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## **Theoretical Studies on the Isomers and Their Stable Conformations of 2–Butanimine**

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## Theoretical Studies on the Isomers and Their Stable Conformations of 2-Butanimine<sup>#</sup>

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### Abstract

**Motivation.** Using the B3LYP/cc-pVDZ method based on the density functional theory (DFT), the isomers and their conformations of 2-butanimine are studied in this paper. Two isomers and four stable conformations are found. The transition states of isomerization reactions and transformations from a conformation into another are also found in the molecular potential energy surface (PES). The frequency analysis method is used on all of the isomers, the stable conformations and the transition states to verify whether they are minima or saddle points. All calculations are repeated with the MP2/cc-pVDZ method.

**Method.** By means of B3LYP method combining Becke's three-parameter hybrid functional method with Lee-Yang-Parr's correlation functional (LYP) and Berny energy gradient method, all degrees of freedom of target molecules were optimized at cc-pVDZ basis set level. The structures of each stationary point including the minimum points and the possible saddle points in the PES of 2-butanimine were carried out. All of the stationary points were confirmed by vibrational analysis. In order to examine the results, the structural optimization and vibrational analysis of 2-butanimine were carried out by using MP2 method with cc-pVDZ basis set. The results are essentially consistent with that of the DFT calculations. In the calculations, the charge of each point is zero and the spin multiplicity is one.

**Results.** Two isomers are found in the molecular PES of 2-butanimine. Each isomer has another two stable conformations. The transition states of isomerization reactions and transformation from a conformation into another also are found in the molecular PES of 2-butanimine.

**Conclusions.** There are two isomers (*cis*-isomer and *trans*-isomer, namely isomer 1 and isomer 2 respectively) in the molecular PES of 2-butanimine. Each isomer has another two stable conformations. The isomer 1 is most stable. Because the steric effect of imino-group N-H of isomer 2, the energy of the isomer 2 is a little higher than that of isomer 1 (the difference is 0.689 kJ/mol). There are three *cis-trans*-isomerization reactions of the N<sub>2</sub>-H<sub>3</sub> bond. Because the activation barriers are very high, the reactions occur difficultly. There are six rotation transition states in the transformation from a conformation into another. Because the difference of energy among the isomers and conformations is very small and the rotation barriers are very low, it is difficult to distinguish and determine the structure of 2-butanimine in the synthesis products.

**Keywords.** 2-Butanimine; isomer; stable conformation; isomerization reaction; B3LYP/cc-pVDZ; MP2/cc-pVDZ.

### Abbreviations and notations

PES, potential energy surface

DFT, density functional theory

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## 1 INTRODUCTION

2-Butanimine is an unstable imine with a C=N double bond and plays an important role in experiment as an organic intermediate and catalyst. Chemists have been very interested in the synthesis [1,2], structural determination [3,4], and theoretical investigation [1,5,6] of 2-butanimine. The synthetic condition of 2-butanimine is very rigorous, it was synthesized by means of vacuum gas-solid reaction (VGSR) of *N,N*-dichloro-2-butanimine and KOH in a glass column, the column temperature and sample pressure were optimized by measuring FTIR spectra of the reaction products in a separate experiment [1,2]. Because of the existence of the imino-group, the substituted butane will produce a complex and variable molecular potential energy surface (PES). Obviously, it's significant to understand the distribution of the stable forms and the energy relation of their transformation to each other. It also has the directing significance to synthesis and application of the 2-butanimine and the imino-alkanes. The previous experimental and theoretical studies about 2-butanimine have just been limited to a part of the isomers, and there are different conclusions. In this study, the molecular PES is searched completely and all stationary points are predicted by theoretical techniques.

## 2 COMPUTATIONAL METHODS

By means of B3LYP method combining Becke's three-parameter hybrid functional method [7] with Lee-Yang-Parr's correlation functional (LYP) [8,9] and Berny energy gradient method [10], all degrees of freedom of target molecules were optimized at the cc-pVDZ basis set level. The structures of each stationary point including the minimum points and the possible saddle points in the PES of 2-butanimine were carried out. All of the stationary points were confirmed by vibrational analysis. In order to examine the results, the structural optimization and vibrational analysis of 2-butanimine were carried out by using MP2 method [11,12] with cc-pVDZ basis set. The results are essentially consistent with that of the DFT calculations. In the calculations, the charge of each point is zero and the spin multiplicity is one. All computations were performed with the Gaussian 03 program [13].

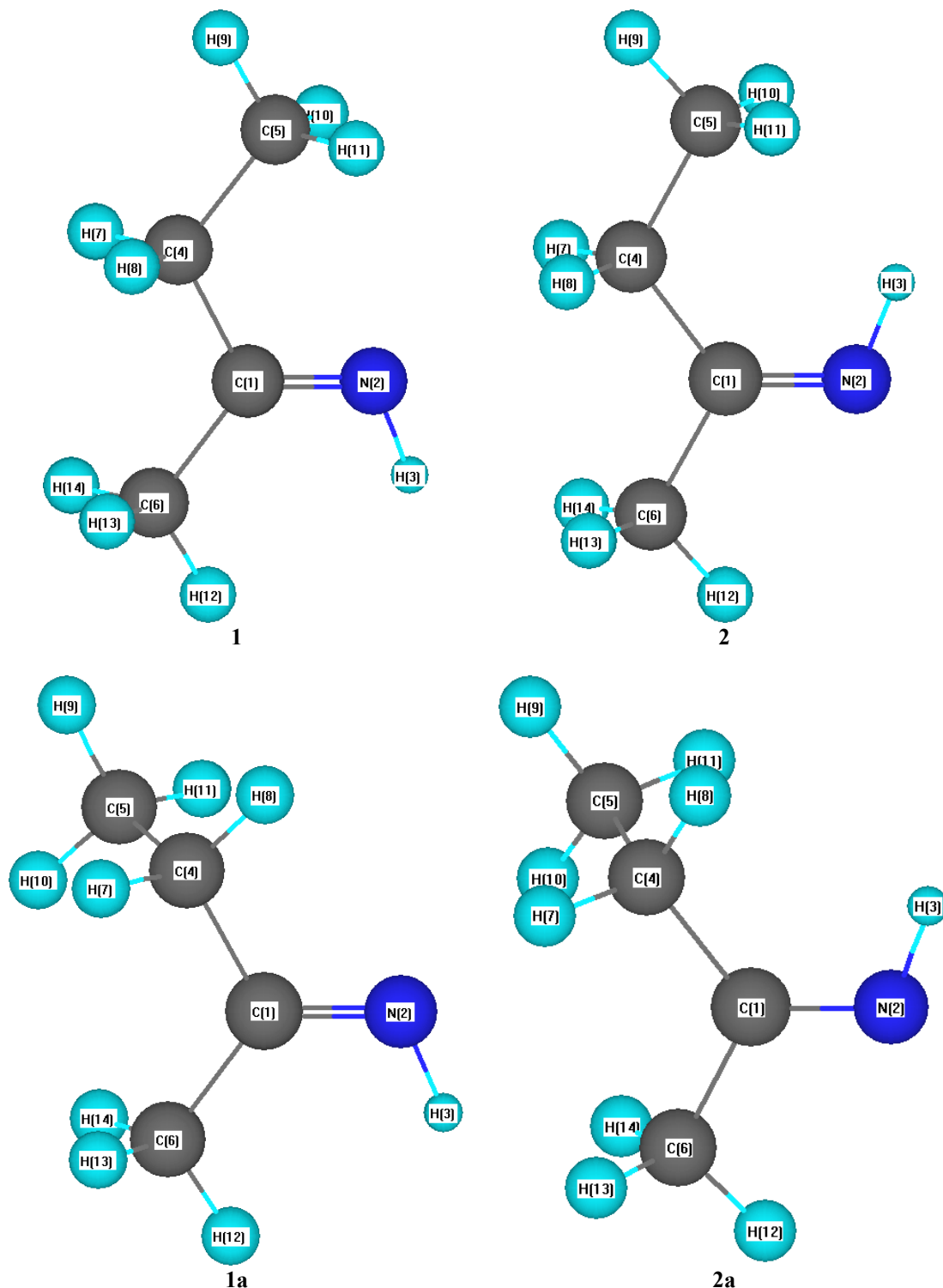
## 3 RESULTS AND DISCUSSION

There are 15 stationary points in the molecular PES of 2-butanimine, including 6 minima points and 9 saddle points.

### 3.1 Isomers and Their Stable Conformations

The calculated results show that there are two isomers (**1** and **2**, as shown in Figure 1) for  $(C_2H_5)(CH_3)C=NH$  in the molecular PES. The isomers **1** and **2** are a pair of *cis-trans*-isomers,

which have the  $C_s$  symmetry. Their difference only is that the N–H bond and the methyl group containing the  $C_6$  atom are in the *cis*-orientation or in the *trans*-orientation.



**Figure 1.** The structures and atom numberings for partial stable forms of 2-butanamine.

In the isomer **1**, when the methyl group containing the  $C_5$  atom rotates around the  $C_1$ – $C_4$  single bond counterclockwise toward the position of the  $H_7$  atom, the conformation **1a** is obtained (see

Figure 1). The dihedral angle  $\angle C_5C_4C_1C_6$  is  $-69.1^\circ$ . By the same operation to the isomer **2**, the conformation **2a** is obtained, and it is the *trans*-form of the conformation **1a**. When the methyl group containing the  $C_5$  atom rotates around the  $C_1$ — $C_4$  single bond clockwise toward the position of the  $H_8$  atom in the isomer **1**, the conformation **1b** is obtained. By the same rotation to the isomer **2**, the conformation **2b** is obtained, and it is the *trans*-form of the conformation **1b**. The conformation **1b** and **2b** are enantiomers of the conformation **1a** and **2a**, respectively. Thus the structural parameters and energies of the conformation **1b** and **2b** are same with the conformation **1a** and **2a**, respectively. And all of them have not symmetry. Their difference is that the methyl group containing the  $C_5$  atom points to inside of the paper plane in the conformation **1a** and **2a**, but the methyl group containing the  $C_5$  atom points to outside of the paper plane in the conformation **1b** and **2b**. The isomer **1**, **2**, the conformation **1a**, **2a** and the conformation **1b**, **2b** are three pairs of *cis*-*trans*-forms. The selected structural parameters for these isomers and conformations are provided in Tables 1–3 (the values in parentheses were obtained by using MP2 method with cc-pVDZ basis set). Because of enantiomers, we only present the structural parameters of isomer **1**, **2** and conformation **1a**, **2a**.

**Table 1.** The bond lengths of various stationary points in the molecular PES of  $(C_2H_5)(CH_3)C=NH$  at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

l (nm)	<b>1</b>	<b>2</b>	<b>1a</b>	<b>2a</b>	<b>TS1</b>	<b>TS4</b>	<b>TS8</b>
$C_1-N_2$	0.1277 (0.129)	0.1277 (0.129)	0.1278 (0.129)	0.1279 (0.1291)	0.1245 (0.125)	0.1270 (0.129)	0.1278 (0.129)
$N_2-H_3$	0.1030 (0.103)	0.1020 (0.103)	0.1030 (0.103)	0.1030 (0.103)	0.0990 (0.099)	0.1030 (0.103)	0.1030 (0.103)
$C_1-C_4$	0.1510 (0.151)	0.1520 (0.152)	0.1510 (0.151)	0.1520 (0.151)	0.1530 (0.153)	0.1520 (0.152)	0.1530 (0.152)
$C_1-C_6$	0.1510 (0.151)	0.1510 (0.151)	0.1510 (0.151)	0.1510 (0.151)	0.1530 (0.153)	0.1510 (0.151)	0.1510 (0.151)
$C_4-C_5$	0.1520 (0.152)	0.1520 (0.152)	0.1530 (0.153)	0.1530 (0.153)	0.1520 (0.152)	0.1530 (0.153)	0.1530 (0.153)
$C_4-H_7$	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)
$C_4-H_8$	0.1100 (0.110)	0.1100 (0.110)	0.1090 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)	0.1100 (0.110)

According to our initial guess, when a hydrogen atom of the methyl group containing the  $C_6$  atom is staggered with the two H atoms linking with the  $C_4$  atom in the isomer **1** (meantime the methyl group containing the  $C_6$  atom and the imino-group also have the staggered orientation), the conformation is more stable, but an evaluation of the vibrational frequency of this conformation yields an imaginary frequency indicating that it is not a minimum in the potential energy surface of 2-butanimine. Similarly, is it also a stable conformation when the ethyl group consisted of the  $C_4$  and  $C_5$  atoms in the isomer **1** stretches for the reverse direction (still retaining the  $C_s$  symmetry), and the methyl group containing the  $C_5$  atom and the two H atoms linking with the  $C_6$  atom are eclipsed (see the **TS8** in Figure 2)? As the calculation indicated, it is also not a minimum in the PES of 2-butanimine (see the discussion of the saddle points in the next section).

**Table 2.** The bond angles of various stationary points in the molecular PES of (C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)C=NH at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

$\theta(^{\circ})$	<b>1</b>	<b>2</b>	<b>1a</b>	<b>2a</b>	<b>TS1</b>	<b>TS4</b>	<b>TS8</b>
$\angle C_1N_2H_3$	110.1 (108.5)	110.4 (108.9)	110.0 (108.4)	109.7 (108.1)	179.9 (180.0)	110.1 (108.6)	110.0 (108.5)
$\angle N_2C_1C_4$	119.1 (118.8)	126.3 (126.4)	118.0 (117.9)	124.9 (125.1)	123.0 (123.0)	117.8 (117.4)	116.7 (116.4)
$\angle N_2C_1C_6$	125.4 (125.7)	118.4 (118.3)	125.2 (125.4)	118.2 (118.0)	123.1 (123.4)	125.6 (125.9)	124.7 (124.9)
$\angle C_1C_4C_5$	114.9 (114.2)	115.8 (115.1)	113.7 (112.9)	113.7 (113.1)	113.9 (113.1)	112.1 (111.2)	117.6 (116.8)
$\angle C_1C_4H_7$	107.8 (107.9)	107.7 (107.7)	109.1 (109.0)	108.9 (108.7)	107.9 (108.0)	110.2 (110.2)	106.8 (107.0)
$\angle C_1C_4H_8$	107.8 (107.9)	107.7 (107.7)	107.0 (107.1)	108.6 (108.8)	107.9 (108.0)	107.8 (108.1)	106.8 (107.0)
$\angle C_1C_6H_{12}$	111.5 (111.4)	110.0 (110.0)	111.4 (111.1)	109.7 (109.3)	110.2 (110.1)	111.8 (111.7)	110.8 (110.5)
$\angle C_1C_6H_{13}$	110.7 (110.4)	110.8 (110.5)	110.5 (110.7)	110.7 (110.8)	110.7 (110.4)	110.4 (110.2)	111.2 (111.0)
$\angle C_4C_5H_9$	110.6 (110.6)	110.6 (110.7)	110.5 (110.7)	110.6 (110.7)	111.2 (111.3)	111.1 (111.3)	110.1 (110.1)
$\angle C_4C_5H_{10}$	111.0 (110.7)	111.6 (110.2)	112.3 (111.9)	111.9 (111.5)	110.9 (110.5)	111.3 (110.9)	112.2 (111.9)
$\angle C_4C_5H_{11}$	111.0 (110.7)	111.6 (110.2)	110.9 (110.6)	111.0 (110.7)	110.9 (110.5)	109.8 (109.4)	112.2 (111.9)

A detailed analysis of the energies shows that the energy of isomer **1** is lowest in all of isomers and conformations, which indicates that the isomer **1** is most stable, but the energy difference between the isomer **1** and other is small. As listed in the Table 4, the highest difference is only 5.559 kJ/mol. The energy of the isomer **2**, which is the *trans*-isomer of the isomer **1**, is a little higher than that of isomer **1** (the difference is 0.689 kJ/mol). Analyzing the cause, this likely relates to the steric effect of imino-group N–H.

In Figure 1, the distance between the N<sub>2</sub> atom and the H<sub>12</sub> atom in the isomer **1** is 0.2659 nm, which is close to the sum of the van der Waals radii of N atom and H atom. But in the isomer **2**, the distance between the N<sub>2</sub> atom and the H<sub>12</sub> atom is 0.2496 nm, which is a little lower than this value. Therefore there is the steric hindrance between the N<sub>2</sub> atom and methyl hydrogen atom in the isomer **2**.

The energies of the conformation **1a** and **2a**, which are another pair of *cis*–*trans*–forms, are higher than that of the first pair of *cis*–*trans*–isomers, but similarly the difference between them is very small, the energy of the *trans*–form (the conformation **2a**) is only 0.024 kJ/mol higher than that of the *cis*–form (the conformation **1a**). Because the third pair of *cis*–*trans*–forms, namely the conformation **1b** and **2b**, is the enantiomers of the conformation **1a** and **2a**, their energies are equal to the energies of the conformation **1a** and **2a**, respectively.

**Table 3.** The dihedral angles of various stationary points in the molecular PES of  $(C_2H_5)(CH_3)C=NH$  at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

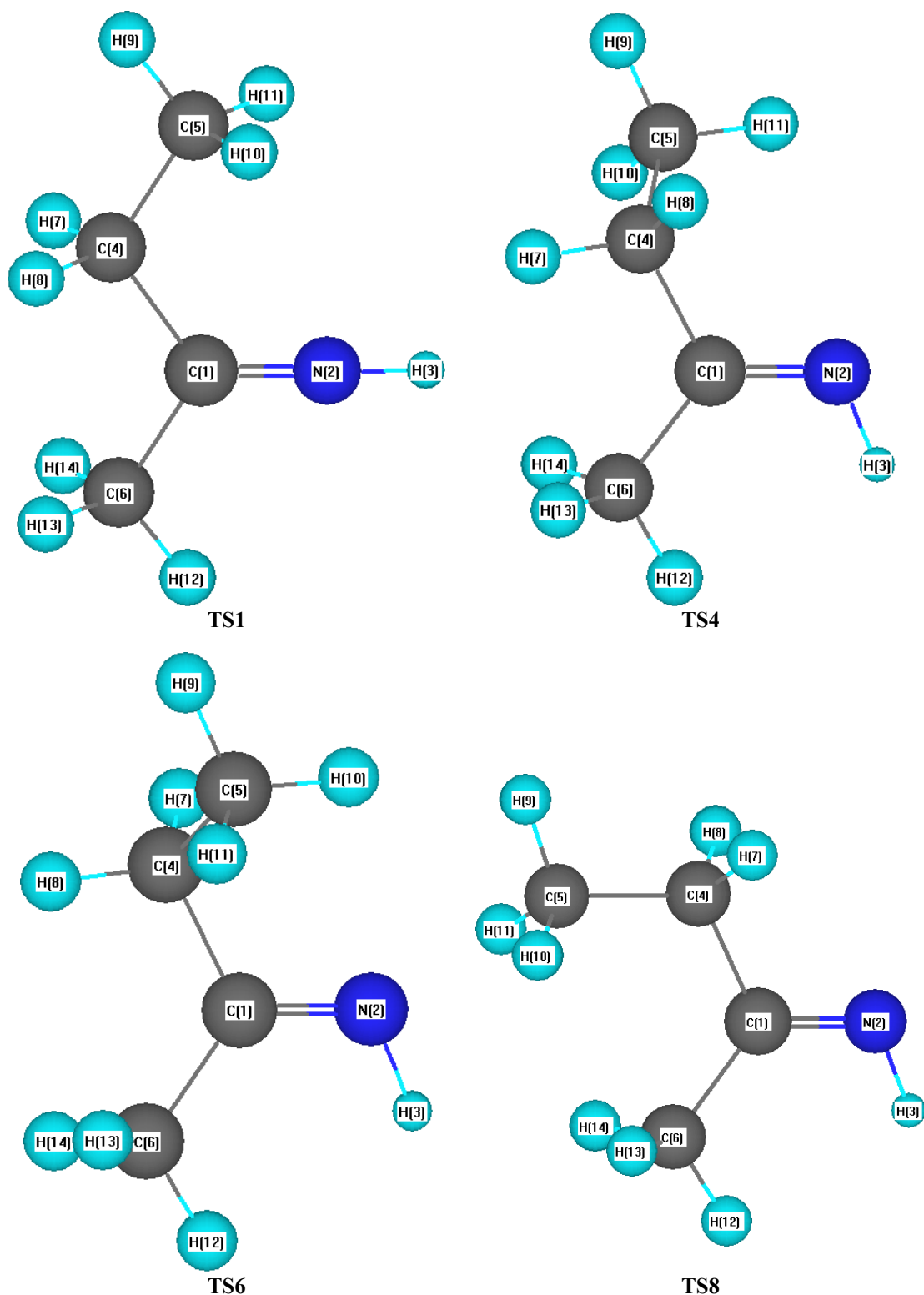
$\theta$ (°)	<b>1</b>	<b>2</b>	<b>1a</b>	<b>2a</b>	<b>TS1</b>	<b>TS4</b>	<b>TS8</b>
$\angle H_3N_2C_1C_4$	180.0 (180.0)	0.0 (0.0)	-179.5 (-179.8)	0.3 (-0.1)	0.0 (0.0)	-179.0 (-179.0)	180.0 (180.0)
$\angle H_3N_2C_1C_6$	0.0 (0.0)	180.0 (180.0)	0.5 (-0.5)	180.0 (180.0)	180.0 (180.0)	0.2 (0.0)	0.0 (0.0)
$\angle N_2C_1C_4C_5$	0.0 (0.0)	0.0 (0.0)	110.9 (117.5)	111.1 (118.7)	0.0 (0.0)	63.7 (60.8)	180.0 (180.0)
$\angle N_2C_1C_4H_7$	123.8 (123.4)	123.7 (123.4)	-126.9 (-120.8)	-127.1 (-120.0)	123.6 (123.2)	-173.1 (-176.4)	-56.0 (-56.4)
$\angle N_2C_1C_4H_8$	-123.8 (-123.4)	-123.7 (-123.4)	-10.7 (-4.4)	-11.1 (-3.6)	-123.6 (-123.2)	-56.6 (-59.4)	56.0 (56.4)
$\angle N_2C_1C_6H_{13}$	121.0 (120.9)	120.9 (120.8)	121.1 (130.6)	121.7 (127.6)	121.0 (120.9)	120.0 (120.3)	120.8 (120.6)
$\angle N_2C_1C_6H_{14}$	-121.0 (-120.9)	-120.9 (-120.9)	-120.8 (-110.8)	-119.8 (-114.5)	-121.0 (-120.9)	-122.5 (-122.0)	-120.8 (-120.6)
$\angle C_4C_1C_6H_{12}$	180.0 (180.0)	180.0 (180.0)	-179.7 (-171.3)	-179.0 (-173.5)	180.0 (180.0)	178.0 (178.2)	180.0 (180.0)
$\angle C_1C_4C_5H_9$	180.0 (180.0)	180.0 (180.0)	-177.3 (-176.1)	-177.9 (-176.5)	180.0 (180.0)	-177.3 (-177.9)	180.0 (180.0)
$\angle C_1C_4C_5H_{10}$	59.4 (59.3)	60.4 (60.3)	63.0 (64.0)	62.4 (63.6)	59.3 (59.2)	62.5 (61.7)	60.7 (60.6)
$\angle C_5C_4C_1C_6$	180.0 (180.0)	180.0 (180.0)	-69.1 (-61.8)	-68.9 (-61.2)	180.0 (180.0)	-115.6 (-118.4)	0.0 (0.0)
$\angle H_7C_4C_1C_6$	-56.2 (-56.6)	-56.3 (-56.6)	53.0 (60.0)	52.9 (60.2)	-56.4 (-56.8)	7.6 (4.5)	124.0 (123.6)
$\angle H_8C_4C_1C_6$	56.2 (56.6)	56.3 (56.6)	169.3 (176.4)	168.9 (176.5)	56.4 (56.8)	124.1 (124.4)	-124.0 (-123.6)
$\angle H_7C_4C_5H_{10}$	-63.0 (-62.7)	-62.1 (-61.8)	-59.1 (-57.5)	-59.3 (-57.5)	-62.7 (-62.3)	-60.7 (-61.0)	-61.8 (-61.5)
$\angle H_7C_4C_5H_{11}$	178.3 (178.8)	177.2 (177.6)	179.8 (178.1)	-179.8 (-177.9)	178.6 (179.2)	179.9 (179.9)	176.9 (177.2)

**Table 4.** The relative energies (kJ/mol) of various minimum points in the molecular PES of  $(C_2H_5)(CH_3)C=NH$  at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

minimum point	<b>1</b>	<b>2</b>	<b>1a</b>	<b>2a</b>	<b>1b</b>	<b>2b</b>
relative energy	0.000 (0.000)	0.689 (0.801)	5.559 (4.742)	5.525 (4.745)	5.559 (4.742)	5.525 (4.745)

### 3.2 Transition States

There are 3 reaction transition states in the isomerization of the three pairs of *cis-trans*- forms, meanwhile there are 6 rotation transition states in the processes of the transformations to each other of the isomers and stable conformations. Similarly, because of the enantiomers, only the parameters of part of transition states are listed in Tables 1–3. The results of vibrational analysis show that every transition state has a unique imaginary vibration mode. The corresponding imaginary frequencies are listed in Table 5. The direction of the vibrational vector of every imaginary vibration is correct which points to a pair of corresponding stationary points.



**Figure 2.** The structures and atom numberings for partial transition states in the molecular PES of 2-butanamine.

**Table 5.** The imaginary frequencies ( $icm^{-1}$ ) of various transition states in the molecular PES of  $(C_2H_5)(CH_3)C=NH$  at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

saddle point	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9
imaginary	1192.8	1192.8	1192.8	70.1	66.4	70.1	66.4	110.3	93.6
frequency	(1192.8)	(1240.0)	(1240.1)	(69.8)	(71.8)	(69.8)	(71.8)	(120.7)	(103.4)



There is **TS1** in the process of the *cis*–*trans*–isomerization reaction from the isomer **1** to **2** (see Figure 2). In the structure of **TS1**, the four C atoms, the N atom and the H atom linking with the N atom are located in a same symmetric plane, and the C<sub>1</sub>, N<sub>2</sub>, H<sub>3</sub> atoms are almost in a line. The two H atoms linking with the C<sub>4</sub> atom and two H atoms linking with the C<sub>6</sub> atom are eclipsed.

**TS1** belongs to the C<sub>s</sub> point group, the vibrational analysis shows that the value of imaginary frequency is 1206.5 icm<sup>-1</sup>, and its vibration mode is presented as follows: the N<sub>2</sub>–H<sub>3</sub> bond swings up and down using the N<sub>2</sub> atom as the axis in the symmetric plane, the positive and negative directions of its vibrational vector point to a pair of *cis*–*trans*–isomers, respectively (namely isomers **1** and **2**). At the same time, the C<sub>1</sub>–N<sub>2</sub> bond swings slightly using the C<sub>1</sub> atom as the axis in the opposite direction of the N<sub>2</sub>–H<sub>3</sub> vibration. The calculation shows that because the activation barrier of the isomerization reaction is higher (that of positive and negative reaction are 124.666 kJ/mol and 123.977 kJ/mol, respectively), it is difficult to occur. In the same way, there is **TS2** in the process from the conformation **1a** to **2a**, and **TS3** from the conformation **1b** to **2b**. **TS2** and **TS3** are a pair of enantiomers. Similar to **TS1**, the imaginary vibration direction of two transition states points to their corresponding *cis*–*trans*–forms. The activation barrier of two isomerization reactions is also higher (see Table 6).

**Table 6.** The activation barriers (kJ/mol) of various isomerization reactions of (C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)C=NH at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

reaction	<b>1</b> → <b>2</b>	<b>1a</b> → <b>2a</b>	<b>1b</b> → <b>2b</b>
corresponding transition state	<b>TS1</b>	<b>TS2</b>	<b>TS3</b>
ΔE <sup>‡</sup> (+)	124.666 (137.179)	119.082 (132.436)	119.082 (132.436)
ΔE <sup>‡</sup> (-)	123.977 (136.378)	119.116 (132.433)	119.116 (132.433)

**TS4** is a rotation transition state from the conformation **1a** to isomer **1**. In **TS4**, the C<sub>1</sub>, C<sub>4</sub>, C<sub>6</sub>, N atom and the H atom linking with the N atom are located almost in a plane. The dihedral angle ∠C<sub>5</sub>C<sub>4</sub>C<sub>1</sub>N<sub>2</sub>, which is consisted of the C<sub>5</sub> atom and this plane is 60.2°. The methyl group containing the C<sub>5</sub> atom points to inside of the paper plane, and the two H atoms linking with the C<sub>4</sub> atom and the H atom in the methyl group containing the C<sub>6</sub> atom are staggered (see Figure 2). From the conformation **2a** to isomer **2**, the *trans*–form of **TS4** is obtained, which is named **TS5**. The vibrational analysis shows that each of the two forms has a unique imaginary vibration mode. The direction of the vibration mode is that the ethyl group linking with the C<sub>1</sub> atom rotates around the C<sub>1</sub>–C<sub>4</sub> single bond to and fro relative to the others of molecule framework (the others of molecule framework rotate slightly in opposite direction), and points to their corresponding stationary points, namely the isomer **1**, conformation **1a** and the isomer **2**, conformation **2a**, respectively. It verifies

that **TS4** and **TS5** are rotation transition states in correct transformation process. Similarly, when isomer **1** and conformation **1b** transform into each other, there is **TS6**; when the isomer **2** and the conformation **2b** transform each other, there is **TS7**. **TS6** and **TS7** are also a pair of *cis-trans*-forms, meanwhile **TS6** and **TS4**, **TS7** and **TS5** are a pair of enantiomers, respectively.

**TS8** is formed in the transformation process from the conformation **1a** to **1b**. The molecular structure of **TS8** is presented in Figure 2: the four C atoms, N atom and the H atom linking with the N atom are located in the same symmetric plane. The methyl group containing the C<sub>5</sub> atom and the methyl group containing the C<sub>6</sub> atom are eclipsed. **TS9** is a rotation transition state from the conformation **2a** to **2b**. **TS9** and **TS8** are a pair of *cis-trans*-forms, and both of them have the C<sub>s</sub> symmetry. From an object analysis of chemistry, **TS8** and **TS9** seem as the stable conformations, but the vibrational analysis shows that both of them have a unique imaginary vibration mode.

The direction of the imaginary vibration modes of **TS8** and **TS9** is that the ethyl group linking with the C<sub>1</sub> atom rotates around the C<sub>1</sub>—C<sub>4</sub> bond to and fro relative to the others of molecule framework (the others of the framework swing slightly in opposite direction), each of them points to its corresponding stable conformations, which are the conformation **1a**, **1b** and conformation **2a**, **2b**, respectively. It testifies they are rotation transition states in correct transformation process.

The nine transition states can divide into two types. One kind is the reaction transition states that are formed in the *cis-trans*-isomerization processes of the N<sub>2</sub>—H<sub>3</sub> bond, including **TS1**, **TS2** and **TS3**. The other kind is the rotation transition states that are formed in the rotation transformation processes of the partial groups in the molecule framework, including **TS4**, **TS5**, **TS6**, **TS7**, **TS8** and **TS9**.

**Table 7.** The rotation barriers (kJ/mol) of various transformation from a conformation into another of (C<sub>2</sub>H<sub>5</sub>)(CH<sub>3</sub>)C=NH at B3LYP/cc-pVDZ level (the values in parentheses obtained from the MP2/cc-pVDZ calculations)

transformation	<b>1</b> → <b>1a</b>	<b>2</b> → <b>2a</b>	<b>1</b> → <b>1b</b>	<b>2</b> → <b>2b</b>	<b>1a</b> → <b>1b</b>	<b>2a</b> → <b>2b</b>
corresponding transition state	<b>TS4</b>	<b>TS5</b>	<b>TS6</b>	<b>TS7</b>	<b>TS8</b>	<b>TS9</b>
ΔE <sup>‡</sup> (+)	7.962 (7.402)	7.213 (6.966)	7.962 (7.402)	7.213 (6.966)	10.081 (11.607)	6.987 (8.088)
ΔE <sup>‡</sup> (-)	2.403 (2.660)	2.377 (3.022)	2.403 (2.660)	2.377 (3.022)	10.081 (11.607)	6.987 (8.088)

Compared the imaginary frequencies of the nine transition states and the barriers of the isomerization reactions and rotation transformation processes (listed in Tables 5, 6 and 7), it is evident that the activation barriers of *cis-trans*-isomerization reactions of the N<sub>2</sub>—H<sub>3</sub> bond are very high, and the reactions perform very difficultly. For example, the activation barrier from the isomer **1** to **2** is 124.666 kJ/mol and that from the isomer **2** to **1** is 123.977 kJ/mol. But the rotation barriers

of the rotation transformation processes are very low, thus the transformations perform easily. For example, the rotation barrier from the isomer **1** to conformation **1a** is only 7.962 kJ/mol and that from the conformation **1a** to isomer **1** is 2.403 kJ/mol.

## 4 CONCLUSIONS

There are two isomers (*cis*-isomer and *trans*-isomer, namely isomer **1** and isomer **2** respectively) in the molecular PES of 2-butanimine. Each isomer has another two stable conformations. The isomer **1** is most stable. Because the steric effect of imino-group N-H of isomer **2**, the energy of the isomer **2** is a little higher than that of isomer **1** (the difference is 0.689 kJ/mol). There are three *cis-trans*-isomerization reactions of the N<sub>2</sub>-H<sub>3</sub> bond. Because the activation barriers are very high, the reactions occur difficultly. There are six rotation transition states in the transformation from a conformation into another. Because the difference of energy among the isomers and conformations is very small and the rotation barriers are very low, it is difficult to distinguish and determine the structure of 2-butanimine in the synthesis products.

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