Theoretical Study on Radiationless Decay in Butadiene Isomerization Case using First-principles Calculation

R N Fadilla[1,2,*]**, A N Jannah**[3]**, F N Febriana**[3]**, S Munir**[3]**, A H Zaidan**[3]

[1] Research Center for Quantum Engineering Design, Universitas Airlangga, Surabaya 60115, Indonesia

[2] Department of Engineering Physics, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung 40132, Indonesia

[3] Department of Physics, Faculty of Science and Technology, Universitas Airlangga, Surabaya 60115, Indonesia

E-mail: `rizkafadilla@students.itb.ac.id`

Abstract. This study is to learn the radiation-less decay in butadiene isomerization from *skew*- to *trans*- conformation based on energy level diagram. We construct energy level diagram to determine the energy difference of butadiene in transition geometry between ground state and excited state with the basis of first-principles calculations. We use density functional theory for ground state butadiene while configuration interaction and complete active space for the excited state. The result is that the energy difference is 0.005 eV. It implies that there is degeneration occurred at the transition state of butadiene between its ground state and excited state. We conclude that conical intersection may occurs in the butadiene isomerization reaction.

1. Introduction

Understanding reaction involving excited state is challenging compared to that involving ground state. Ground state refers to the most stable state of the system. Most chemical reactions important for living things take place in ground state. While excited state is state which has higher energy than ground state. Studying reaction related to excited state usually involves things which triggers the excitation such as light. Thus, the number of works on excited state is much less than that on ground state.

Radiationless decay occurred in butadiene (C_4H_6) de-excitation is one example of reaction involving excited state. The de-excitation of butadiene is not occurred along with light emission as how de-excitation commonly occurs.[1] This makes de-excitation occurred in butadiene seems to disobey energy conservation law. Due to the unusual phenomenon, butadiene de-excitation becomes an experimental object which has been comprehensively studied.[2, 3, 4, 5, 6, 7] One way to explain this radiation-less decay phenomenon is using conical intersection concept.

Butadiene de-excitation is usually occurred in its isomerization reaction. Butadiene has some possible conformation such as *cis*, *skew*, and *trans*. Among all of them, *trans* is the most stable conformation of butadiene. In room temperature, 96% of butadiene exist in a form of *trans*-butadiene.[8] *Trans*-butadiene is 0.09-0.22 eV more stable than *cis*-butadiene while *Skew*-butadiene is bit more stable than *cis*-butadiene.[1] Due to the small energy difference between

Table 1. Selected geometrical structure parameter of *trans*-butadiene in ground state compared to experimental value. Δ is obtained by subtracting Calc. by Exper.

Parameter	Calc.	Exper.	Δ
Bond length ($\mathring{A}$)			
1-4	1.340	1.349	-0.009
4-6	1.457	1.467	-0.010
Bond angle (°)			
1-4-6	124.3	127.4	-3.1
1-4-5	118.9	120.9	2.0
Dihedral angle (°)			
1-4-5-7	180.0	180.0	0.0

those conformations, isomerization reaction is likely to be occurred.

In this work, we attempt to study butadiene isomerization reaction from *skew* to *trans* conformation with the basis of first-principles calculation. We construct energy level diagram for ground state and excited state. We identify the existence of conical intersection by finding degeneration in our energy level diagram.

2. Computational Detail

We model isomerization of butadiene from *skew*- into *trans*- conformation using energy level diagram. Our molecule of interest are *skew*-, *trans*-, and the transition state connecting *skew*- and *trans*-butadiene. We determine the ground state of our molecule of interest and the corresponding excited states.

We begin by performing a series of ground and transition state calculation routines with the basis of density functional theory (DFT)[9, 10] for our molecule of interest. We perform those calculations using B3LYP exchange-correlation functional [11] and 6-31G(d,p) basis set. We use the same basis set for the rest of calculations. The selected exchange-correlation and basis set have provided a good prediction of ground state structures for the similar case.[12, 13, 14] All the ground state structures are characterized by the number of imaginary frequency obtained from frequency calculation.

To obtain the excited state corresponds to our ground state structures, we utilize configuration interaction (CI) methods. The transition structure connecting *skew*- and *trans*-butadiene in excited state is optimized using Complete Active Space (CAS) method. We perform all the calculations using Gaussian09 software.[15]

3. Results and Discussion

On the ground state structures

Table 1 shows the comparison of geometrical structure parameter of *trans*-butadiene in ground state with experimental values [16]. The results shows that our calculation results generally agrees with experimental data. It implies that our selected exchange-correlation functional and basis set gives a good prediction for this case.

Figure 1 shows energy level diagram of *skew*-butadiene isomerization into *trans*-butadiene. Based on our results, we found that the isomerization reaction involves one transition state. The transition state is characterized by one imaginary frequency.

The energy level diagram (see Figure 1) shows that energy barrier of *skew*- to *trans*-butadiene isomerization reaction is 0.17 eV. It implies that the isomerization may occurs due to molecular
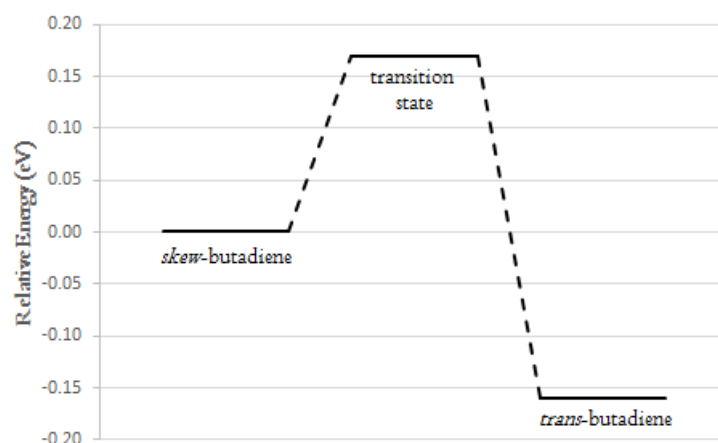
Figure 1. Energy level diagram of *skew*-butadiene, *trans*-butadiene, and the transition state connecting them in ground state.
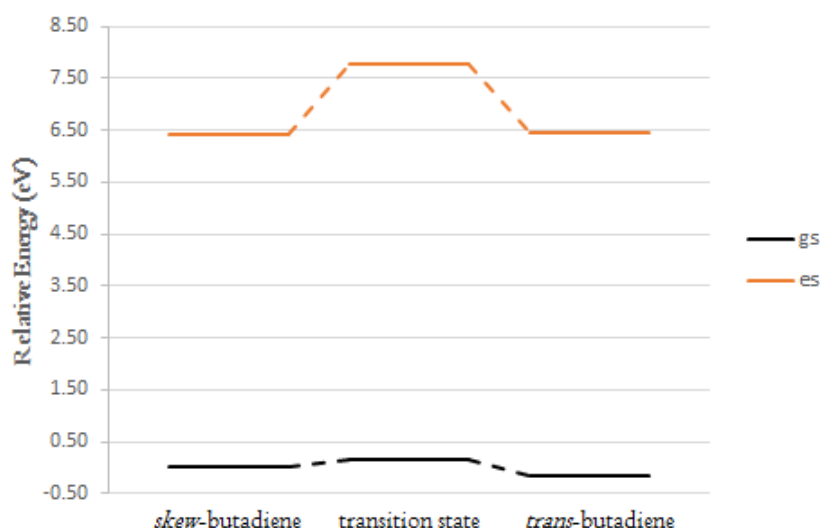

Figure 2. Energy level diagram of *skew*-butadiene, *trans*-butadiene, and the transition state connecting them in ground state (gs) and the corresponding excited state (es).

vibration. Figure 1 also shows the energy barrier of the opposite isomerization reaction which is 0.33 eV. The energy barrier of *skew*- to *trans*-butadiene reaction is smaller than the opposite one. It means that the *skew*- to *trans*-butadiene isomerization reaction is more likely to be occurred compared to the opposite one.

On the excited state structures
Figure 2 shows the energy level diagram of ground state and the corresponding excited state of *skew*-butadiene, *trans*-butadiene, and the transition state connecting them. Energy difference between excited state and the corresponding ground state are 6.43 eV, 6.44 eV, and 7.77 eV for *skew*-butadiene, *trans*-butadiene, and transition state connecting them, respectively. Since the energy difference is greater than 1 eV, we infer that conical intersection may not occur due

Figure 3. Energy level diagram of *skew*-butadiene, *trans*-butadiene, and the transition state connecting them in ground state (gs) and the corresponding excited state (es). The transition structure in excited state has been optimized using CASSCF method.

to the absence of degeneration between ground state and excited state. It means that CI alone cannot be used to show the existence of conical intersection.

Figure 3 shows the energy level diagram with the optimized transition structure in excited state. The results show that the energy of excited state transition structure is 0.005 eV higher than the corresponding ground state. It implies that degeneration occurs in transition state.

Degeneration in transition state of butadiene isomerization reaction involving de-excitation process shows that conical intersection may occurs in this reaction. The energy which is absorbed during excitation is used to reconstruct its transition state structure instead of released in form of light (radiation-less decay). Thus, this reaction still obeys conservation energy law.

4. Conclusion
We have reported the existence of degeneration in transition state of butadiene isomerization reaction. The energy difference of transition structure in ground state and excited state is 0.005 eV. It implies that conical intersection may occurs in this reaction. This explains that the energy which should be released during butadiene de-excitation is used to reconstruct its transition structure hence radiation-less decay occurred.

References
[1] Carey F A and Sunberg R J 2007 *Advanced Organic Chemistry. Part A. Structure and Mechanism* (Berlin: Springer)
[2] Olivucci M, Ragazos I N, Nernardi F, and Robb M A 1993 *J. Am. Chem. Soc.* **115** 3710
[3] Squillacote M and Semple T C 1990 *J. Am. Chem. Soc.* **107** 6842
[4] Srinivasan R 1968 *J. Am. Chem. Soc.* **90** 4498
[5] Dauben W G and Ritscher 1970 J S *J. Am. Chem. Soc.* **92** 2925
[6] Gale D M 1970 *J. Org. Chem.* **35** 970
[7] Bigwood M and Boue S 1974 *J. Chem. Soc. Chem. Commun.* **92** 529
[8] Penny A C 2014 *Organic Chemistry. A Mechanical Approach* (Florida: CRC Press)
[9] Hohenberg P and Kohn W 1964 *Phys. Rev.* **3B** B864-71

[10] Kohn W and Sham L J 1964 *Phys. Rev.* **4A** A1133-38

[11] Becke A D 1993 *J. Chem. Phys.* **98** 5648-52

[12] Fadilla R N, Aisyah N D, Dipojono H K, and Rusydi F 2017 *Proc. Eng.* **170** 113–8

[13] Aisyah N D, Fadilla R N, Dipojono H KD, and Rusydi F 2017 *Proc. Eng.* **170** 119–23

[14] Rusydi F, Agusta M K, Saputro A G S, and Kasai H 2014 *J. Vac. Soc. Jpn* **57** 102–110

[15] Gaussian Inc. 2010 *Gaussian09, Revision C.01* (Wallingford CT: Gaussian, Inc)

[16] Haynes W M 2017 *CRC Handbook of Chemistry and Physics 97th edition* (Florida: CRC Press)