

Ab-initio Study on the Stabilities and Structures of Monosilacyclopropylidenoids

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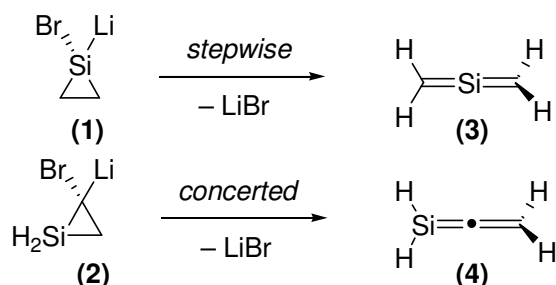
Abstract

Ab-initio levels of theory using 6-31+G(d,p) basis set have been carried out to investigate the isomeric structures, energies and properties of monosilacyclopropylidenoids, C₂H₄SiMX (where M= Na or Li, and X= F, Cl or Br). The theoretical calculations depict that each of them has three stationary structures: silacyclopropylidenoid (**S**), tetrahedral (**T**), and inverted (**I**). All of the silacyclopropylidenoid (**S**) forms are energetically more stable than others except for **S-LiF**, whereas all of the tetrahedral (**T**) forms are the most unstable ones except for **T-NaF**. Energy differences between **S**, **T**, and **I** forms range from 0.60 to 8.70 kcal/mol. Moreover, natural bond orbitals (NBO), and frontier molecular orbitals (FMO) were achieved in this computational study.

Keywords: Ab-initio, reactive intermediates, theoretical computations

Introduction

Cyclopropylidenes have been recognized as highly reactive carbon species and are frequently used as useful intermediates in organic synthesis [1-4]. Likewise, silacyclopropylidenes, the silicon analogues of cyclopropylidenes, a compound in which an electropositive metal (M) and a leaving group (X, usually halogen) are bound to the same silicon atom, and have been predicted to be active intermediates in organosilicon reactions [5-8].



Scheme 1

More recently, we have carried out a series of *ab initio* and DFT calculations on the ring-opening reactions of lithium bromosilacyclopropylidenoids; 1-bromo-1-lithiosilirane (**1**) and 2-bromo-2-lithiosilirane (**2**) to 2-silallene (**3**) and 1-silaallene (**4**), respectively [8]. The theoretical results indicate that the ring-opening of 1-bromo-1-lithiosilirane (**1**) to the complex of 2-silaallene (**3**) can occur in a stepwise fashion with the intermediacy of a free silacyclopropylidene, whereas the ring-opening reaction of 2-bromo-2-lithiosilirane (**2**) to the complex 1-silaallene (**4**) can proceed in a concerted fashion. Moreover, the “classical” tetrahedral structures of **1** and **2** were not located on their potential energy surfaces. Their geometric structures correspond to the distorted-tetrahedron coordination having lowest energy in the studied forms.

In this study, we wish to report the results of structure, energetics, and the properties of C_2H_4SiMX (where $M = Li$ or Na and $X = F, Cl$ or Br) with the help of computational methods.

Computational methods

At first, all structures were fully optimized at MP2/6-31+G(d,p) level of theory [9], and then their vibrational frequencies were computed at the same level of theory

to characterize them as minima (no imaginary frequencies) with help of Gaussian03 package program [10]. The energies reported herein include zero-point energy (ZPE) corrections at MP2/6-31+G(d,p) level. Wiberg bond orders (WBO) [11] were also calculated at HF/6-31+G(d,p) level. The computed structures were visualized by using the GaussView program [12].

Results and Discussion

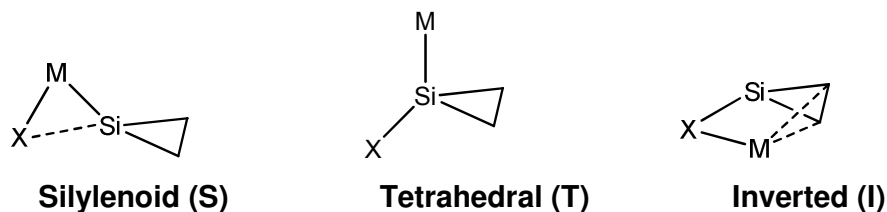


Fig. 1. The illustration of C_2H_4SiMX ($X=F, Cl, Br$, and $M=Li, Na$) complexes.

C_2H_4SiMX ($X=F, Cl, Br$, and $M=Li, Na$) as a silylenoid, can be considered as a complex, which consists of free silacyclopropylidene (1-siliranylidene) and **MX** moieties. Since the ground state of CH_2SiCH_2 is known to be singlet and its calculated singlet-triplet gap is large (42.9 kcal/mol at B3LYP/6-31G(d) level of theory) [8], so only singlet silacyclopropylidene is considered at this work. Because the ring-plane has an unoccupied p-orbital and lone pair electrons on Si atom, its reaction with **MX** moiety causing structural complexity of silylenoids. We calculated the structure of silacyclopropylidene in which case three minimum structures, called silylenoid (**S**), tetrahedral (**T**), and inverted (**I**), were found at MP2/6-31+G(d,p) level of theory, in accordance with $H_2SiNaCl$ (**Fig. 1**). Counter ions, such as $M=Li^+, Na^+$, attach the Si carbon on silacyclopropylidene in different position to give the three minimal structures which have low-energy. However, the structure of **T-NaBr** could not be optimized at MP2/6-31+G(d,p) level of theory.

Characteristic data of these minima are listed in Tables 1-3. It can easily be understood from the tables the three molecules are local minima on Potential Energy Surfaces (PES) due to the positive vibrational frequencies. These tables also give us a chance to compare the bond lengths of the three minima to reference bond lengths. For instance, the bond length of Si-Br, Si-Li, and Li-Br in the structure of **S-LiBr** are elongated 13.6 %, -0.44 %, and 7.3 % as compared to the reference bond

lengths of H₃Si-Br (2.232 Å), H₃Si-Li (2.500 Å), and Li-Br (2.222 Å), respectively. The results show that the Si-Li bond of **S-LiBr** decreases slightly compared to H₃Si-Li (2.500 Å), whereas the most strongly elongated bond in the studied molecule **S-LiBr** is Si-Br with 13.6 %. In addition, we investigated **MX** effect on bond length and angles of free silacyclopropylidene moiety of the three complex as compared to reference bond length of free silacyclopropylidene which was calculated at MP2/6-31+G(d,p) level of theory (**Fig. 2**). Consequently, we determined that the most elongation occurs on Si-C bond of **I-LiF** with 2.46 % as compared to reference bond length 1.909 Å. On the other hand, the most shortening of the same bond is identified on the complex of **T-LiF** by -0.84%. As for bond angles, it can easily be understood that, the C¹SiC² bond angles of **T-LiF** and **T-NaF** increase mostly in comparison with reference bond angle of 46.5 degree.

Table 1 Selected bond lengths and angles (Å), stretching frequencies ν Si-X, and ZPVE-corrected relative energies (a.u) for silylenoidal forms of the C₂H₄SiMX (X=F, Cl, Br, and M=Li, Na) molecules at MP2/6-31+G(d,p) level.

| | S-LiF | S-LiCl | S-LiBr | | S-NaF | S-NaCl | S-NaBr |
|-------------------------------------|--------------|---------------|---------------|-------------------------------------|--------------|---------------|---------------|
| Si-Li | 2.440 | 2.465 | 2.489 | Si-Na | 2.752 | 2.775 | 2.809 |
| Si-X | 1.857 | 2.367 | 2.536 | Si-X | 1.817 | 2.320 | 2.509 |
| Si-C¹ | 1.894 | 1.896 | 1.898 | Si-C¹ | 1.899 | 1.902 | 1.905 |
| Si-C² | 1.894 | 1.896 | 1.898 | Si-C² | 1.899 | 1.902 | 1.905 |
| Li-X | 1.763 | 2.217 | 2.385 | Na-X | 2.266 | 2.592 | 2.742 |
| SiLiX | 49.2 | 60.4 | 62.6 | SiNaX | 41.0 | 51.1 | 53.7 |
| C¹SiC² | 47.6 | 47.4 | 47.3 | C¹SiC² | 47.4 | 47.2 | 47.0 |
| νSi-X | 82.9 | 78.9 | 75.0 | $\Sigma\alpha$ | 47.5 | 46.0 | 44.1 |
| E_{rel} | - | - | - | E_{rel} | - | - | - |
| | 474.405255 | 834.394848 | 2944.809160 | | 628.796506 | 988.788798 | 3099.205079 |

Table 2 Selected bond lengths and angles (Å), stretching frequencies ν Si-X, and ZPVE-corrected relative energies (a.u) for tetrahedral forms of the C₂H₄SiMX (X=F, Cl, Br, and M=Li, Na) molecules at MP2/6-31+G(d,p) level.

| | T-LiF | T-LiCl | T-LiBr | | T-NaF | T-NaCl | T-NaBr |
|-------------------------------------|--------------|---------------|---------------|-------------------------------------|--------------|---------------|---------------|
| Si-Li | 2.474 | 2.467 | 2.465 | Si-Na | 2.773 | 2.762 | - |
| Si-X | 1.684 | 2.135 | 2.313 | Si-X | 1.689 | 2.147 | - |
| Si-C¹ | 1.893 | 1.896 | 1.898 | Si-C¹ | 1.895 | 1.898 | - |
| Si-C² | 1.893 | 1.896 | 1.898 | Si-C² | 1.895 | 1.898 | - |
| Li-X | 3.541 | 3.872 | 3.987 | Na-X | 3.802 | 4.086 | - |
| SiLiX | 25.4 | 30.1 | 32.2 | SiNaX | 23.8 | 29.1 | - |
| C¹SiC² | 47.8 | 47.5 | 47.3 | C¹SiC² | 47.8 | 47.5 | - |
| νSi-X | 113.3 | 103.1 | 70.0 | $\Sigma\alpha$ | 76.0 | 59.8 | - |
| E_{rel} | - | - | - | E_{rel} | - | - | - |
| | 474.395959 | 834.383619 | 2944.795294 | | 628.794281 | 988.782662 | - |

Table 3 Selected bond lengths and angles (Å), stretching frequencies $\nu_{\text{Si-X}}$, and ZPVE-corrected relative energies (a.u) for inverted forms of the $\text{C}_2\text{H}_4\text{SiMX}$ (X=F, Cl, Br, and M=Li, Na) molecules at MP2/6-31+G(d,p) level.

| | I-LiF | I-LiCl | I-LiBr | | I-NaF | I-NaCl | I-NaBr |
|---------------------------------------|--------------|---------------|---------------|-------------------------------------|--------------|---------------|---------------|
| Si-Li | 2.707 | 2.967 | 3.073 | Si-Na | 3.251 | 3.498 | 3.607 |
| Si-X | 1.860 | 2.388 | 2.559 | Si-X | 1.842 | 2.362 | 2.547 |
| Si-C¹ | 1.956 | 1.950 | 1.951 | Si-C¹ | 1.949 | 1.947 | 1.948 |
| Si-C² | 1.956 | 1.950 | 1.951 | Si-C² | 1.949 | 1.947 | 1.948 |
| Li-X | 1.741 | 2.184 | 2.364 | Na-X | 2.177 | 2.539 | 2.707 |
| SiLiX | 42.9 | 52.5 | 54.3 | SiNaX | 32.6 | 42.4 | 44.8 |
| C¹SiC² | 46.2 | 46.3 | 46.3 | C¹SiC² | 46.3 | 46.3 | 46.2 |
| $\nu_{\text{Si-X}}$ | 7.0 | 137.3 | 142.4 | $\Sigma\alpha$ | 88.1 | 123.5 | 124.6 |
| E_{rel} | - | - | - | E_{rel} | - | - | - |
| | 474.406337 | 834.392547 | 2944.806522 | | 628.792403 | 988.782837 | 3099.199379 |

Alternatively, chemical bond disruption and formation can be determined by the Wiberg bond order (WBO) which represent the electron density between two relevant atoms [11]. We calculated several bonds of three minima structures with help of NBO analyses are tabulated in Table 4, 5, and 6. A large WBO value shows that a strong covalent bonding interaction between two related atoms. The results depicts that the Si-M bond of three considered forms of $\text{C}_2\text{H}_4\text{SiMX}$ (M=Li, Na and X=F, Cl, Br) has an ionic rather than covalent nature since the estimated Wiberg bond orders for Si-M are in the range of 0.007 and 0.405. Furthermore, C₁-Si and C₂-Si bonds have the strongest covalent bond interactions within the studied forms of $\text{C}_2\text{H}_4\text{SiMX}$ due to the high bond orders values (in the range of 0.660 and 0.810).

We also calculated the molecular orbitals of the three complexes with help of Natural bond orbital (NBO) analysis at HF/6-31+G(d,p) level. The strongest delocalization in tetrahedral form **T-LiBr** involves the interaction of the Si-Li bonding with the Si-Br anti-bonding. The interaction stabilizes the **T-LiBr** form by 26.85 kcal/mol at HF/6-31+G(d,p) level. In addition to that, the Si-Br bonding interact the Li anti-lone pair with 4.73 and 4.95 kcal/mol in the forms of **S-LiBr** and **I-LiBr** at HF/6-31+G(d,p) level, respectively. Moreover, the same S-Br bonding forms an interaction with C-Si anti-bonding to stabilize the **I-LiBr** with 3.26 kcal/mol. Optimizing of **T-NaBr** was not successful neither at MP2/6-31+G(d,p) (seen in Table 2) nor at HF/6-31+G(d,p) levels, so we only discuss the **S-NaBr** and **I-NaBr** in this part. As a result of NBO analysis, the Si-Br bonding interacts with Na anti-lone pair by 2.31 and 1.78 kcal/mol in **S-NaBr** and **I-NaBr** at HF/6-31+G(d,p) level, respectively.

Table 4. Calculated Wiberg Bond Orders for **S-C₂H₄SiMX** (M=Li, Na and X=F, Cl, Br) at HF/6-31+G(d,p) level of theory.

| | 1LiF | 1LiCl | 1LiBr | | 1NaF | 1NaCl | 1NaBr |
|-------------------|-------|-------|-------|-------------------|-------|-------|-------|
| Si-Li | 0.166 | 0.134 | 0.133 | Si-Na | 0.177 | 0.124 | 0.115 |
| Si-X | 0.341 | 0.426 | 0.516 | Si-X | 0.368 | 0.512 | 0.546 |
| Si-C ¹ | 0.781 | 0.809 | 0.810 | Si-C ¹ | 0.768 | 0.800 | 0.802 |
| Si-C ² | 0.781 | 0.809 | 0.810 | Si-C ² | 0.768 | 0.800 | 0.802 |
| Li-X | 0.025 | 0.073 | 0.085 | Na-X | 0.014 | 0.042 | 0.054 |

Table 5. Calculated Wiberg Bond Orders for **T-C₂H₄SiMX** (M=Li, Na and X=F, Cl, Br) at HF/6-31+G(d,p) level of theory.

| | 2LiF | 2LiCl | 2LiBr | | 2NaF | 2NaCl | 2NaBr |
|-------------------|-------|-------|-------|-------------------|-------|-------|-------|
| Si-Li | 0.405 | 0.320 | 0.133 | Si-Na | 0.402 | 0.306 | - |
| Si-X | 0.466 | 0.731 | 0.516 | Si-X | 0.546 | 0.705 | - |
| Si-C ¹ | 0.763 | 0.801 | 0.810 | Si-C ¹ | 0.751 | 0.791 | - |
| Si-C ² | 0.763 | 0.801 | 0.810 | Si-C ² | 0.751 | 0.791 | - |
| Li-X | 0.011 | 0.013 | 0.085 | Na-X | 0.012 | 0.014 | - |

Table 6. Calculated Wiberg Bond Orders for **I-C₂H₄SiMX** (M=Li, Na and X=F, Cl, Br) at HF/6-31+G(d,p) level of theory.

| | 3LiF | 3LiCl | 3LiBr | | 3NaF | 3NaCl | 3NaBr |
|-------------------|-------|-------|-------|-------------------|-------|-------|-------|
| Si-Li | 0.011 | 0.009 | 0.010 | Si-Na | 0.010 | 0.007 | 0.007 |
| Si-X | 0.311 | 0.411 | 0.460 | Si-X | 0.332 | 0.429 | 0.460 |
| Si-C ¹ | 0.660 | 0.682 | 0.685 | Si-C ¹ | 0.665 | 0.693 | 0.697 |
| Si-C ² | 0.660 | 0.682 | 0.685 | Si-C ² | 0.665 | 0.693 | 0.697 |
| Li-X | 0.030 | 0.097 | 0.115 | Na-X | 0.011 | 0.053 | 0.072 |

The results of the relative stability of the silylenoid, tetrahedral, and inverted forms are clear at the MP2/6-31+G(d,p) calculations summarized in Table 1, 2, 3 and Figure 2. From the results, the structures of **S-MX** (X=F, Cl, Br, and M=Li, Na) is the most stable of three considered structure types in gas phase, except for **S-LiF**. Moreover, the tetrahedral forms of **2MX** (X=F, Cl, Br, and M=Li, Na) is the most unstable structure of the three, except for **T-NaF**. Silylenoid forms of **S-LiCl**, **S-LiBr**, **S-NaCl**, and **S-NaBr** are determined to be of lower energy than the inverted form of **I-LiCl**, **I-LiBr**, **I-NaCl**, and **I-NaBr** by 1.44, 1.65, 3.74, and 3.56 kcal/mol at MP2/6-31+G(d,p) theory of level, respectively. Our calculations show that the tetrahedral form of **T-NaBr** is not a minimum on the potential energy surface, whereas the others are at MP2/6-31+G(d,p) theory of level. The optimized tetrahedral forms **T-LiCl**, **T-LiBr**, and **T-NaCl** have more energy than the silylenoids forms by 7.04, 8.70, and 3.87 at MP2/6-31+G(d,p) theory of level, respectively.

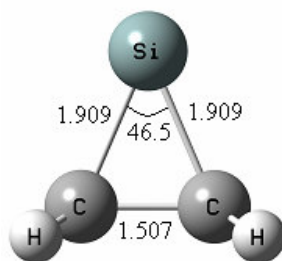


Fig. 2. Optimized geometry of free silacyclopropylidene; interatomic distances in angstrom bond angle in degree.

The frontier molecular orbitals play an important role in the electric, optical and other prosperities, as well as in UV-Vis spectra and chemical reactions. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [13-17]. Fig. 3 indicates the distribution and energy levels of HOMO-LUMO orbitals calculated at MP2/6-31+G(d,p) level for three local minima of selected two structures *Cyclo-C₂H₄Si-LiBr* and *Cyclo-C₂H₄Si-NaCl*. As seen from Fig. 3, HOMO of the three forms are mainly on the Si and C atoms, whereas lowest unoccupied molecular orbital (LUMO) of the molecules substantially localized on metal (Li and Na) atoms of title molecules. The **S-LiBr** has the highest HOMO-LUMO gap with 0.299 eV, whereas the lowest HOMO-LUMO gap of title molecules is on the **T-NaCl**. The small energy separations mean low excitation energies for many of excited states and low chemical hardness for **T-NaCl**.

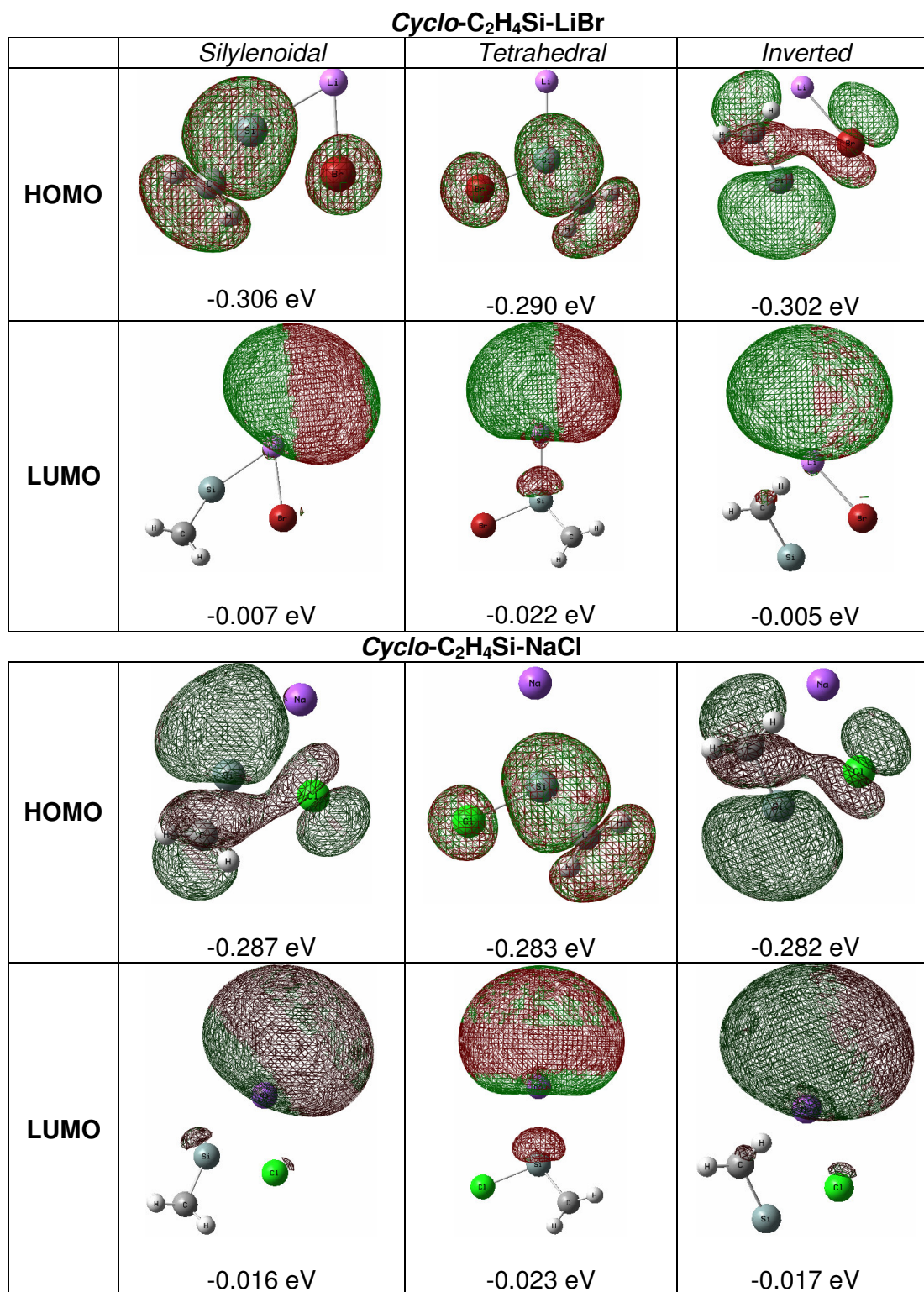


Fig. 3. HOMO-LUMO of *Cyclo-C₂H₄Si-LiBr* and *Cyclo-C₂H₄Si-NaCl* at MP2/6-31+G(d,p) level.

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