

SOLVENT INFLUENCE ON THE STABILITY AND PROPERTIES OF Si₄H₄ ISOMERS BY COMPUTATIONAL METHODS

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ABSTRACT:

In this investigation, we explored solvent influence on the stability and properties of different isomers of Si₄H₄ molecule in both gas and solution phases. Our calculation was performed at the M062X/Def2-TZVPP level of theory. For solution phase calculations, self-consistent reaction field (SCRf) approach was used by the polarizable continuum model (PCM). The solvation model applied the radii and non-electrostatic terms of the solvent model density (SMD). The eight selected solvents were Chloroform, o-NitroToluene, CycloHexanone, TetraHydroFuran, n,n-DiMethylFormamide, DiMethylDiSulfide, PropanoNitrile and DiChloroEthane. The stability of the isomers were investigated in both phases and the solvation energy values of them were calculated. Solvent effect on the frontier orbital energy and HOMO-LUMO gap was clarified. The most instance vibration of the most stable isomer was determined and solvent influence on the wavenumber of this vibration was explored. Lastly, natural bond analysis (NBO) was used for the illustration of the Si-Si chemical bonds, strongest interaction and natural atomic charges of the most stable isomer.

Keywords: tetrasilacyclobutadiene, solvent effect, frontier orbitals, natural bond analysis (NBO).

INTRODUCTION:

The wide-ranging silicon chemistry and probable advanced uses such as semiconducting materials were lead to the preparation and characterization of the family of tetrasilacyclobutadiene (Si₄R₄) substances. Numerous unusual tetrasilacyclobutadiene or tetragermacyclobutadiene analogues together with a planar-rhombic or puckered Si₄ ring [1, 2], a rather folded Ge₄ ring [3], or a puckered Si₃Ge ring with ylide structure [4] were reported. Theoretical studies of the simplest member of the Si₄R₄ family (Si₄H₄) were explored a puckered Si₄ ring with D_{2d} symmetry for this molecule [5, 6]. The central silicon skeleton from the simplest Si₄H₄ to the complex Si₄(EMind)₄ (EMind = 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-shydrindacen-4-yl) compound contains various low-symmetry configuration deviations of the reference square-planar geometry.

The solvent effect is one of the basic subjects of chemistry and leads to extensive changes in the molecular behaviors via inducing some changes to the interactions between solute and solvent molecules [7-9]. To consider the solvent effect in quantum mechanical (QM) calculations of electronic structure, several methods were developed [10, 11]. Solvent impact on the structural and spectroscopic properties of various chemical systems was investigated [12-29]. Also, the solvent effect on the barrier height has been discovered in various systems [30-35].

In this study, we illustrate solvent influence on the stability and properties of Si₄H₄ isomers by computational method. The solvent effect on the frontier orbital energy, HOMO-LUMO gap and the most intensity vibrational mode of the most stable isomer was explored. Also, the Si-Si chemical bonds, strongest interaction and natural atomic charges of the most stable isomer were illustrated by natural bond analysis (NBO).

Computational Methods

All calculations were conducted with the Gaussian 09 suite program [36].

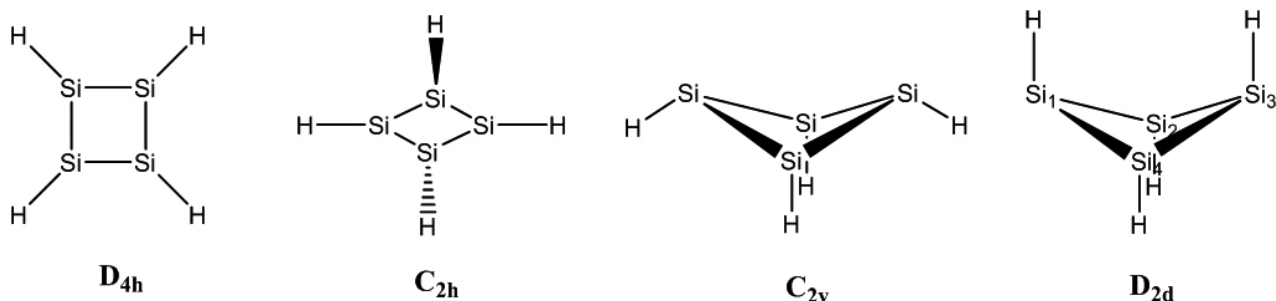


Figure 1. The structures of Si₄H₄ molecule in the D_{4h}, C_{2h}, C_{2v} and D_{2d} symmetries.

The standard Def2-TZVPP basis set [37] was utilized in the calculations. Geometry optimization was performed utilizing with the hybrid functional of Truhlar and Zhao (M06-2X) [38]. A vibrational analysis was carried out at each stationary point found confirming its identity as an energy minimum. The population analysis was also conducted by the natural bond orbital method [39] at B3LYP/Def2-TZVPP level of theory using NBO 6.0 program[40] under Gaussian 2009 program package.

For the solvation effects study we have used a self-consistent reaction field (SCRf) approach, in particular using the polarizable continuum model (PCM) [41]. The solvation model utilized the radii and non-electrostatic terms of the solvent model density (SMD) presented by Truhlar et al.[42].

RESULTS AND DISCUSSION

1. Energetic aspects.

Figure 1 indicates the structures of Si₄H₄ molecule in the D_{4h}, C_{2v}, C_{2h} and D_{2d} symmetries. These structures are optimized at the M062X/Def2-TZVPP level of theory. Absolute energy and relative energy of these isomers in both gas and solution phases are summarized in Table 1. The comparison of these values reveals stability trend of these isomers as D_{2d} > C_{2v} > C_{2h} > D_{4h} in both phases. It can be found the relative energy values decrease in solution phase in compared to gas phase. On the other hand, relative energy values are depend on the solvent polarity. These values decrease in more polar solvents. The observed relations of the relative energy vs. dielectric constant of solvent are fitted by quadratic formulas. The corresponding fitting equations are:

$$\begin{aligned} \Delta E(D_{4h}) &= 0.0008 \varepsilon^2 - 0.044 \varepsilon + 34.228; & R^2 &= 0.9152 \\ \Delta E(C_{2h}) &= 0.0002 \varepsilon^2 - 0.0126 \varepsilon + 7.6698; & R^2 &= 0.9277 \\ \Delta E(C_{2v}) &= 0.0004 \varepsilon^2 - 0.0205 \varepsilon + 4.111; & R^2 &= 0.9263 \end{aligned}$$

Table 1. Absolute energy (E, Hartree), relative energy (ΔE , kcal/mol) and solvation energy (E_{solv} , kcal/mol) values of the Si_4H_4 molecule in the D_{4h} , C_{2v} , C_{2h} and D_{2d} symmetries in gas and solution phases at the M062X/Def2-TZVPP level of theory. ϵ is dielectric constants of the solvent.

E					
	ϵ	D_{4h}	C_{2h}	C_{2v}	D_{2d}
gas	-	-1160.0221	-1160.2117	-1160.2171	-1160.2247
Chloroform	4.71	-1160.1739	-1160.2161	-1160.2218	-1160.2283
THF	7.43	-1160.1731	-1160.2150	-1160.2208	-1160.2271
DMS	9.60	-1160.1729	-1160.2147	-1160.2205	-1160.2268
DiChloroEthane	10.13	-1160.1732	-1160.2151	-1160.2209	-1160.2271
CycloHexanone	15.62	-1160.1726	-1160.2144	-1160.2202	-1160.2264
o-NitroToluene	25.67	-1160.1727	-1160.2143	-1160.2202	-1160.2263
PN	29.32	-1160.1736	-1160.2152	-1160.2211	-1160.2272
DMF	37.22	-1160.1728	-1160.2144	-1160.2203	-1160.2264

ΔE					
	D_{4h}	C_{2h}	C_{2v}	D_{2d}	D_{4h}
gas	127.14	8.15	4.76	127.14	0.00
Chloroform	34.13	7.64	4.06	34.13	0.00
THF	33.91	7.58	3.96	33.91	0.00
DMS	33.83	7.56	3.93	33.83	0.00
DiChloroEthane	33.81	7.55	3.92	33.81	0.00
CycloHexanone	33.71	7.52	3.87	33.71	0.00
o-NitroToluene	33.64	3.84	7.50	33.64	0.00
PN	33.63	7.49	3.82	33.63	0.00
DMF	33.61	7.49	3.82	33.61	0.00

E_{solv}				
	D_{4h}	C_{2h}	C_{2v}	D_{2d}
Chloroform	-95.25	-2.75	-2.93	-2.23
THF	-94.72	-2.06	-2.28	-1.49
DMS	-94.60	-1.88	-2.12	-1.28
DiChloroEthane	-94.84	-2.11	-2.35	-1.51
CycloHexanone	-94.46	-1.66	-1.92	-1.03
o-NitroToluene	-94.46	-1.62	-1.89	-0.97
PN	-95.04	-2.19	-2.46	-1.53
DMF	-94.56	-1.69	-1.97	-1.02

The solvation energy values of these structures are gathered in Table 2. These values show that the stability of these structure increases in solution phase in compared to gas phase. This stability decrease in more polar solvents. It can be found D_{4h} structure has most stability in solution phase in compared to other isomers.

2. Molecular orbital analysis

The frontier orbital energy and HOMO-LUMO gap values of the various isomers of Si_4H_4 molecules are calculated. The calculated values in the Table 2 show that the stability of frontier orbitals decreases in solution phase in compared to gas phase.

It can be observed, the HOMO-LUMO gap values increase in the solution phase in compare to gas phase. The largest HOMO-LUMO gap values is found in the D_{2d} isomer. As a results, the principles of minimum energy (MEP), and maximum hardness (MHP) are obeyed in these isomers in the basis of these principle, whereas an isomer changes from the most stable to other less stable species in most cases, the energy increases, and the HOMO-LUMO gap decreases [43-47].

3. Vibrational analysis

A vibrational analysis was carried out at each stationary point found confirming its identity as an energy minimum. These calculations show the numbers of imaginary frequencies of D_{4h} , C_{2v} and C_{2h} symmetries are six, one and one, respectively. The vibrational modes of these frequencies are (E_u , A_{2u} , B_{1g} , B_{2g} , B_{2u}), B_1 and A_u , respectively. These vibrational modes are presented in Figure 2. The D_{2d} structure have not imaginary frequency.

Si_4H_4 molecule has 18 vibrational modes. The most intensity of the vibrational mode of the most stable isomer (D_{2d} isomer) is indicated in Figure 3. This vibrational mode has B_2 symmetry representation, and attributed to asymmetric stretching of Si-H bonds. The wavenumber values of them are listed in Table 3.

It can be observed that these values are smaller in solution phase compared to the gas phase. The observed shift of the frequency values is mostly attributed to the polarization effect and maybe due to unlike couplings in the gas and solution phases.

Table 2. frontier orbital energy (a.u), HOMO-LUMO gap (eV) values of the Si₄H₄ molecule in the D_{4h}, C_{2v}, C_{2h} and D_{2d} symmetries in gas and solution phases at the M062X/Def2-TZVPP level of theory.

E(HOMO)				
	D_{4h}	C_{2h}	C_{2v}	D_{2d}
gas	-0.15742	-0.24354	-0.24005	-0.26736
Chloroform	-0.18582	-0.24083	-0.23801	-0.26497
THF	-0.18591	-0.24061	-0.23783	-0.26476
DMS	-0.18595	-0.24052	-0.23778	-0.26471
DiChloroEthane	-0.18596	-0.24050	-0.23777	-0.26466
CycloHexanone	-0.18599	-0.24041	-0.23770	-0.26461
o-NitroToluene	-0.18603	-0.24034	-0.23768	-0.26455
PN	-0.18605	-0.24033	-0.23769	-0.26444
DMF	-0.18605	-0.24031	-0.23764	-0.26449

E(LUMO)				
	D_{4h}	C_{2h}	C_{2v}	D_{2d}
gas	-0.09822	-0.08190	-0.08948	-0.07355
Chloroform	-0.08470	-0.07714	-0.08570	-0.07054
THF	-0.08439	-0.07663	-0.08529	-0.07025
DMS	-0.08427	-0.07644	-0.08514	-0.07014
DiChloroEthane	-0.08425	-0.07641	-0.08512	-0.07012
CycloHexanone	-0.08415	-0.07618	-0.08493	-0.06985
o-NitroToluene	-0.08405	-0.07602	-0.08485	-0.06975
PN	-0.08402	-0.07600	-0.08485	-0.06986
DMF	-0.08401	-0.07594	-0.08476	-0.06970

HOMO-LUMO gap				
	D_{4h}	C_{2h}	C_{2v}	D_{2d}
gas	1.611	4.398	4.097	5.274
Chloroform	2.752	4.454	4.145	5.291
THF	2.763	4.462	4.151	5.293
DMS	2.767	4.465	4.154	5.295
DiChloroEthane	2.768	4.465	4.154	5.294
CycloHexanone	2.771	4.469	4.157	5.300
o-NitroToluene	2.775	4.471	4.159	5.301
PN	2.776	4.472	4.159	5.295
DMF	2.777	4.473	4.160	5.301

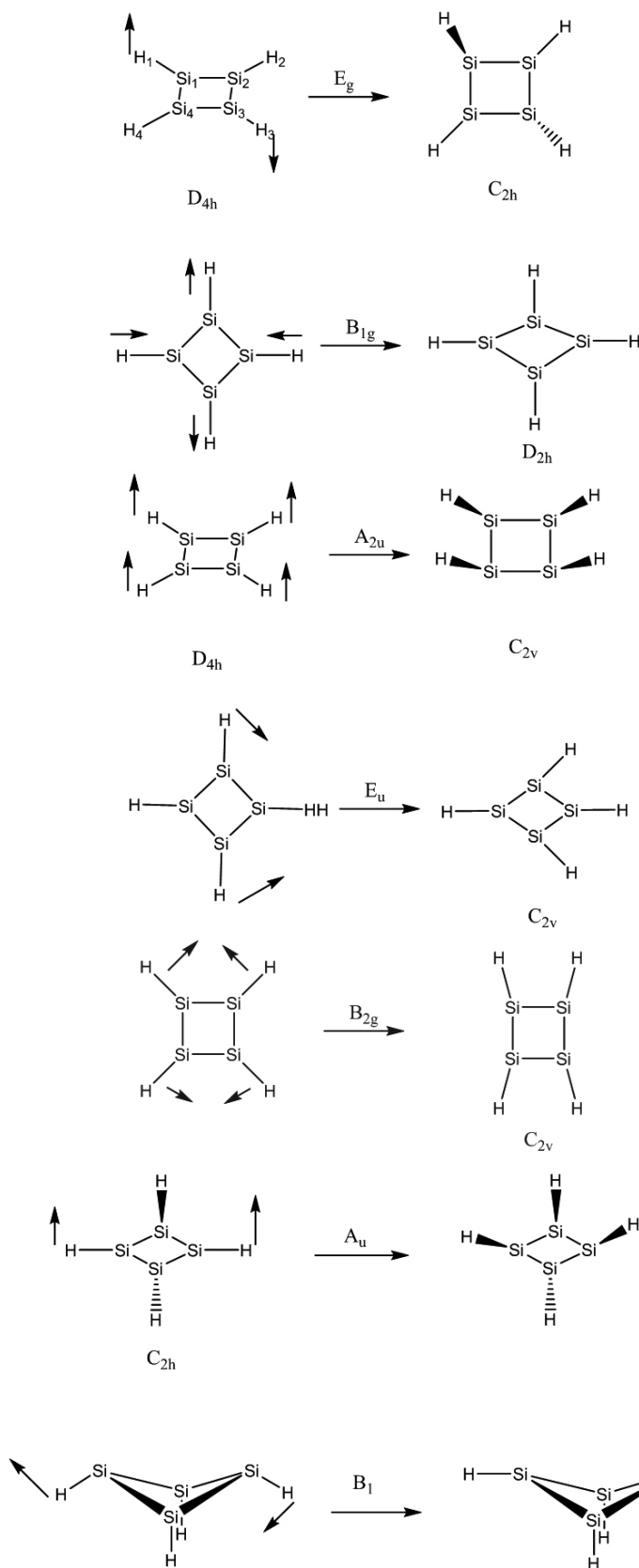


Figure 2. Vibrational modes of imaginary frequencies of Si_4H_4 structures in D_{4h} , D_{4h} , C_{2v} , C_{2h} symmetries.

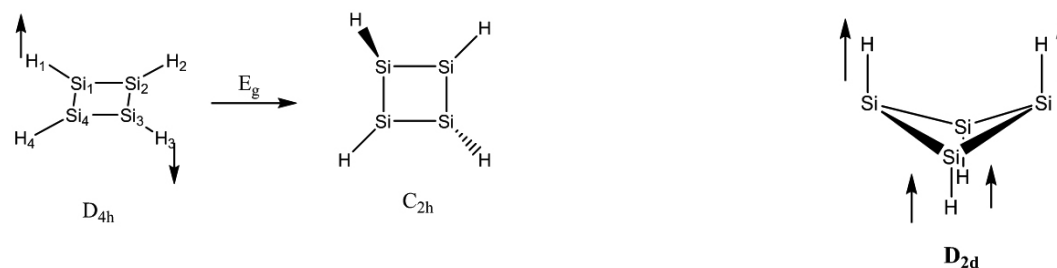


Figure 3. The most intensity of the vibrational mode of the Si_4H_4 molecule in D_{2d} symmetry.

Table 3. Wavenumber values of the most intensity of vibrational modes (cm^{-1}) of the Si_4H_4 molecule in the D_{2d} symmetry in gas and solution phases at the M062X/Def2-TZVPP level of theory.

	ν
gas	2184.53
Chloroform	2181.82
THF	2181.95
DMS	2182.01
DiChloroEthane	2181.88
CycloHexanone	2183.62
o-NitroToluene	2183.62
PN	2181.69
DMF	2183.50

4. Natural bond orbital analysis

Natural bond orbital (NBO) analysis is useful for explore of the bonding characterization in the molecules. NBO calculation of the most stable isomer of Si_4H_4 molecule (D_{2d} isomer) reveals that Si atom in this molecules involves $[\text{core}]3s^{1.40}3p^{2.43}$ hybridization. The hybridization of atomic orbitals of Si-Si bond in this isomer is:

$$\sigma(\text{Si1-Si2}): 0.7071(sp^{2.12})_{\text{Si1}} + 0.7071(sp^{2.12})_{\text{Si2}}$$

The occupancy of this NBO equals to 1.86954 e.

On the other hand, NBO analysis shows the Si1-Si3 and Si2-Si4 bonds in this isomer. The hybridization of atomic orbitals of this Si-Si bond in this isomer is:

$$\sigma(\text{Si1-Si3}): 0.7071(sp^{1.10})_{\text{Si1}} + 0.7071(sp^{1.10})_{\text{Si3}}$$

The occupancy of this NBO equals to 1.80724e.

The strongest interactions of donor (NBO) \rightarrow acceptor (NBO) of the most stable isomer of Si_4H_4 molecule (D_{2d} isomer) occurs as $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si3-Si4})$, $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si1-Si2})$, $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si1-Si4})$, and $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si2-Si3})$. The $E(2)$ value of these interactions was 14.45 kcal/mol.

CONCLUSIONS:

The quantum mechanics investigation of structures of Si_4H_4 molecule in the D_{4h} , C_{2v} , C_{2h} and D_{2d} symmetries at the M062X/Def2-TZVPP level of theory in solution and gas phases revealed:

1. Stability trend of the investigated isomers was changed as $D_{2d} > C_{2v} > C_{2h} > D_{4h}$ in both phases.
2. The HOMO-LUMO gap values were increases in the solution phase in compare to gas phase. The largest HOMO-LUMO gap value was found in the D_{2d} isomer. The principles of MEP and MHP were conformed in the studied isomers.

3. The most intensity of the vibrational mode of the most stable isomer (D_{2d} isomer) had B_2 symmetry representation, and was attributed to asymmetric stretching of Si-H bonds. The wavenumber of this vibration was smaller in solution phase in compared to the gas phase.

4. The strongest interaction of donor (NBO) \rightarrow acceptor (NBO) of this isomer occurs as $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si3-Si4})$, $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si1-Si2})$, $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si1-Si4})$, and $\sigma(\text{Si2-Si4}) \rightarrow \sigma^*(\text{Si2-Si3})$. The $E(2)$ value of these interactions are 14.45 kcal/mol.

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