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DFT investigation of dihydrogen transfer from 1,2-diazene. Structure and reactivity of the disubstituted cyclopentene

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Abstract

In this work, we theoretically study the hydrogenation reaction of disubstituted cyclopentene **1a-d** by the (Z)-1,2-diazene **2** and by (E)-1,2-diazene **2'**. DFT/B3LYP calculations with 6-311G** standard basis set, explain the possibility and the stereoselectivity of these reactions. The transition states of the reaction between (Z)-1,2-diazene **2** and disubstituted cyclopentene **1a-d** have been calculated and discussed.

Keywords: DFT, hydrogenation reactions, cyclopentene.

Introduction

The hydrogenation chemical reactions of alkenes have a great interest in the various fields of chemistry [1-15]. The thermodynamic and kinetic study of a chemical transformation requires knowledge of the reactants structure, products structure and reaction intermediates such as bond length, bond angles, etc. Generally, there are two kinds of hydrogenation reactions, by chemically transfer of two hydrogen atoms from (Z) and (E) -1,2-diazene N_2H_2. Or the hydrogenation of cycloalkenes may be conducted using H_2 with a metal catalysis such as Ni, Pd, etc… [16-20]. In this work, we are interested to study the hydrogenation reaction by chemically transfer of the two hydrogen atoms from (Z) and (E)-1,2-diazene.

We found interesting to study from both the thermodynamic and orbital point of views the possibility and the stereoselectivity of hydrogenation reactions between the disubstituted cyclopentene **1a-d** by the (Z) -1,2-diazene **2** and by (E) -1 ,2-diazene **2'** (see Figure 1). In each case of these reactions, we determine the corresponding transition states.

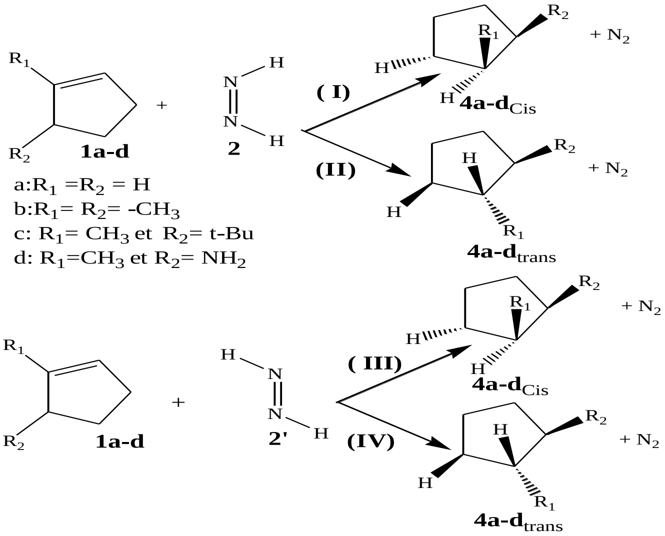


Figure 1: Reaction between cyclopentene **1a** and disubstitued cyclopentene **1b-d** with 1,2-diazene

2. Calculation methods

This study was carried out using the Gaussian 03 program [21]. The calculations were performed at DFT level with the standard basis set 6-311G**. We used the B3LYP functional in which the exchange energy is calculated by Becke's three parameters method and the correlation method of Lee, Yang and Parr [22-24]. The choice of the DFT method is justified by its efficiency in the treatment of this systems type [25]. Computations of harmonic vibrational frequencies have been executed to verify the nature of the corresponding stationary points. The stationary points are classified as minima in the case, when no imaginary frequencies are found, and as a transition state if only one imaginary frequency is obtained [26]. In order to ensure that the transition states connect products, the intrinsic reaction coordinate (IRC) method [27] at the HF/6-311G** and at B3LYP/6-311G** level of theory have been applied to each transition state of every reaction. Zero-point energies (ZPE) have been computed at the HF/6-311G** and at the B3LYP/6-311G** level of theory, and the thermal corrections of each species has been added at 298,15K.

3. Results and discussion

3.1. Thermodynamic study

We study from thermodynamic point of view the posibility and the stereoselectivity of reactions between (Z)-1,2-diazene **2** and cyclopentene **1a-d** and the reactions between (E)-1,2-diazene **2'** and cyclopentene **1a-d** (Figure 2 and figure 3).

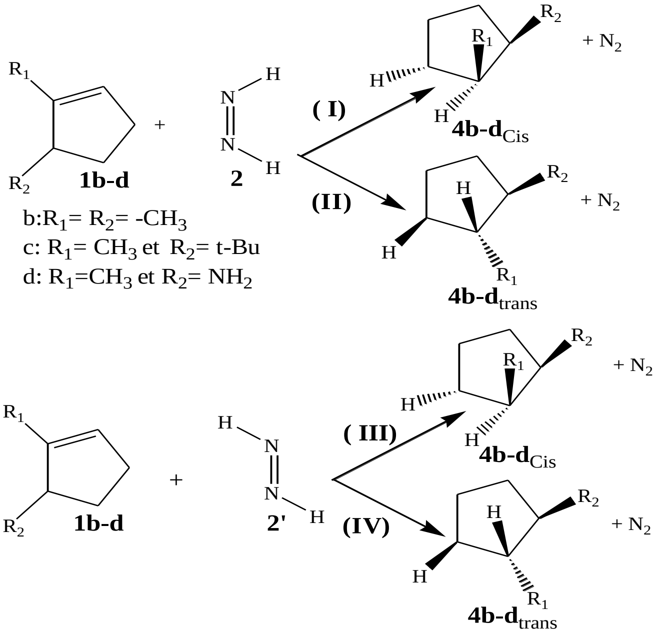


Figure 2 : Reaction between disubstitued cyclopentene **1b-d** with 1,2-diazene

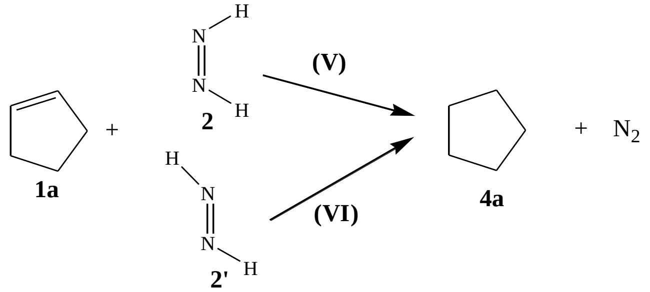


Figure 3: Reaction between cyclopentene **1a** and 1,2-diazene

We determine under standard conditions of temperature and pressure (298,15K et 1atm), the variation of Gibbs free energy ΔG_r, the variation of energy ΔE_r, the variation of enthalpy ΔH_r and ZPE (Zero point energy) of reactions (I), (II), (III) and (IV) (Table 1).

As shown in Table 1, values of free reaction energy ΔG_r are negative, so these reactions are possible from thermodynamic point of view. We notice that the values of Gibbs free energy ΔG_r corresponding to reactions (I) and (II) are respectively higher, in absolute values, than those correspond to the reactions (III) and (IV). This implies that reactions (I) and (II) are more favorable from thermodynamic point of view than reactions (III) and (IV). But we found that (E)-1,2-diazene **2’** is more stable than (Z)-1,2-diazene **2** by 5.49 kcal/mol and 5.35 kcal/mol in energy, respectively of at DFT/B3LYP with the standard basis set 6-31G* and 6-311G** (Table 2). The proportion of isomer (Z) is very low in the mixture reaction as shown previously [24].

But we found that during the addition of (Z)-1,2-diazene **2** on disubstitued cyclopentene type **1b-d** reactions (I) and (II) become thermodynamically more stable as compared to reactions (III) and (IV) between (E)-1,2-diazene **2'** and cyclopentene **1b-d**.

We also notice that the values of Gibbs free energy reaction corresponding to reaction (II) are always higher in absolute values than those of reaction (I). This allows us to predict that the trans compounds **4b-d**$_{trans}$ are the favored products of the reaction between cyclopentene **1b-d** and (Z)-1,2-diazene **2**. Similarly, we can notice that reactions (IV) always give the favored products of the reaction between cyclopentene **1b-d** and (E) -1,2-diazene **2'**. We also notice that the values of energy reaction ΔE_r corresponding to reactions (II) and (IV) are larger, in absolute values, than the variation energies ΔE_r corresponding to reactions (I) and (III), respectively. This confirms again that the favored products of the reaction are the trans type **4b-d**$_{trans}$.

In the case of both the reactions between cyclopentene **1a** and (Z)-1,2-diazene **2** and the reaction between cyclopentene **1a** and (E)-1,2-diazene **2'**, we obtain a single product **4a** (Figure 3). But the thermodynamic values show that the reaction (V) is more favorable from thermodynamic point of view than the reaction (VI) (Table 1).

Table 1 : Thermodynamic results of ΔE_r, ΔG_r, ΔH_r and ZPE for reactions (I-VI) (kcal.mol^{-1}).

Reactions	products	ΔE_r + ZPE	ΔH_r	ΔG_r
		B3LYP/6-311G**		
Reaction (I)	**4b**$_{cis}$	-58.13	-58.31	-56.32
	4c$_{cis}$	-56.96	-57.02	-55.44
	4d$_{cis}$	-59.76	-59.95	-57.94
Reaction (II)	**4b**$_{trans}$	-60.43	-60.53	-58.97
	4c$_{trans}$	-59.96	-59.14	-57.91
	4d$_{trans}$	-59.76	-61.96	-60.30
Reaction (III)	**4b**$_{cis}$	-52.77	-52.95	-50.98
	4c$_{cis}$	-51.60	-51.66	-50.10
	4d$_{cis}$	-54.40	-54.59	-52.60
Reaction (IV)	**4b**$_{trans}$	-55.70	-55.17	-53.62
	4c$_{trans}$	-53.77	-53.78	-52.56
	4d$_{trans}$	-56.50	-56.60	-54.96
Reaction (V)	**4a**	-63.03	-63.00	-62.06
Reaction (VI)	**4a**	-57.68	-57.64	-56.72

Table 2: Calculated energies (hartrees) of the molecules. (1 hartree = 627.49 kcal.mol^{-1})

Compound	E	G	H	ΔE	ΔH	ΔG
	B3LYP/ 6-311G**					
(Z)-1,2-diazene **2**	-110.633120	-110.657613	-110.632175	5.35	5.35	5.34
(E)-1,2-diazene **2'**	-110.641660	-110.666127	-110.640716	0.00	0.00	0.00

3.2. Transition states

The thermodynamic results show that the hydrogenation reactions between cyclopentene **1a-d** and (Z)-1,2-diazene **2** are more favored than the reaction between cyclopentene **1a-d** and (E)-1,2-diazene **2'**. So we continue our transition states between cyclopentene **1a-d** and (Z)-1,2-diazene **2**.

First, we determine the transition state of the reaction between cyclopentene **1a** and (Z)-1,2-diazene **2**. As shown in Figure 4, the reaction between cyclopentene **1a** and (Z)-1,2-diazene **2** passes through the formation of a complex similar to the structure found by Mac Kee et al [28] for the reaction between ethene and (Z) -1,2-diazene **2**.

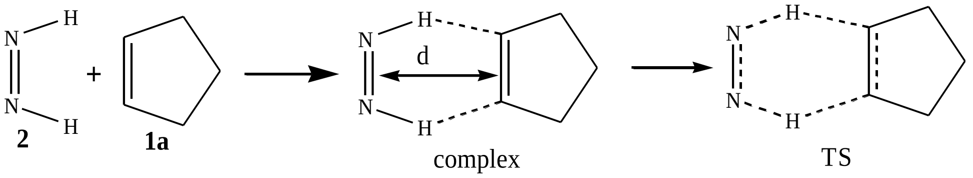


Figure 4: Intermediate reaction formed between (Z) -1,2-diazene **2** and cyclopentene **1a**. complex and TS

The geometries of cyclopentene, complex and transition state are given in Figure 5. As it appears on the Newmann representation following C_2C_3 carbon of cyclopentene **1a**, the cyclopentene is almost planar. In the complex, the dihedral angle between two cycles is 101.1°. The results show that whatever the approach of (Z)-1,2-diazene **2** on the cyclopentene **1a**, we found only one transition state shown in Figure 4 and Figure 5.

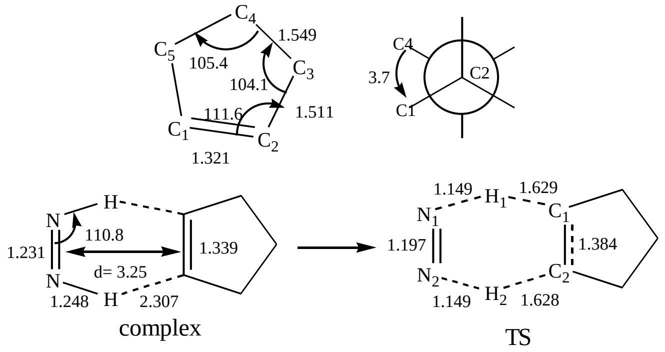


Figure 5: geometries (angle and distance) of compounds

The energy profile of reaction between cyclopentene **1a** and (Z)-1,2-diazene **2** is given in Figure 6.

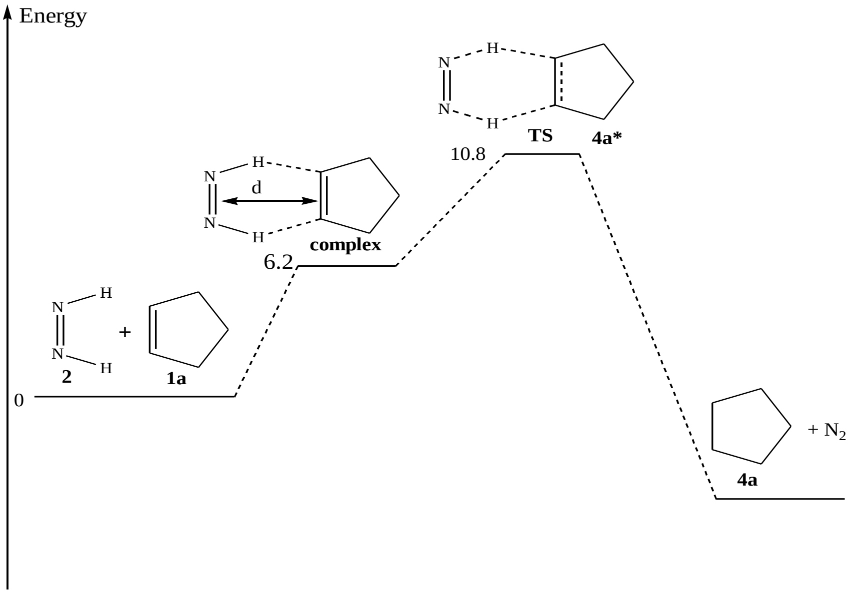
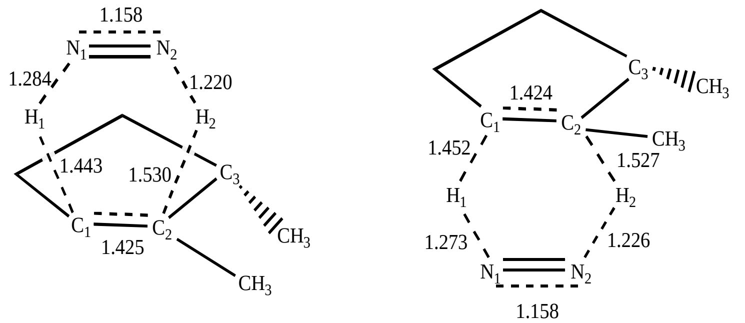


Figure 6: Energetic parameters of the reaction between (Z)-1,2-diazene **2** and cyclopentene **1a**. (B3LYP/ 6-311G **).

We subsequently determine the transition states of the reaction between the disubstituted cyclopentene **1b-d** and (Z)-1,2-diazene **2**. As shown in Figure 7, we find transition states of compounds **4b-d***$_{trans}$(endo) and **4b-d***$_{cis}$(exo) leading respectively to compounds **4b-d**$_{trans}$ and **4b-d**$_{cis}$. The corresponding energies are reported in Table 4.



Exo approach of (Z)-1,2-diazene
TS **4b***$_{cis}$(exo) leading to the cis isomer

Endo approach of (Z)-1,2-diazene
TS **4b***$_{trans}$(endo) leading to the trans isomer

Figure 7: Description of transition states **4b***$_{trans}$(endo) and **4b***$_{cis}$ (exo) leading respectively to **4b**$_{trans}$ and **4b**$_{cis}$ (distances Å). (B3LYP/6-311G **)

In both cases, the transition state **4b***$_{trans}$(endo) and **4b***$_{cis}$(exo) respectively leading from endo and exo approaches of (Z)-1,2-diazene **2**, the N_1, N_2, H_1, H_2, C_2, C_1 atoms are still almost coplanar:
For the transition state **4b***$_{trans}$**(endo)** (N_1, H_1, C_1, C_2) = 3.67°, (N_2, H_2, C_2, C_1) = 4.76°
For the transition state **4b***$_{cis}$**(exo)** (N_1, H_1, C_1, C_2) = -2.42°, (N_2, H_2, C_2, C_1) = -7.24°

Table 3: E* (kcal.mol^{-1}) energies of transition states relative to reactants energies.

	B3LYP/6-311G**
2 + **1b** $\longrightarrow$ **4b***$_{trans}$**(endo)**	11.7
2 + **1b** $\longrightarrow$ **4b***$_{cis}$**(exo)**	13.1
2 + **1c** $\longrightarrow$ **4c***$_{trans}$**(endo)**	12.8
2 + **1c** $\longrightarrow$ **4c***$_{cis}$**(exo)**	14.2
2 + **1d** $\longrightarrow$ **4d***$_{trans}$**(endo)**	10.4
2 + **1d** $\longrightarrow$ **4d***$_{cis}$**(exo)**	11.2

As shown in Table 4, the activation energy for the formation of stereoisomer **4b**$_{cis}$, **4c**$_{cis}$ and **4d**$_{cis}$ from the exo forms is respectively higher than the activation energy for the formation of stereoisomers **4b**$_{trans}$, **4c**$_{trans}$ and **4d**$_{trans}$ from the endo forms. This explains again that the formation of stereoisomers such as **4b**$_{trans}$, **4c**$_{trans}$ and **4d**$_{trans}$ are respectively favorable than stereoisomers **4b**$_{cis}$, **4c**$_{cis}$ and **4d**$_{cis}$. For example in figure 8, we have shown in the energy profile the formation of stereoisomers **4d**$_{cis}$ and **4d**$_{trans}$.

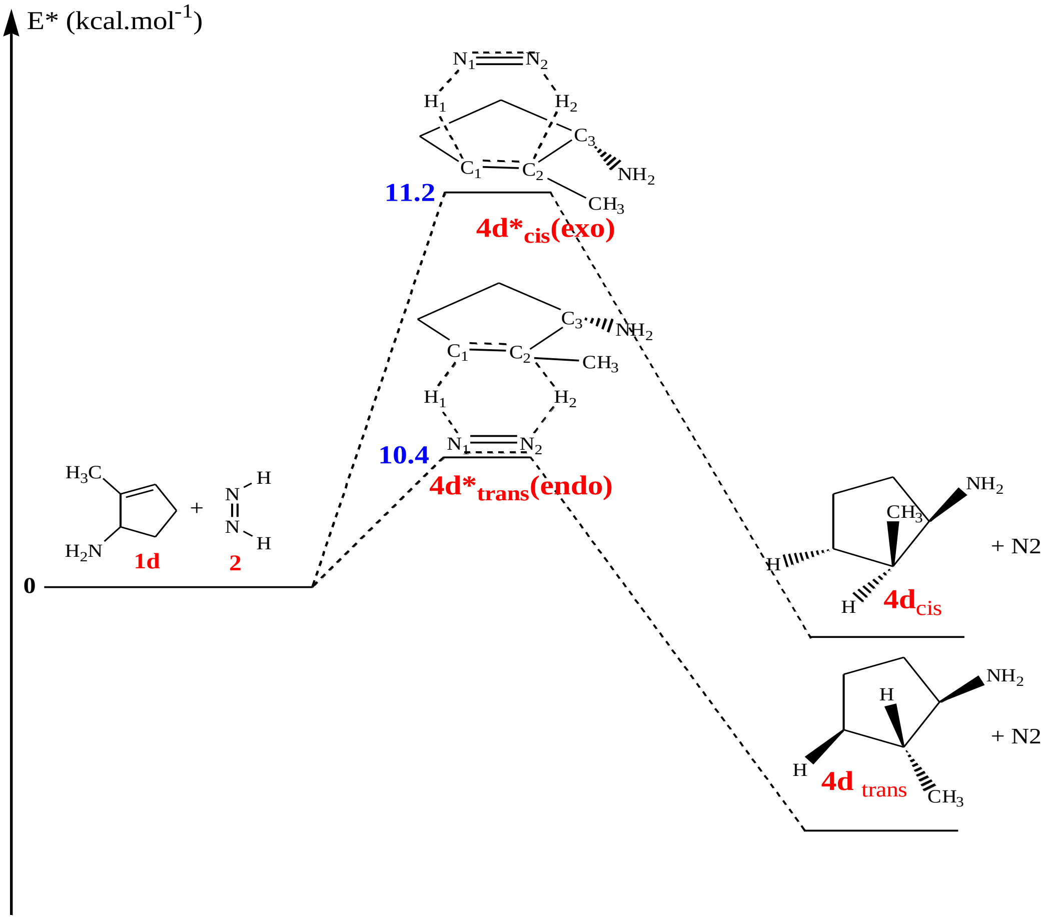


Figure 8: Energy profile of reactions leading to stereoisomers **4d**$_{trans}$ and **4d**$_{cis}$ in DFT/B3LYP with the standard basis 6-311G **.

So we can say that stereoisomers type **4b-d**$_{trans}$ are the thermodynamic and the kinetic products of the reaction between cyclopentene **1b-d** and (Z)-1,2-diazene **2**.
The formation of bond lengths shows that the bond C_1-H_1 is shorter than that bond C_2-H_2. These distances are quite similar to that found by Mc Kee et al for the reaction between (Z)-1,2-diazene **2** and ethene [28] (Table 4).

Table 4: Bond lengths C_1-H_1 and C_2-H_2 in the transition state for the formation of conformers **4b-d**$_{cis}$(exo) and **4b-d**$_{trans}$(endo).

	B3LYP/6-311G**	
	C_1H_1	C_2H_2
Réaction I		
4b*$_{cis}$ (exo) **4c*$_{cis}$ (exo)** **4d*$_{cis}$ (exo)**	1.44 1.45 1.44	1.53 1.52 1.53
Réaction II		
4b*$_{trans}$ (endo) **4c*$_{trans}$ (endo)** **4d*$_{trans}$ (endo)**	1.45 1.45 1.45	1.52 1.52 1.53

3.3. Study of the frontier orbitals

Based on the calculation method DFT/B3LYP, we determine the energies of the LUMO and the HOMO of the cyclopentene type **1a-d**, (Z) -1,2-diazene**2** and (E) -1, 2-diazene **2'** (table 5). According to the theory of frontier orbitals, we note that the preferential interaction is between the LUMO of the cyclopentene **1a** and the HOMO of the (Z)-1,2-diazene **2**, since we observe a favorable overlap between the LUMO of cyclopentene **1a** and the HOMO of the (Z)-1,2-diazene **2**. But the overlap between the LUMO of cyclopentene **1a** and the HOMO of (E)-1,2-diazene **2'** is not very favorable (Figure 9). This explains reasonably that the reaction between (Z) -1,2-diazene **2** and cyclopentene **1a** is more favorable than in the case of the reaction between (E)-1,2-diazene **2'** and cyclopentene **1a**.

We subsequently determine the electrophilicity values of these molecules **1a-d**, **2** and **2'** (Table 5). We notice that the compounds **1a** and **1d** are more electrophilic than the molecules **1b** and **1c**.

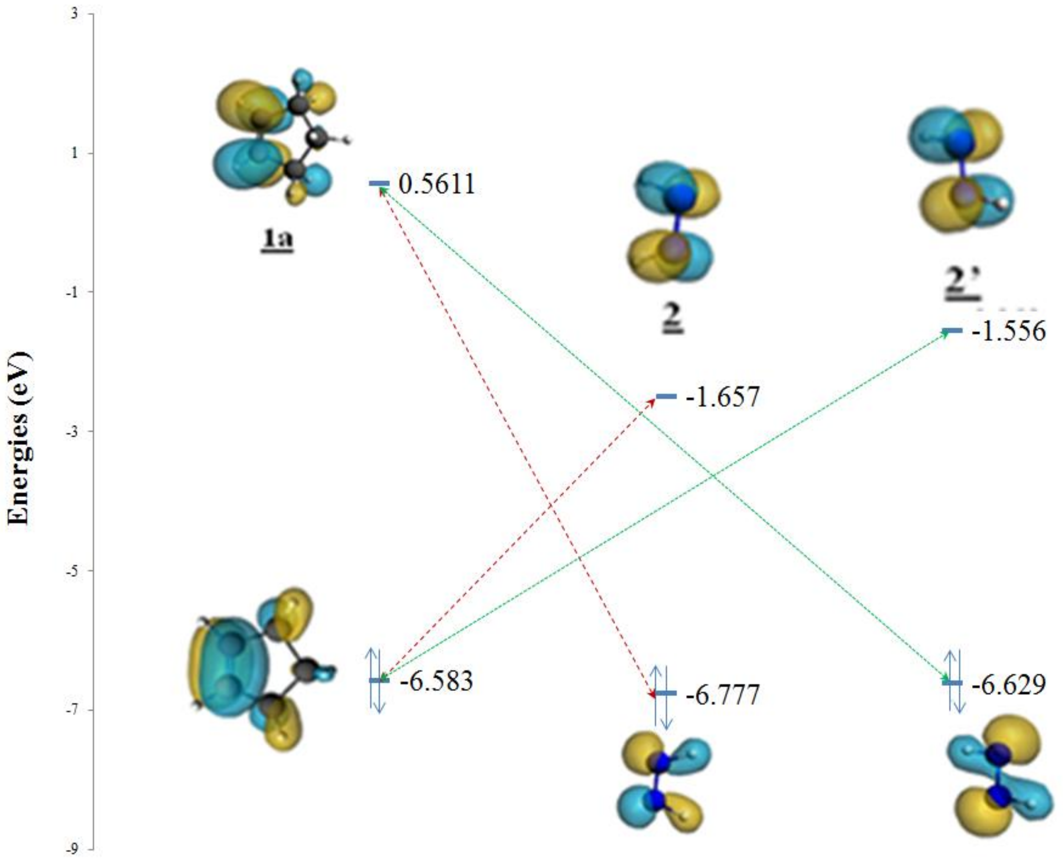


Figure 9: Orbital diagram between cyclopentene **1a** and (Z)-1,2-diazene **2** and interaction between cyclopentene **1a** and (E)-1,2-diazene **2'**. Energies in (eV), value of the isocontour = (0.006 a.u). B3LYP (6-311G**)

Table 5: Energy (eV) of frontier orbitals the cyclopentene **1a**, (Z) -1,2-diazene **2** and (E) -1,2-diazene **2'**. (1a.u = 27.21 eV)

	LUMO (eV)	HOMO (eV)	$\mu = (E_{HOMO} + E_{LUMO})/2$ [29,30]	$\eta = E_{LUMO} - E_{HOMO}$ [29,30]	$\omega = \mu^2/2\eta$ [29,30]	ω(eV) [29,30]
B3LYP/6-311G**						
2	-1.657	-6.777	-0.1549	0.1881	0.0638	1.737
2'	-1.556	-6.629	-0.1504	0.1864	0.0606	1.651
1a	0.5611	-6.583	-0.1106	0.2625	0.0233	0.634
1b	0.0097	-5.624	-0.1031	0.2070	0.0257	0.699
1c	0.0046	-6.320	-0.1160	0.2324	0.0289	0.788
1d	0.4767	-6.387	-0.1086	0.2522	0.0233	0.636

Conclusion

In this study, the hydrogenation reactions between cyclopentene **1a-d** and 1,2-diazene **2** have been investigated using quantum chemical methods. Our theoretical results show that these reactions are possible from thermodynamic point of view. Moreover the reactions between cyclopentene **1a-d** and (Z)-1,2-diazene **2** are thermodynamically more favorable than the reactions between cyclopentene **1a-d** and (E)-1,2-diazene **2'**. We also found that the trans products type **4b-d**$_{trans}$ are more favorable from thermodynamic point of view than the cis products type **4b-d**$_{cis}$.

The transition states show that the kinetic products of the hydrogenation reactions are the trans conformers type **4b-d**$_{trans}$ and the stereoisomers coming from the endo forms are favorable than stereoisomers coming from the exo forms.

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