

Studying on the Addition Reaction Mechanism of Ethylene and Butadiene Based on Density Functional Theory

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Abstract

According to the first principle calculation, the addition reaction mechanism of ethylene and butadiene is determined. The reactant, transition state (TS) and product of this addition reaction are confirmed by optimization calculation and frequency analysis. To verify the correctness of the reaction process, we also calculated the reaction path. Result demonstrates that the addition reaction of ethylene and butadiene is an exothermic reaction. Charge transfer is used to explain this novel reaction. The activation energy of the addition reaction of ethylene and butadiene is 0.83 eV, and the heat release of the whole reaction is 2.01 eV. The molecular structure, charge distribution and energy of butadiene and ethylene are investigated at the molecular level. The calculated activation energy is helpful for understanding the cyclic addition reaction of butadiene and ethylene, providing theoretical guidance for experiments and deepening people's understanding of this reaction.

Introduction

Ethylene is a synthetic plastic, fiber, rubber, ethanol (alcohol) of basic chemical raw materials, also is one of the world's biggest chemical products production, ethylene industry is the core of the petroleum chemical industry, Therefore, ethylene output is also an important measure of national petrochemical labeling. Ethylene has the role of promoting fruit ripening, which is often used as a ripening agent. Butadiene, a colorless faint aromatic gas, anesthetic, especially stimulate the mucous membrane, easy to liquefy, is the main raw material for the production of rubber. Butadiene molecular contains two C = C bonds, which can undergo addition reaction. Cyclohexene is an important organic chemical raw material. It is generally used in the synthesis of pesticides, pharmaceutical intermediates and polymers.

Addition reaction refers to the reaction in which carbon atoms at both ends of the double bond (or triple bond) in organic molecules combine directly with other atoms or groups to form new compounds. The addition reaction of butadiene and ethylene is a typical Diels-Alder reaction[1], which was used as an example in the frontier molecular orbital theory proposed by K.Fukui and the energy-related theory proposed by R.B.Woodward and R.Hoffman[2].

Wu reported that the synthesis of polybutadiene skeletons from ethylene units is a method for the synthesis of advanced rubber materials, which has been a research challenge due to the different polymerization mechanisms of the two monomers[3].Su also studied the copolymerization of butadiene and ethylene with rhodium trichloride as the starting material[4]. Sautet tested the low-temperature coordination modes of butadiene and ethylene on Pt (110), Pt (111) and Pd (111) surfaces based on Hückel calculation [5]. Gul reported the preparation of acrylonitrile styrene/butadiene vinyl acetate melt blends using linear low density polyethylene as modifier[6].Using density functional theory, Ma investigated the adsorption of cyclohexene on the surface of nAu/Pt(100) (n = 0,1,2) [7]. Vandichel studied the epoxidation of cyclohexene in a vanadium-catalyzed acetylacetone system with tert-butyl hydrogen peroxide as the oxidant, with the aim of identifying the most active epoxidized species and further investigating the most reasonable epoxidized mechanism [8].

However, the TS, reaction path and reaction energy barrier for the addition reaction of ethylene and butadiene to form cyclohexene have not been studied based on the first principle calculation. Therefore, based on density functional theory (DFT) calculation, we have conducted an in-depth study on the reaction path of the addition reaction of butadiene and ethylene to generate cyclohexene. The reactant, product, and TS are optimized and the reaction mechanism is analyzed, which will help people to have a deeper understanding of the mechanism of this addition reaction. It can also provide theoretical guidance for experimental synthesis of cyclohexene.

Computing Methods

First principles calculations are performed with the hybrid functional DFT (B3LYP)[9] implemented in the Gaussian 09 program[10, 11]. B3LYP is a gradient-corrected hybrid DFT with exchange-correlation functional in Becke's three-parameter form, which includes a mixture of HartreeFock exchange with the Vosko, Wilk and Nusair (VWN) functional III for local correlation and the correlation functional of Lee, Yang, and Parr (LYP) for non-local correlation[12]. The mixed basis set of the 6-31G (d, p) is adopted. Geometry optimization and frequency calculation of all stationary points (reactant, product, and TS) for the addition reaction of ethylene and butadiene are performed at the same theoretical level. Initially, the structures of ethylene and butadiene are optimized respectively. Then, the adsorption site is chosen and putting ethylene and butadiene on the same plane to construct the adsorption complex, which is the reactant of the addition reaction, and cyclohexene as the product of the addition reaction. After the reactant and product are optimized and their energy stability has been confirmed with harmonic frequency analysis, the TS is searched by using the quadratic synchronous transit (QST2) method [13]. The obtained TS is confirmed with TS optimization algorithm and another frequency calculation. All structures are fully optimized to local minima except for the TS that is optimized with the constrained optimization. Vibrational frequencies are used to confirm the minima geometries and the TS. Intrinsic reaction coordinate (IRC) calculation is performed at the same level to confirm the connection of the product and reactant [14]. Thus, the entire reaction path has been constructed. Energy barrier or activation energy is determined by the energy difference between the transition state and the reactant. In the calculation, the standard self-consistent energy convergence is 1.0×10^{-6} Hartree. The standard maximum displacement and maximum force convergence in the calculation are 1.8×10^{-3} Å and 4.5×10^{-4} Hartree/Bohr, respectively.

Results And Discussion

1 Geometric structure

1.1 Geometric structure of ethylene and butadiene

We built the initial structures of ethylene and butadiene, and obtained stable structures with optimization calculations. The energy stability of them has been confirmed because no imaginary frequency has been found.

Fig. 1 (left) is the geometric structure of ethylene. The length of C-C bond is 1.331 Å, and the four C-H bonds are 1.088 Å. It can be seen from the figure that there are only two different bonds, namely C=C and C-H. Two C atoms are distributed in the center of ethylene, while four H atoms are evenly distributed and symmetrical around it.

Fig. 1 (right) is the geometric structure of butadiene. One can find that four C and six H atoms are in the same plane, four C atoms are symmetrically distributed, and there are six H atoms around them. There are three different bonds: C=C, C-C and C-H. There are two C=C bonds and one C-C bond. The length of C-C bond is 1.470 Å, the lengths of two C=C bonds are 1.339 Å. The length of C-H bond is between 1.086 Å and 1.091 Å.

1.2 Geometric structure of reactant and product

Fig. 2 (left) is the geometric structure of reactant which is composed by ethylene and butadiene. In this reactant, the length of three C=C bond is 1.326 Å, one C-C bond is 1.548 Å, and C-H bond is 1.098 Å. We obtained stable structure of cyclohexene with optimization calculation by the same base set, as shown in Fig. 2 (right). They are stable in terms of energy because no imaginary frequency is found for them.

Cyclohexene consists of 6 carbon atoms forming a carbon ring structure composed of one C=C bond and five C-C bonds. As can be seen from Fig. 2, the length of C=C bond is 1.337 Å. The length of two C-C bonds adjacent to C=C bond is 1.510 Å while the rest of three C-C bonds is 1.535~1.537 Å.

2 Addition reaction of ethylene and butadiene

2.1 Reaction path of cyclization addition reaction

The reactant was ethylene and butadiene, and the corresponding cyclohexene was used as the product. The quadratic synchronous transit (QST2) method was used to find the connection TS between the reactant and product. The obtained TS was verified by TS optimization and frequency analysis again. The imaginary frequency reached -525.79 cm^{-1} . All structures were optimized to local minimum, in addition to constrained optimization of TS. Then the intrinsic reaction coordinate (IRC) of the addition reaction was calculated in order to clarify the correlation among the reactant, transition state and product.

Fig.2 (middle) shows the obtained geometric structure of TS. The reaction path (IRC) of the cyclization addition reaction of ethylene and butadiene to generate cyclohexene is shown in Fig. 3. Notably, the final structures at both ends of the reactant and product does not fully reach the optimized reactant and product, because when the potential energy surface within the scope of special flat on both ends, the value of the imaginary is difficult to achieve tolerance. Finally, we got the reactant and product, which were same as those final structures at both ends of IRC used as the initial structures for optimization. The energy of reactant and product is -234.5744 Hartree and -234.64829 Hartree (1Hartree=27.21 eV), respectively. Clearly, the energy of the product is lower than that of the reactant, indicating that

cyclohexene is more stable than the complex configuration composed of ethylene and butadiene. Therefore, the addition reaction is exothermic process.

The reaction path diagram shows that the energy of the system increases gradually as the addition reaction proceeds. For comparison, we set the energy of the reactant is zero. Thus, both TS and product are the energy relative to the reactant. When calculating the IRC, we set maximum point to 30. The energy of TS reaches the maximum (-234.5438966 Hartree), and the relative energy is 0.83014 eV. Therefore, the activation energy of the reaction is 0.83014eV, and the energy of the product is -2.00948 eV. Thus, the addition reaction is exothermic and the released heat is -2.00948 eV. In this study, as long as the activation energy of 0.83014 eV is overcome, the cyclization addition reaction can proceed smoothly. This addition reaction first absorbs 0.83014 eV energy to reach the saddle point, then releases 2.83962eV energy, and finally produces cyclohexene, the product of this reaction.

As the reaction goes on, the total energy of the system also increases with the increase in C=C distance. The total energy peaks when the C=C distance (12-C and 11-C) of ethylene, (1-C and 2-C; 6-C and 7-C) of butadiene increase to above 1.383 Å. Meanwhile, C=C breaks to form C-C. The new bond (1-C and 6-C) becomes C=C, and the new C-C bonds (12-C and 2-C) and (11-C and 7-C) form. Then the total energy of the system gradually decreases thereafter. When the length of C-C bonds (12-C and 2-C, 11-C and 7-C) reaches 1.537 Å, and the length of C-C bond (11-C and 12-C) reaches 1.535 Å, the energy of the system is minimum and a stable product is formed.

2.2 Charge analysis

We calculated the Hirshfeld charges for reactant, TS and product of the addition reaction of ethylene and butadiene, and the results are shown in Fig. 4. Table 1 lists each atom charges. One can find that all C atoms are negatively charged and H atoms are positively charged. As the reaction progresses, the charge of 2-C and 7-C atoms near to ethylene in butadiene increases, reaching their maximum charge at the saddle point, and then gradually decreases. It was shown that the charge attraction of C atoms (2-C and 7-C) in butadiene and H atoms (13-H and 16-H) in ethylene promoted the reaction.

Table 1 Each atom charges in reactant, TS and product of the addition reaction			
Atom	Reactant	TS	Product
1-C	-0.0408616875	-0.0569083349	-0.0531786904
2-C	-0.0884282225	-0.0574409716	-0.0491419752
3-H	0.0421699251	0.0372900504	0.0349435528
4-H	0.0407763630	0.0376494274	0.0313732398
5-H	0.0406293505	0.0384217735	0.0299666151
6-C	-0.0407844490	-0.0569204949	-0.0531711009
7-C	-0.0877578878	-0.0574312833	-0.0491375007
8-H	0.0423793747	0.0372978506	0.0349362140
9-H	0.0396327415	0.0376512249	0.0299600942
10-H	0.0402902564	0.0384210525	0.0313942812
11-C	-0.0796287049	-0.0705928255	-0.0486416634
12-C	-0.0803709040	-0.0705929957	-0.0486431845
13-H	0.0417853656	0.0355099620	0.0267049724
14-H	0.0441093333	0.0360721779	0.0279635145
15-H	0.0450477460	0.0360585920	0.0267047942
16-H	0.0410113996	0.0355147947	0.0279668371

As shown in Fig. 5, for reactant composed by ethylene and butadiene, the HOMO and LUMO are completely located on the butadiene, with the E_g (energy gap) of 5.64 eV. The hybridization is mainly p-p hybridization to form the π bond, which is the phase overlap. We also examine the HOMO and LUMO for product and find that the HOMO and LUMO mainly locate on 1-C, 2C and 6-C atoms, while the HUMO locate on a small part on 5-H and 9-H atoms. And the hybridization is mainly p-p hybridization to form the π bond, and the hybridization is also s-s and s-p hybridization. E_g generally refers to the energy difference between the valence (HOMO) and the conduction levels (LUMO) in insulators and semiconductors. Therefore, the E_g is one of the most important factors in determining the electrical conductivity of the materials. The E_g of system is increased from 5.64 eV to 7.28 eV, implying that the electrical conductance of the product system is decreased. It also shows that the product is more chemically stable than the reactant.

Conclusions

In summary, we identified the reaction path for addition reaction mechanism of ethylene and butadiene based on the first principle calculation. The cyclic addition reaction is completed with only one step. The energy barrier of the reaction is 0.083 eV, implicating that cyclohexene can be easily synthesized through addition reaction of ethylene and butadiene under appropriate conditions. The ethylene and butadiene can react to form cyclohexene by overcoming a 0.083 eV barrier. The cyclohexene molecule is obtained with an only one-step reaction. The IRC demonstrates that the whole process of the addition reaction is exothermic with 2.00 eV of reaction energy. The reaction is supported by the wonderful charge distribution. The reaction shows close relationship with the charge distribution of the C atoms near to ethylene in butadiene that promoted the reaction. The calculated activation energy is helpful for understanding the cyclic addition reaction of butadiene and ethylene, providing theoretical guidance for experiments and deepening people's understanding of this reaction.

Declarations

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Authors' contributions: Kangning Li contributed to the conception of the study, performed the data analyses and wrote the manuscript. Weilin Ma contributed significantly to analysis and manuscript preparation. Wenli Xie helped perform the analysis with constructive discussions.

Data availability: The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability: Not applicable.

Declarations

Ethics approval: Not applicable.

Consent to participate: All the co-authors consent the publication.

Consent for publication: All the co-authors consent the publication.

Conflict of interest: The authors declare no competing interests

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Figures

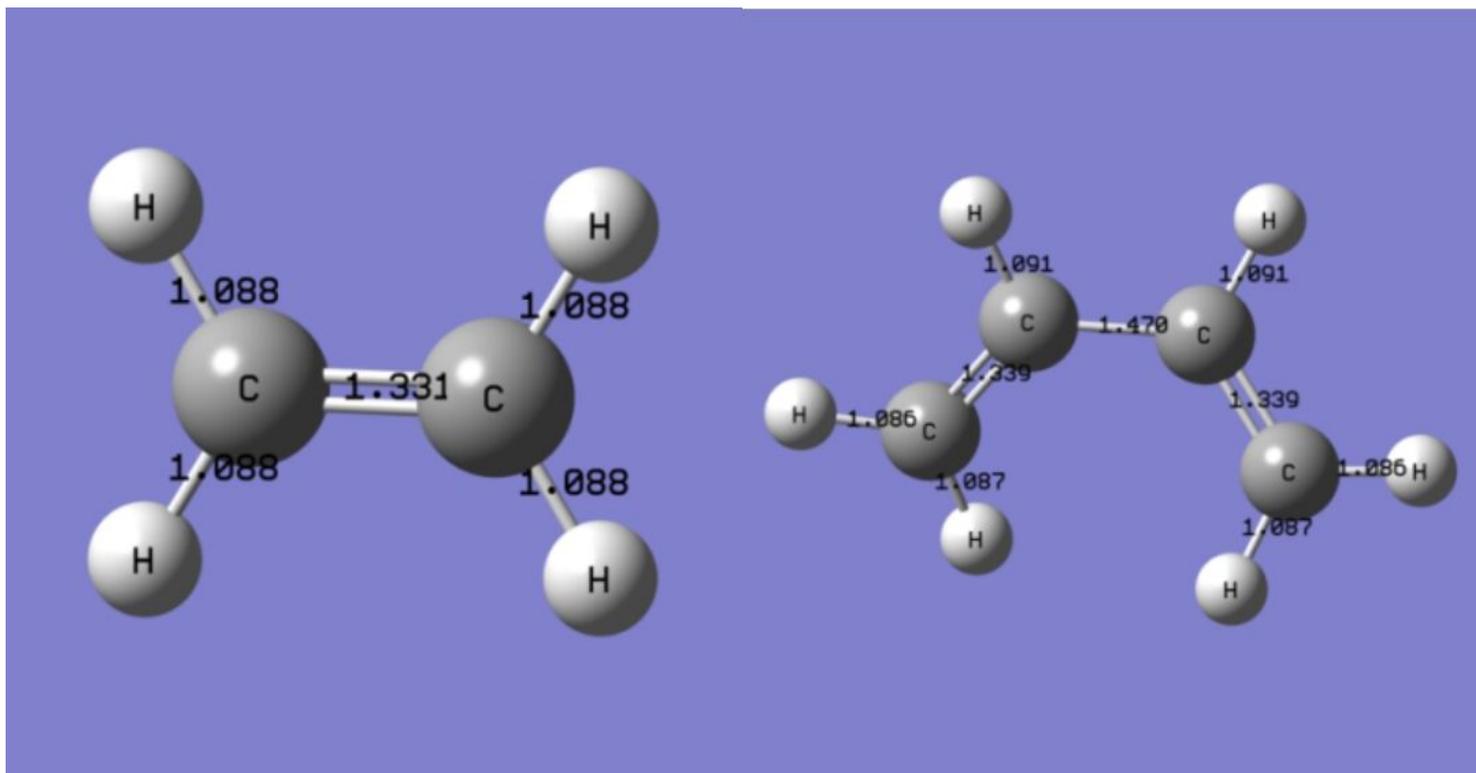


Figure 1

Optimized ethylene and butadiene

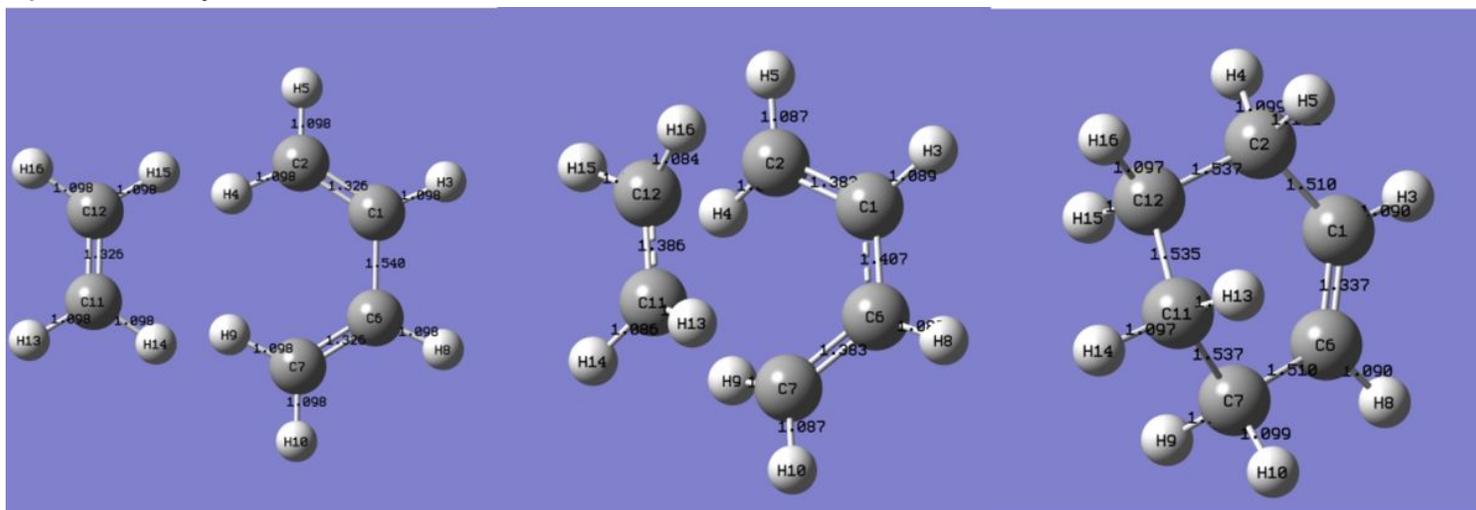


Figure 2

Geometric structures of reactant, TS and product

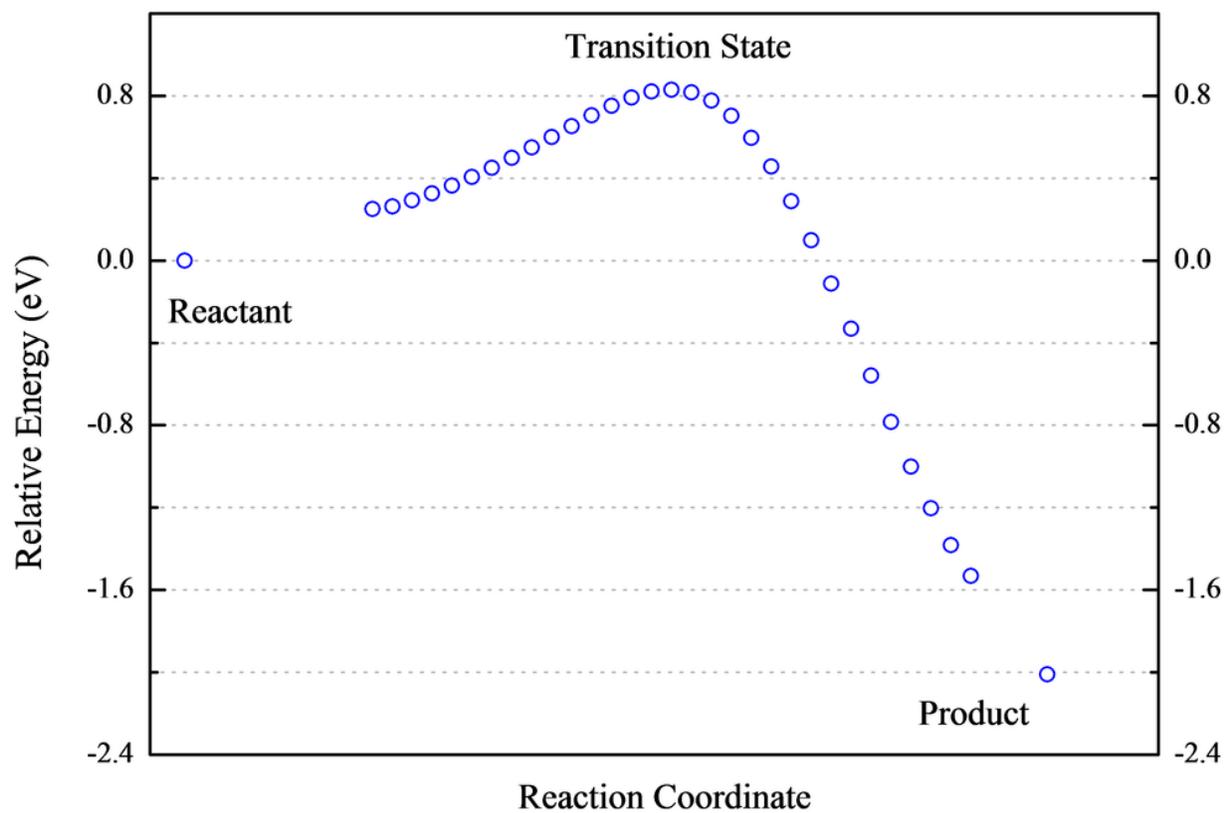


Figure 3

The reaction path of the addition reaction of ethylene and butadiene

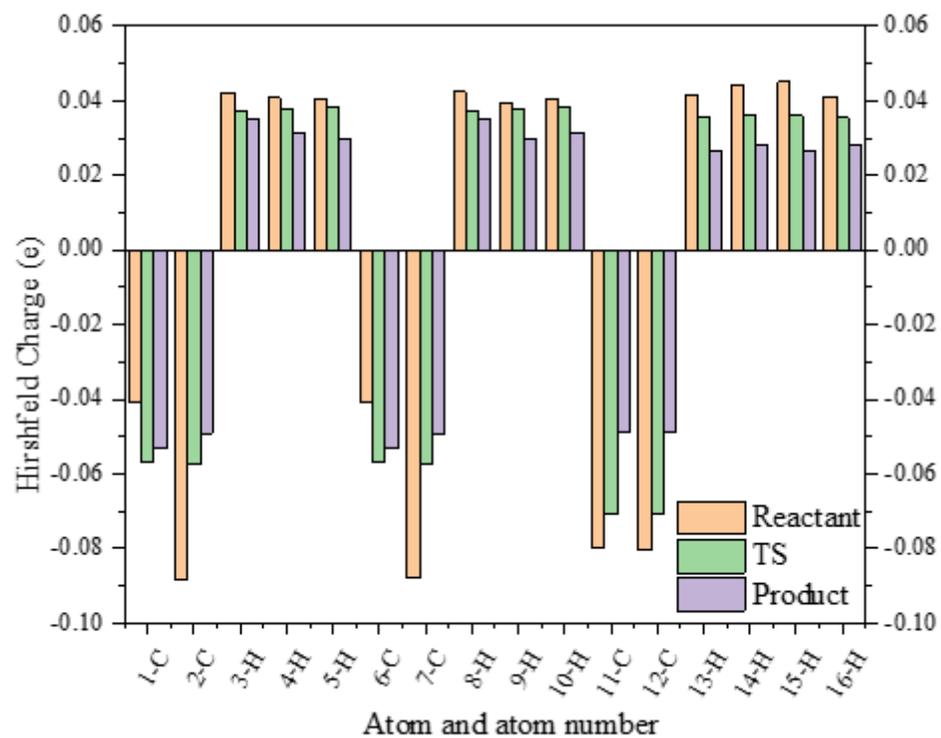
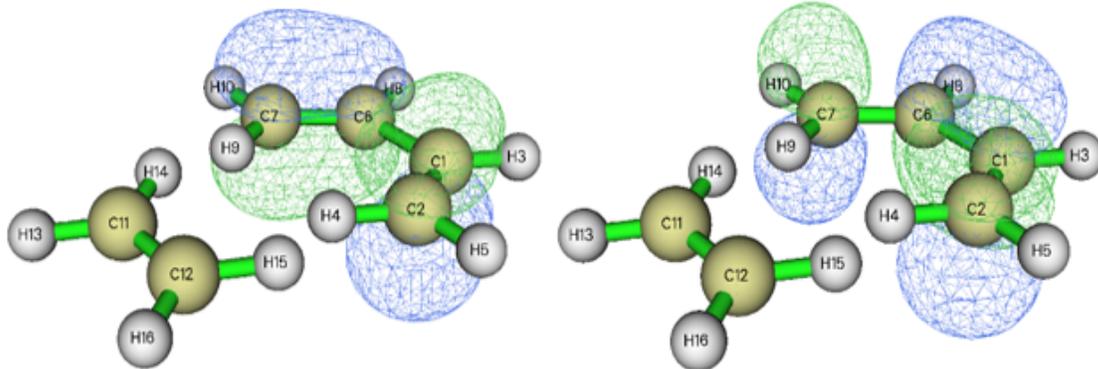


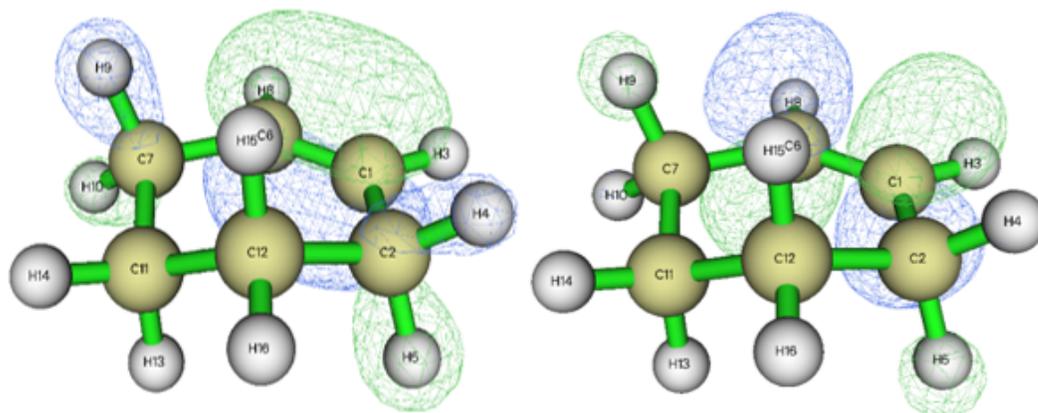
Figure 4

The Hirshfeld charges for reactant, TS and product of the addition reaction



R-HOMO

R-LUMO



P-HOMO

P-LUMO

Figure 5

The HOMO and LUMO of reactant (R) and product (P).