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Kinetic DFT study of the mechanism of the [3+2] reaction of a five-membered cyclic nitrone with 2-butene isomers

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Abstract: A theoretical DFT investigation of the [3+2] cycloaddition reaction of 3,4-dihydro-2H-pyrrole-1-oxide (nitrone) with two alkenes, cis- and trans-2-butene, was performed at the B3LYP/6-31G(d) level of theory. The energy gaps of the frontier molecular orbitals of the reactants indicate that interactions take place between the HOMOs of the butene isomers and the LUMOs of the nitrone. The regioselectivity and selectivity determined by the calculations of the Parr function indices revealed the most reactive sites of both the nitrone and the 2-butene isomers. The detailed reaction mechanism has been established, and the analysis revealed that the reaction is characterized by only one transition state and follows a concerted asynchronous mechanism. Products P2 and P4 are the most stable and favorable products kinetically and thermodynamically. Good agreement with the experimental data was found.

Keywords: DFT, [3+2] cycloaddition, B3LYP, Fukui, Parr functions.

1. Introduction

1,3-Dipolar cycloaddition (1,3-CD) reactions are the methods of choice for the synthesis of five-membered heterocycles in organic chemistry [1-6]. 1,3-Dipolar reactions are also part of a large family of cycloadditions [7]. This type of was first well defined by Huisgen as the reaction between the 1,3-dipole and the dipolarophile [8]. The 1,3-dipolar cycloaddition of nitrones with alkenes is among the most commonly used routes in various fields of organic chemistry because of the easy accessibility of nitrones and the multitude of stereogenic centers created during the formation of N, O-heterocycles. It is a widely used reaction for the synthesis of natural products, biological products and, very commonly, pharmaceutical products [9-11]. On the other hand, nitrones are highly important in organic synthesis; thus, they are known to be very good partners in [3+2] cycloaddition reactions [12]. They are essentially defined as dipolar compounds that contain the azomethine-*N*-oxide group. These compounds react with a wide variety of dipolarophiles, such as olefins [13]. They are also intermediate compounds of many products of biological interest [14]. The therapeutic efficacy of nitrones was discovered at the very beginning of the 1930s, and since then, several nitrones have been synthesized and used in medicine [15]. A study on their ability to scavenge free radicals in vitro or in vivo has been reported [16]. There have also been some reports on their antimicrobial activity [17].

Heterocyclic molecules play a very important role in the processes of life and are of major interest in industrial development in the fields of dyes, pharmaceuticals, pesticides, natural products, etc. This is the reason why scientists have devoted enormous effort and time to finding efficient synthesis methods for a wide variety of heterocyclic compounds, including biologically active molecules, often resorting to cycloaddition reactions.

The mechanism of the 1,3-dipolar reaction of alkenes has attracted much interest and more attention since their early discovery from both

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experimental and theoretical chemists and thus has been intensively studied [18].

For example, Maftei et al. described a very useful synthetic method for accessing triazole derivatives of *Cinchona* alkaloids via 32 CA reactions. They investigated the synthetic potential of 6′-Amino-cinchonine 1,6′-Amino-cinchonidine and its derivatives and whether they could be successfully converted into azides, and they successfully constructed triazoles [19].

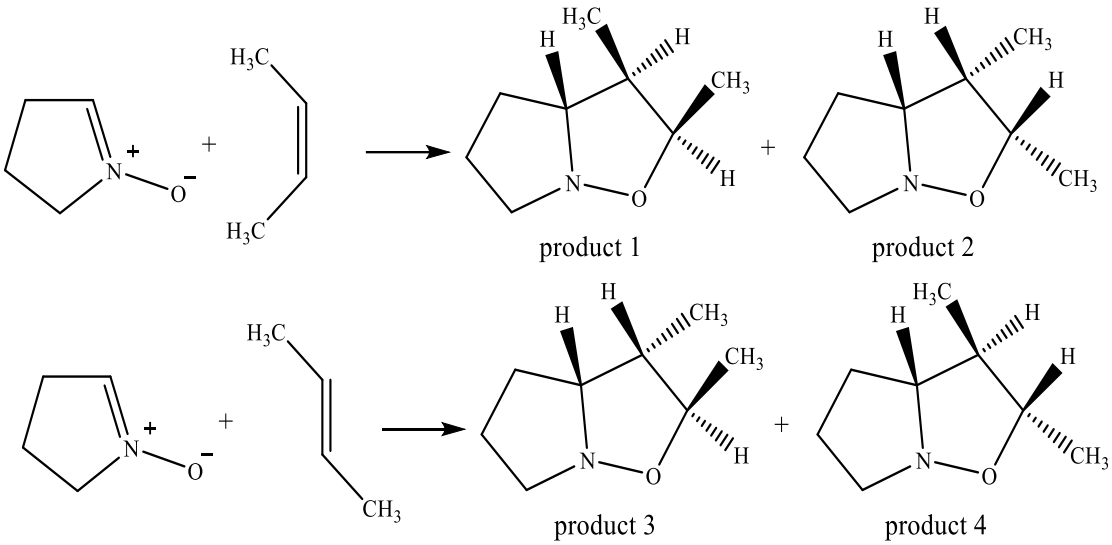
Moreover, Al-Matarneh et al. synthesized several new compounds with cyano groups substituted with two quinoline derivatives via [3 + 2] cycloadditions of several quinolinium ylides and fumaronitrile. They tested eleven selected compounds against sixty human cancer cells. Among the studied compounds, 9a exhibited excellent growth inhibition. The molecular docking results revealed the anticancer properties of compound **9a**, as explained by its ability to bind with tubulin [20].

In addition, Mitka et al. theoretically probed the possible mechanism of the 1,3-dipolar cycloaddition of C-arylnitrones with perfluoro 2-methylpent-2-ene via the B3LYP/6-31G(d) level of theory. Their theoretical findings revealed that the studied reactions involve a concerted one-step mechanism. They attempted to localize a zwitterionic intermediate in vain [21].

Zawadzińska et al. conducted experimental and theoretical investigations of the [3 + 2] cycloaddition reactions of a series of aryl-substituted nitrile *N*-oxides with trichloronitropropene. They reported that the studied reactions are exergonic, irreversible and kinetically controlled. These results show that these reactions follow an asynchronous concerted mechanism [22].

In this work, a theoretical study of the [3+2] cycloaddition reaction between a nitrone and *cis /trans*-2-butene was conducted. The different aspects of stereo- and regioselectivity are addressed and well analyzed on the basis of several theoretical approaches at the B3LYP/6-31G(d) level of theory. The detailed mechanism and possible products involved in this reaction have been well determined and thoroughly probed on the basis of transition state theory.

The general scheme of the studied reaction in this work is as follows:



Scheme 1. Reactions of 3,4-dihydro-2*H*-pyrrole-1-oxide (nitrone) with *cis /trans*-2-butene.

As shown in this scheme, two cycloadducts are formed from the [3+2] reaction of this nitrone with the *cis*-2-butene as well as with the *trans*-2-butene.

2. Computational Method

The calculations were performed with the B3LYP/6-31G(d) theoretical method implemented in Gaussian09 software [23]. This hybrid method is well known as the abbreviation of the terms; Becke's 3-parameter refers to the exchange functional, and Lee-Yang-Parr refers to the correlation functional [24]. Even though this method has been used for decades, it is still a suitable and rapid way to obtain a very good explanation and useful information about mechanisms in organic chemistry, especially for

cycloaddition reactions. Many combined experimental and theoretical studies reported the accuracy and feasibility of B3LYP in combination with the basis set 6-31G(d) [25-28]. The optimizations of the equilibrium geometries were well performed via the Berny algorithm [29]. The localization of the transition states for the two cyclization modes for each reaction in the gas phase and in the solvent, dichloromethane via the PCM solvation model [30] was followed by a frequency calculation to ensure that the minimum corresponds to a single imaginary frequency.

Using HOMO and LUMO energies, global indices such as; affinity A, ionization potential I, gap (ΔE), electronic chemical potential μ, hardness η, and electrophilicity ω can be calculated as shown below [31-38]:

$$A = -E_{\mathrm{LUMO}} \quad (1)$$

$$\mathrm{I} = -E_{\mathrm{HOMO}} \quad (2)$$

$$\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} \quad (3)$$

$$\mu = \frac{1}{2}(E_{\mathrm{LUMO}} + E_{\mathrm{HOMO}}) \quad (4)$$

$$\eta = \frac{1}{2}(I - A) \quad (5)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

$$N = E_{HOMO} - E_{HOMO(TCE)} \quad (7)$$

where E_{HOMO} is the HOMO energy of the system and $E_{HOMO(TCE)}$ is the HOMO energy of tetracyanoethylene (TCE) taken as a reference, where $E_{HOMO(TCE)}$= - 0.34427a.u.

The Parr indices were calculated as [39-41]:

$$P_k^- = \rho_s^{rc}(k) \text{ for electrophilic attack} \quad (8)$$

$$P_k^+ = \rho_s^{ra}(k) \text{ for nucleophilic attack} \quad (9)$$

where $\rho_s^{rc}(k)$ is the cation atomic spin density, and $\rho_s^{ra}(k)$ is the anion atomic spin density. Each atomic spin density provides local nucleophilic and electrophilic Parr functions to the neutral system.

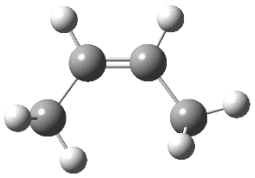
Using $P^-(k)$ and $P^+(k)$, it is possible to define the local electrophilicity ω_k and the local nucleophilicity N_r indices as follows:

$$\omega_k = \omega\rho_k^+ \quad (10)$$

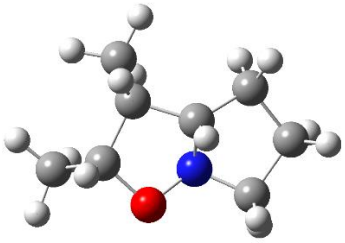
$$N_k = N\rho_k^- \quad (11)$$

3. Results and discussion

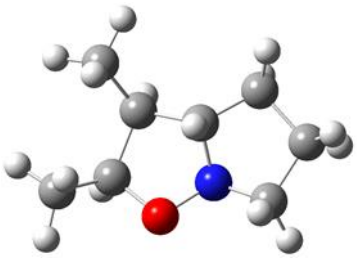
In each case, the studied reaction yields two cycloadducts (stereoisomers) on the basis of selectivity. The optimized structures of the reactants, transition states and products are illustrated in Figure 1.



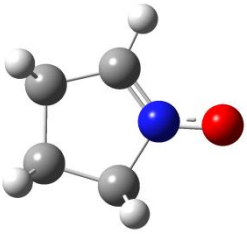
***Cis*-2-butene**



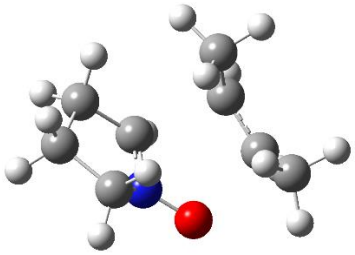
Product 1



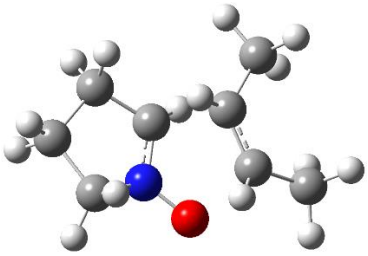
Product 2



Nitrone



TS1



TS2

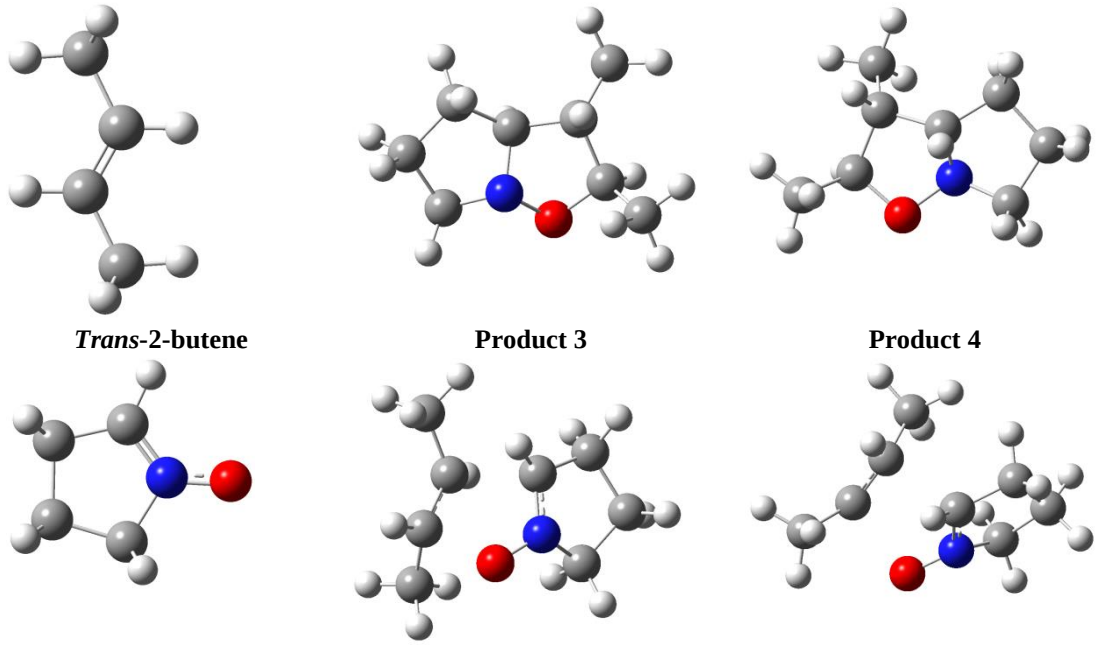


Figure 1. Optimized structures for the reaction of nitrone with *cis* /*trans*-2-butene at the B3LYP/6-31G(d) theory level.

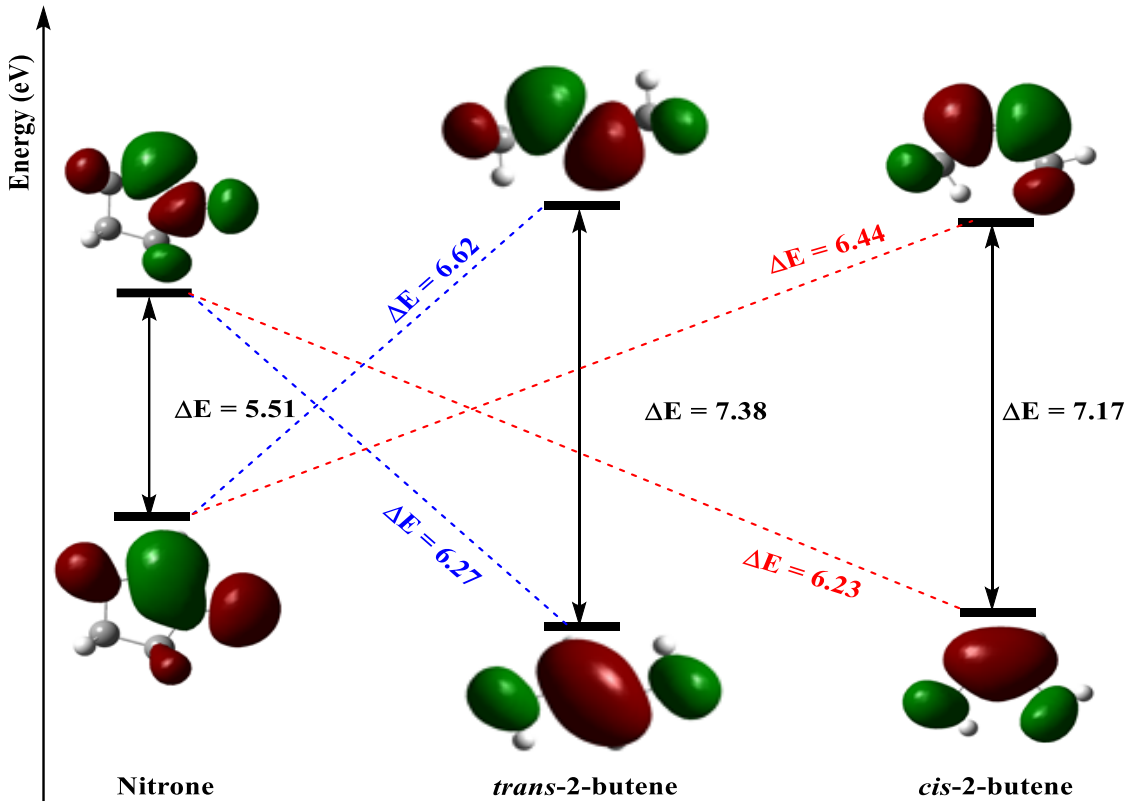


Figure 2. HOMO/LUMO plots and gap values for the studied reactants.

3.1. Global indices

To predict the electrophilicity and nucleophilicity of the reactants under study, the global reactivity indices, namely, the electronic chemical potential μ, electrophilicity ω, and nucleophilicity N, were calculated (Table 1).

Table 1. The global electronic properties (eV) of the reactants at the B3LYP/6-31 G(d) level.

	Nitrone	*Cis*-2-butene	*Trans*-2-butene
E_{HOMO}	-5.63	-6.35	-6.39
E_{LUMO}	-0.12	0.81	0.99
μ	-2.87	-2.77	-2.70
η	5.51	3.58	7.38
ω	0.75	1.07	0.50
N	3.74	3.01	2.97
Gap	5.51	7.17	7.38

Table 1 shows that the nucleophilicity index *N* value of nitrone (dipole) is much greater than that of alkenes (dipolarophiles). However, the electrophilicity index ω value of the nitrone is less than 0.75 eV. Nitrones with a nucleophilicity value exceeding 3.0 eV are classified as strong nucleophiles [42]. In addition, the small difference in electrophilicity between the two reactants (nitrone and alkenes) clearly shows that this 1,3-dipolar cycloaddition reaction is characterized by a weakly polar character [43].

Figure 2 presents the HOMO and LUMO shapes as well as the different calculated gaps related to the possible reactions between the nitrone and the two 2-butene isomers.

Figure 2 shows that the gap between $HOMO_{nitrone}$ and $LUMO_{butenes}$ is slightly greater than the gap corresponding to the differences between $LUMO_{nitrone}$ and $HOMO_{butenes}$.

3.2. Parr indices

To determine the regioselectivity of the reactions studied, the Parr indices as well as the local electrophilicity and nucleophilicity indices were calculated on the basis of the Mulliken atomic spin density (ASD).

Table 2. Parr functions P_k^+, P_k^-, local electrophilicity ω_k^+ and nucleophilicity N_k using the ASD for nitrone at the B3LYP/6-31G(d) calculation level.

Atom k	P_k^+	P_k^-	ω_k^+	N_k
C1	0.00	0.00	0.00	0.01
C2	-0.04	-0.01	-0.03	-0.02
C3	-0.04	-0.02	-0.03	-0.09
N10	0.36	-0.07	0.27	-0.24
O11	0.15	0.66	0.11	**2.46**
C12	0.48	0.38	0.36	**1.42**

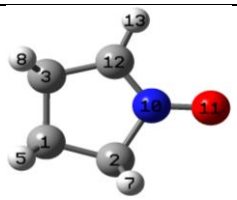


Table 3. Parr functions P_k^+, P_k^-, local electrophilicity ω_k^+ and nucleophilicity N_k using the ASD for *cis*-2-butene at the B3LYP/6-31G(d) calculation level.

Atom k	P_k^+	P_k^-	ω_k^+	N_k
C1	0.45	0.45	**0.48**	1.35
C3	-0.04	-0.01	-0.04	-0.02
C7	0.44	0.46	**0.47**	1.38
C9	-0.02	-0.01	-0.02	-0.02

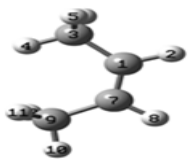
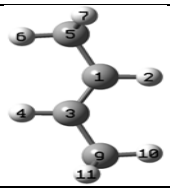


Table 4. Parr functions P_k^+, P_k^-, local electrophilicity ω_k^+ and nucleophilicity N_k using the ASD for *trans*-2-butene at the B3LYP/6-31G(d) calculation level.

Atom k	P_k^+	P_k^-	ω_k^+	N_k
C1	0.49	0.44	**0.24**	1.32
C3	0.49	0.44	**0.24**	1.32
C5	-0.04	-0.01	-0.02	-0.03
C9	-0.04	-0.01	-0.02	-0.03



The Parr functions and the local indices for nitrone and *cis /trans*-but-2-ene are grouped in Tables 2-4. The results in Table 2 show that the oxygen atom O11 and the carbon atom C12 are the most nucleophilic sites of this nitrone.

Tables 3 and 4 show that the carbon atoms C1 and C7 of cis-2-butene (dipolarophile) and C1, and C3 of trans-2-butene are the most electrophilic sites. Therefore, interactions occur between C1, and C7 and between C1, and C3 of the dipolarophiles and

between O11 and C12 of the dipole, as summarized in Scheme 2.

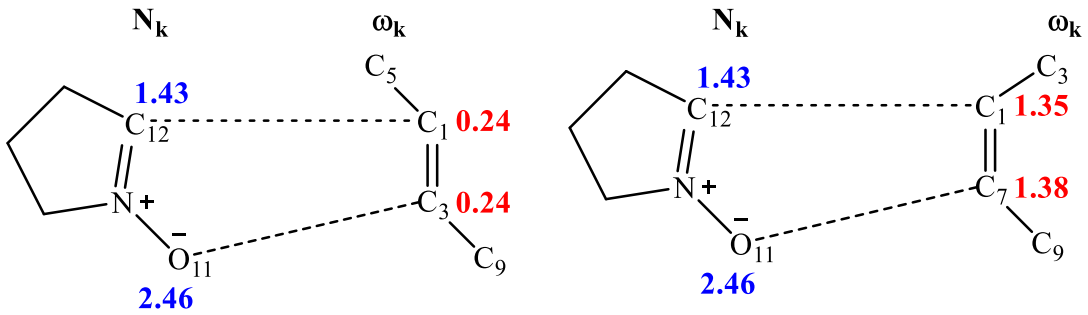
3.3. Reaction pathway

The values of the different energy forms for the reactions studied are grouped in Table 5.

The analysis of the results shown in Table 5 is quite interesting, and some important information can thus be drawn. The activation energies (ΔE) of the transition states TS1, TS2, TS3 and TS4 obtained via the B3LYP method in the gas and solvent phases are positive and on the order of 20 kcal/mol for the energy and enthalpy, and on the order of 30 kcal/mol for the Gibbs free energy.

The enthalpy of formation of the four stereoisomers P1-4 is negative; thus, these reactions are exothermic. The negative values of Gibbs free energy are also negative; hence, the obtained products P1-4 are stable, and their formation is thermodynamically favorable.

The energetic profiles of cis /trans-2-butene with the studied nitrone are shown in Figures 3 and 4. The letters s and g in the denomination of transition states TS and products P indicate the gas and solvent phases, respectively.



Scheme 2. Reactions between nitrone and 2-butene isomers via the Parr function.

Table 5. Energetics (in kcal/mol) of the reaction of nitrone with *cis/trans*-2-butene in gas and solvent (CH_2Cl_2) phases at B3LYP/6-31G(d).

	Gas			Dichloromethane		
	ΔE	**ΔH**	**ΔG**	**ΔE**	**ΔH**	**ΔG**
	***Cis*-2-butene + nitrone**					
TS1	18.23	20.11	32.37	20.81	22.69	34.85
TS2	15.31	17.07	29.20	17.76	19.52	31.60
Product 1	-15.65	-11.46	2.10	-12.20	-8.04	5.53
Product 2	-17.07	-12.99	0.34	-13.70	-9.64	3.62
	***Trans*-2-butene + nitrone**					
TS3	18.74	19.98	32.40	21.22	22.47	34.89
TS4	18.27	19.52	31.83	20.91	22.12	34.24
Product 3	-15.86	-12.40	1.09	-12.45	-9.04	4.38
Product 4	-15.67	-12.08	1.54	-12.19	-8.63	4.94

The energy diagrams, in Figures 3 and 4, which characterize the steps of the studied reactions, reveal two possible pathways for each alkene, *cis /trans*-2-butene, leading to the formation of two stereoisomers (P1 and P2 for the *cis*-reaction and P3, and P4 for the *trans*-reaction). The reactions proceed through a single step, and therefore, the mechanism is concerted, i.e., the two bonds responsible for the cyclization are formed at the same time.

3.4. Energetic and structural comparison

Table 6 lists the energy values of the TSs and products of reaction 1 in the two gas and solution phases and their respective differences.

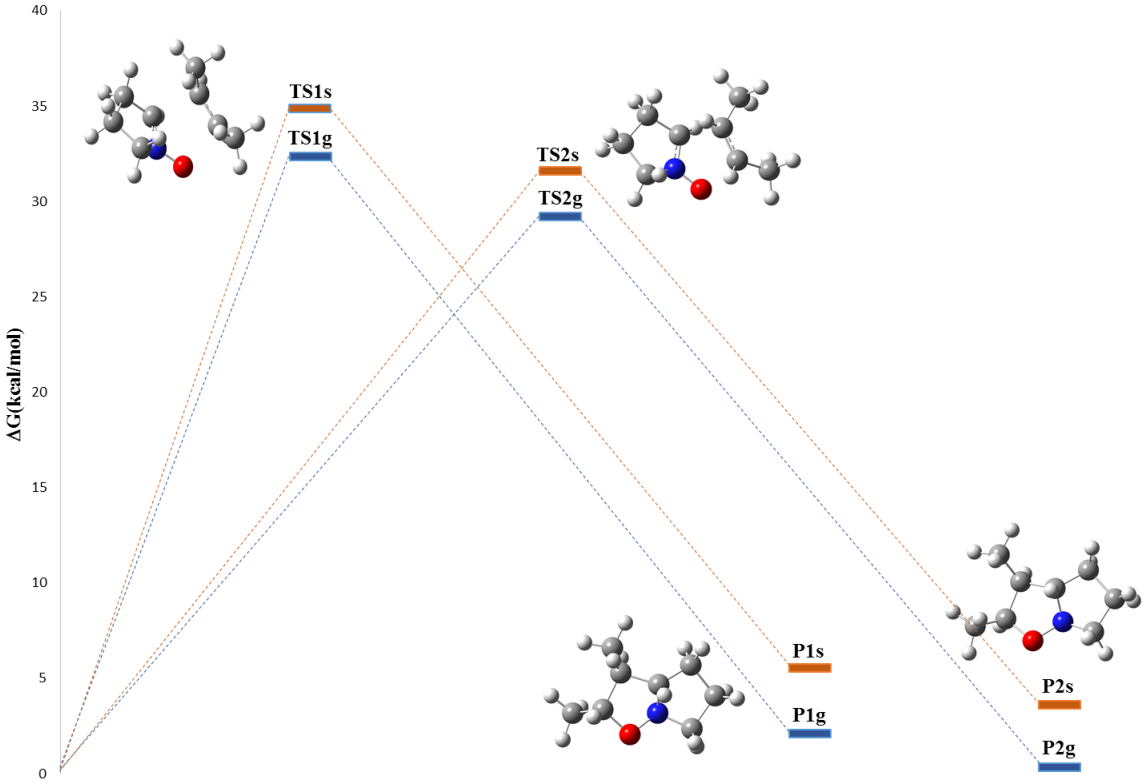


Figure 3. Energy profile of the reaction of nitrone with *cis*-2-butene in the gas and solvent phases at the B3LYP/6-31G(d) level.

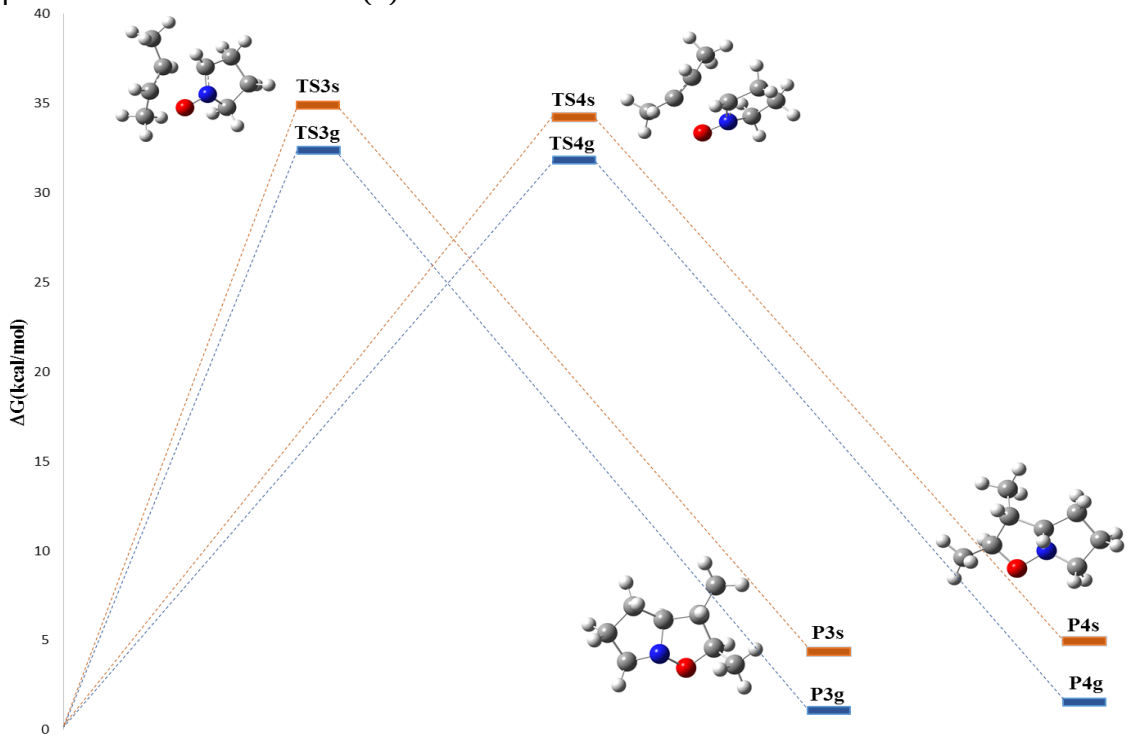


Figure 4. Energy profile of the reaction of nitrone with *trans*-2-butene in the gas and solvent phases at the B3LYP/6-31G(d) level.

Table 6. Energy difference values (kcal/mol) obtained for the two phases at the B3LYP/6-31G(d) level.

	Gaz			**Solution**					
	ΔE	**ΔH**	**ΔG**	**ΔE**	**ΔH**	**ΔG**	**ΔΔE**	**ΔΔH**	**ΔΔG**

	***Cis*-2-butene + nitrone**								
TS1	18.23	20.11	32.37	20.81	22.69	34.85	2.58	2.58	2.48
TS2	15.31	17.07	29.20	17.76	19.52	31.60	2.45	2.45	2.40
P1	-15.65	-11.46	2.10	-12.20	-8.04	5.53	3.45	3.42	3.43
P2	-17.07	-12.99	0.34	-13.70	-9.64	3.62	3.37	3.35	3.28
	***Trans*-2-butene + nitrone**								
TS3	18.74	19.98	32.4	21.22	22.47	34.89	2.48	2.49	2.49
TS4	18.27	19.52	31.83	20.91	22.12	34.24	2.64	2.6	2.41
P3	-15.86	-12.4	1.09	-12.45	-9.04	4.38	3.41	3.36	3.29
P4	-15.67	-12.08	1.54	-12.19	-8.63	4.94	3.48	3.45	3.40

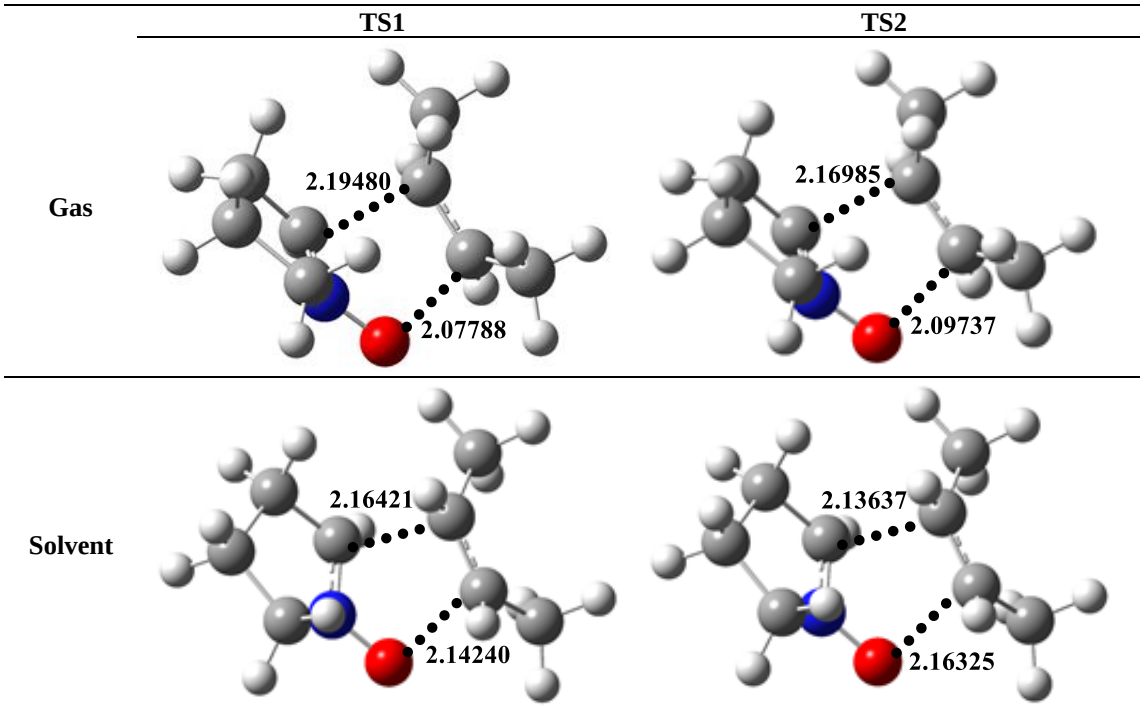
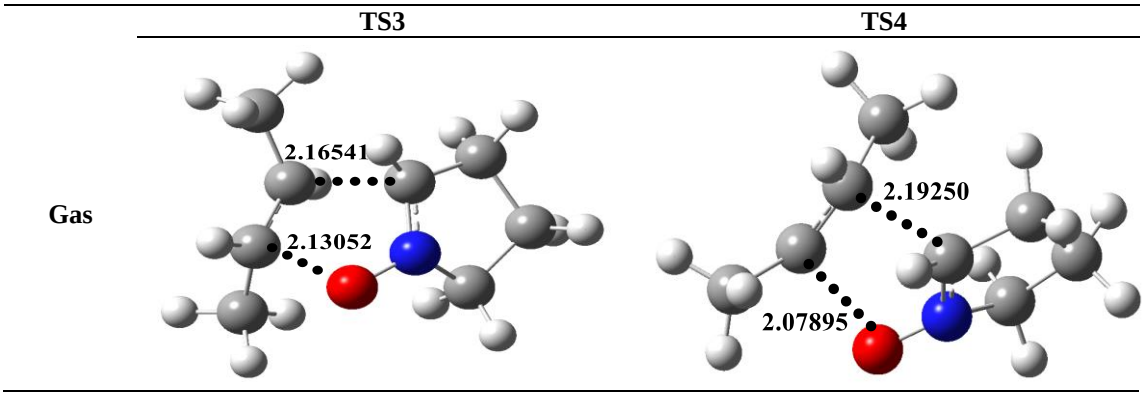


Figure 5. Bond lengths in both phases for the reaction with *cis*-2-butene at the B3LYP/6-31G(d) level.



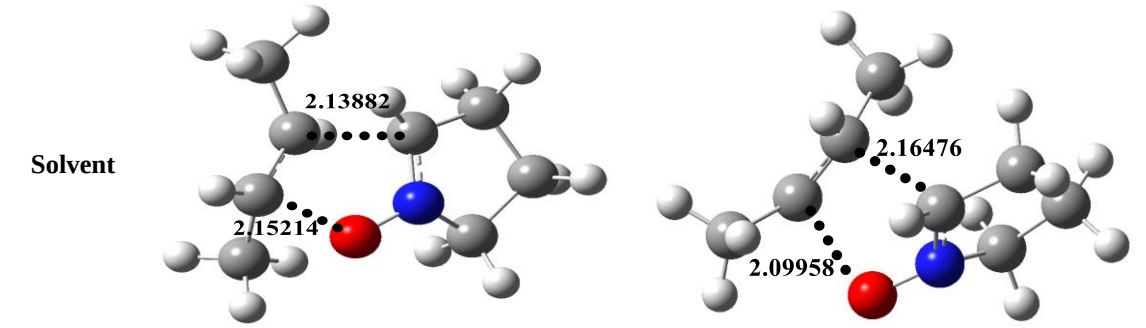


Figure 6. Bond lengths in both phases for the reaction with *trans*-2-butene at the B3LYP/6-31G(d) level.

For example, in TS3, the C-C bond length decreases from 2.165 Å in the gas state to 2.139 Å in solution, and the C-O bond length increases from 2.131 Å in the gas state to 2.152 Å in solution. The same can be found for TS4, where the C-C bond length decreases from 2.193 Å in the gas state to 2.165 Å in solution, and the C-O bond length increases from 2.079 Å in the gas state to 2.100 Å in solution.
Therefore, in both cases, going from gas to solution results in stretching of the C-C bond and a reduction in the C-O bond. This is due mainly to solvation effects.

4. Conclusions

In this work, a theoretical study was carried out at the level of the B3LYP theory and 6-31G(d) basis set in both gas and solution phases (dichloromethane solvent) of the 1,3-dipolar cycloaddition reaction between the nitrone 3,4-dihydro-2*H*-pyrrole-1-oxide and *cis/trans*-2-butene. The global reactivity indices, such as electrophilicity and nucleophilicity, calculated in the ground state of the reactants allowed us to classify the nitrone as a nucleophile and the two alkenes studied as electrophiles. The local Parr reactivity indices indicate that the carbon and oxygen atoms of the nitrone and the carbons of the double bond of the 2-butene stereoisomers are involved in the cyclization. This regioselectivity is in good concordance with the experimental observations. The geometric analysis of the bonds at the transition states shows that the formation of bonds is synchronous. The study of thermicity via calculations of enthalpy revealed that the reactions are exothermic. The lower activation barriers obtained prove that the stereoisomers P2 and P4 are kinetically favored, whereas the Gibbs free energies reveal that they are thermodynamically stable. The energetic profiles indicate that these 1,3-dipolar cycloaddition reactions proceed via a one-step concerted mechanism. The obtained theoretical results are in good agreement with the experimental outcomes.

ACKNOWLEDGEMENT

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