5
4	3004.1	3792.5	3023.5	4336.0



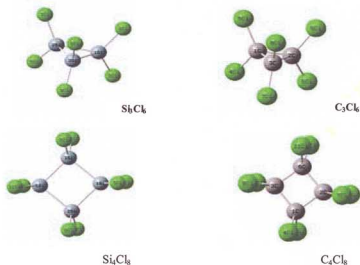


Table 4.

Calculated results for the three- and four-membered rings and chains. Bond length in Å, total electronic energy and natural bond orbital energy ( $\epsilon_{\text{XCl}}$ ,  $\epsilon_{\text{XCl}}$ ) in hartree, and s character of the hybrid orbital along the XX bond and XCl bond at X ( $S_{\text{XX}}$ ,  $S_{\text{XCl}}$ ) are given.

		$R_{\text{CC}}$	$R_{\text{CCl}}$	E	$S_{\text{CC}}$	$S_{\text{CCl}}$	$\epsilon_{\text{CC}}$	$\epsilon_{\text{CCl}}$
$\text{C}_3\text{Cl}_6$	HF	1.518	1.742	-2870.391	0.250	0.240	-0.870	-0.986
$\text{C}_3\text{Cl}_8$	HF	1.608	1.781	-3789.337	0.306	0.225	-0.955	-0.952
$\text{C}_4\text{Cl}_8$	HF	1.582	1.755	-3827.204	0.272	0.232	-0.910	-0.968
$\text{C}_4\text{Cl}_{10}$	HF	1.506	1.760	-4745.955	0.328	0.226	-1.032	-0.985
		$R_{\text{SiSi}}$	$R_{\text{SiCl}}$	E	$S_{\text{SiSi}}$	$S_{\text{SiCl}}$	$\epsilon_{\text{SiSi}}$	$\epsilon_{\text{SiCl}}$
$\text{Si}_3\text{Cl}_6$	HF	2.356	2.047	-3623.903	0.253	0.244	-0.582	-0.964
$\text{Si}_3\text{Cl}_8$	HF	2.361	2.054	-4543.026	0.295	0.236	-0.661	-0.970
$\text{Si}_4\text{Cl}_8$	HF	2.381	2.049	-4831.930	0.264	0.235	-0.635	-0.972
$\text{Si}_4\text{Cl}_{10}$	HF	2.377	2.055	-5751.013	0.283	0.218	-0.660	-0.902

Table 4 shows that the CCl bond of chlorocyclopropane is shorter than that in

chloropropane by 0.039 Å. However, the CC bond of hexachlorocyclopropane is also shorter

than that of octachloropropane by 0.09 Å due to the serious bent-bond situation in small ring [17,20]. For comparison, the contractions of SiCl and SiSi bondlengths in hexachlorocyclotrisilane are only 0.005 Å and 0.007 Å. For four-membered and bigger rings, the bond lengths behave "normally" in that the XCl bond shortening accompanies the XX bond lengthening. The  $R_{CC}$  of octachlorocyclobutane is 0.076 Å longer than that of decachlorobutane, and  $R_{CCl}$  is 0.005 Å shorter (Table 4). The corresponding values for octa chlorocyclotetrasilane are 0.004 Å and 0.006 Å. Again, the SiCl shortening effect is weaker than that of a CCl bond.

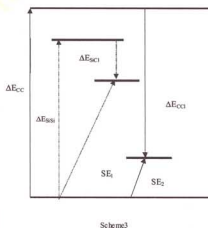
Table 4 also shows the s character of the hybrid orbital along the XX and XCl bonds for carbon and silicon atoms in the three-membered ring. The high strain results in less s character in the XX bonds and more s character in the XCl bonds in comparison with those in the  $X_2Cl_4$  linear chain system [21-27]. The difference in s character for the hybrid orbitals along the CC bond is 0.056, in contrast, with the 0.015 difference for the hybrid orbitals along the CCl bond. The corresponding values for SiSi and SiCl are -0.042 and +0.008, respectively. The strain also raises the NBO energy of the XX bond and lowers that of the XCl bond when comparing the ring and the chain. Therefore, the XCl bond stabilization can partially compensate for XX bond weakening, as shown in scheme 3. The quantity  $\Delta X$  in the Figure is defined as the difference between the quantity X in the ring and in the chain.

The value of  $\Delta E_{XX}$  destabilization energy can be estimated qualitatively by the change in natural orbital energy ( $\Delta E_{XX}$ ) multiplied by the occupation, i.e. 0.51 ( $0.085 \times 6$ ) hartree for hexachlorocyclopropane and 0.474 ( $0.079 \times 6$ ) hartree for hexachlorocyclotrisilane. However the value of  $\Delta E_{XCl}$  stabilization is 0.408 ( $0.034 \times 12$ ) hartree for the former and 0.072 ( $0.006 \times 12$ ) hartree for the latter. The resulting value of ( $\Delta E_{CC} + \Delta E_{CCl}$ ) is 2410.209  $\text{KJmol}^{-1}$  for hexachlorocyclopropane, and that of

( $\Delta E_{SiSi} + \Delta E_{SiCl}$ ) is 1433.533  $\text{KJmol}^{-1}$  for hexachlorocyclotrisilane. We also estimated the values for the four-membered rings for comparison. They are 3276.624  $\text{KJmol}^{-1}$  and 3465.66  $\text{KJmol}^{-1}$  for the pair. The difference within the pair reduces on going from  $n=3$  to  $n=4$ . The results here are in qualitative agreement with the more rigorous SE defined in Table 3. We do not expect the quantities ( $\Delta E_{XX} + \Delta E_{XCl}$ ) estimated here from NBO analysis to quantitatively agree with the formal SE results, since they are based on different definitions.

#### 4. Conclusion

The value of the natural orbital energy difference ( $\Delta E_{XX} + \Delta E_{XCl}$ ) agrees qualitatively with both the isodesmic and homodesmotic SE results, namely that 1 is more strained than 2. The  $\Delta E_{XCl}$  energy component provides the insight that the main difference is due to the compensatory effect from SiCl bond stabilization in 1, which



Scheme 3. diagram for XX and XCl bond orbital energy contributions ( $\Delta E_{XX} + \Delta E_{XCl}$ ) to the strain energy (SE) for chlorocyclopropane (solid line) in comparison with those for chlorocyclotrisilane (dotted line).  $\Delta x$  is defined

as the difference between the quantity  $x$  for the ring and that for the chain.

is much less effective than that of the CCl bonds in **2** (0.072 hartree vs. 0.408 hartree). The difference in the interior destabilization from  $\Delta E_{XX}$  is less important, with 0.51 hartree for  $\Delta E_{SiSi}$  and 0.474 hartree for  $\Delta E_{CC}$ . Thus, SiSi bond weakening in **1** is less serious than CC bond weakening in **2**. This analysis here is qualitative in nature, since the total energy is not a simple sum of the natural bond orbital energies. It is in a similar attitude to the often used analysis of Walsh diagrams based on orbital energies to identify the key orbitals responsible for the molecular geometry, which is actually dictated by the total energy. The information thus obtained is often exaggerated and simplified.

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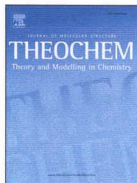
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