



Research article

QTAIM and IRC studies for the evaluation of activation energy on the C=P, C=N and C=O Diels-Alder reaction

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ABSTRACT

In Diels-Alder reaction of 1,3-butadiene with hetero-dienophiles, the substitution of a carbon by a heteroatom as N, O and P on the dienophile decreases the activation energy, particularly for the phosphorus. All these reactions are concerted, proven by the DFT/B3LYP method using the cc-pVDZ basis. The intrinsic reaction coordinate (IRC) analysis confirms concerted reaction and the Quantum Theory of Atoms in Molecules (QTAIM) analysis shows that there are critical points BCP in the transition state structures with positive values for the interaction links.

1. Introduction

The Hetero-Diels-Alder (DA) reaction is one of the most important methods of heterocyclic synthesis [1]. It is a very attractive method in organic synthesis, in particular in the six-membered carbocycles and natural product synthesis [2]. The extension of the Diels-Alder reaction to compounds that contain C=P, C=N and C=O functional groups is a recent development [3, 4, 5, 6]. Markl and his coworker reported the first Diels-Alder reaction involving the $-C=C=C=P-$ moiety of phosphinine as diene [7]. Although Mathey et al. demonstrated that phosphinine was also capable of reacting as a dienophile, the reaction occurs at the C=P bond [8]. Different aspects of the Diels-Alder reaction of non-phosphorus compounds have been frequently reviewed [9] but so far there has been no systematic analysis specifically of the Diels-Alder reaction of organophosphorus compounds having a C=P functionality [10, 11]. This work aims to evaluate the effect of carbon substitution by a heteroatom in the Diels-Alder reaction for both ethylene and diene [6, 12, 13, 14].

We investigate the influence of the binding nature π of the hetero-dienophile on the activation energy of the following Diels-Alder reaction by substituting a carbon atom with a heteroatom Z (Figure 1).

2. Methods of computation

The density functional theory (DFT) method with the hybrid exchange-correlation functional- (B3LYP) [15, 16] was used because of an increasing number of recent studies showing strong agreement with the experimental results of Diels-Alder reactions [17, 18, 19]. The basis set cc-pVDZ were used for the optimization of reactants and transition states (TS). The corresponding energies were calculated at the same B3LYP/cc-pVDZ (d) level. The location of the transition states geometries was confirmed by the presence of a single imaginary frequency in the Hessian matrix. The calculations were performed with Gaussian 09 software [20]. The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles that connect each TS with the two corresponding minima of the proposed mechanism [21].

3. Results and discussion

Analysis of the reactivity of the Diels-Alder reaction of dienophile with heteroatom Z and 1,3-butadiene. The bond length for the structure of the transition state in Å.

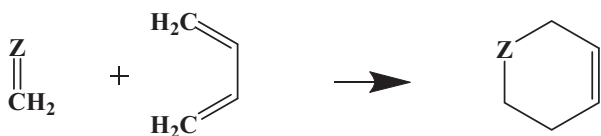
From the structures shown in Figure 2, it is shown that the Diels-Alder adduct channel along the pathway (reaction 1) corresponds to the C4C5 and C1N14 forming bond processes, whereas the pathway (reaction 2) corresponds to the C1C2 and C5O14 and pathway (reaction 3)

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With Z = NH (Reaction 1), Z=O (Reaction 2) or PH (Reaction 3).

Figure 1. Cycloaddition pathways of DA reactions of hetero-dienophile and 1,3-butadiene.

corresponds to the C4C5 and C1P14 ones. Eight transition states, namely TS-N, TS-O and TS-P.

It is found that the distances C-Z (with Z a heteroatom) in the transition states are longer than the corresponding bonds in the dienophile. Thus, a disappearance of π links in dienophiles and the appearance of σ links in transition structures. We also observe the lengthening of the double bonds in the structures of the transition states compared to their diene counterparts, while the C-C single bond in the transition state is narrowing compared to the single bond in the diene, which shows the beginning of the formation of the next unsaturated six-membered ring (Figure 3).

The bond length for TS-N for C1-N14 is 1.902 and C4-C5 is 2.528 significant the start of formation of a covalent bond, the same for other transition states geometries [22].

We note from Table 1 that a heteroatom's change of the carbon of the dienophile remarkably decreases the activation energy. A small difference in activation energy for reactions 1 and 2 (TS-N and TS-O) 16.040 kcal/mol and 18.800 kcal/mol, but a drop in energy is noted for reaction 3 (TS-P) 5.490 kcal/mol, the activation energy for reaction de Diels-Alder with ethylene is 27 kcal/mol [23, 24].

Therefore, the insertion of a heteroatom in the dienophile facilitates the formation of the Diels-Alder adduct on all the phosphorus. The relative energies for the three products P-N, P-O and P-P of three reactions are negative.

The potential energy surface schemes (PESs), corresponding to the reaction channels for the three Diels-Alder reactions, are illustrated in Figure 4.

The intrinsic reaction coordinate (IRC) Plots corresponding to the favored P-P product shows a concerted reaction (Figure 5).

An analysis of the two transition mechanisms by the Natural Bond Orbital (NBO) [25, 26] was carried out to explain their relative stabilizations. It reveals significant $\pi_{\text{dienophile}} \rightarrow \pi^*_{\text{diene}}$ and $\pi_{\text{diene}} \rightarrow \pi^*_{\text{dienophile}}$ interactions (Table 2) and it is worthy of notice that the three-transition structure varies significantly in the stabilization energies associated with the $\pi^*_{\text{C1-O14}} \rightarrow \pi^*_{\text{C2-C3}}$ and $\pi^*_{\text{C1-C2}} \rightarrow \pi^*_{\text{C3-C4}}$ interactions. TS-O and TS-P been stabilized more effectively.

The results found in Table 3 above show that the $|E_{\text{HOMO}}^{\text{Diene}} - E_{\text{LUMO}}^{\text{Dienophile}}|$ gaps are smaller than the $|E_{\text{HOMO}}^{\text{Dienophile}} - E_{\text{LUMO}}^{\text{Diene}}|$ gaps, indicating that the

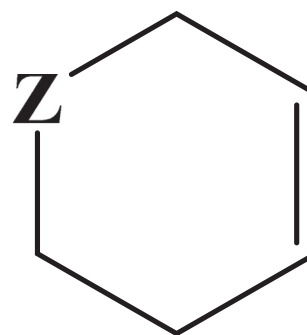


Figure 3. Diels-Alder adduct.

Table 1. Energies (E), relative energy (ΔE) of reactants, transition states, and cycloadducts.

Species	Total energy (a.u) ^a	Relative energy (Kcal/mol)
1,3-butadiene	-155.995	0.000
R-N	-94.633	0.000
R-O	-114.508	0.000
R-P	-381.239	0.000
TS-N	-250.602	16.040
TS-O	-270.472	18.800
TS-P	-537.225	05.490
P-N	-250.683	-34.810
P-O	-270.549	-29.470
P-P	-537.300	-41.760
TS-C	—	27.000

^a TS: transition state; a.u: atomic unit.

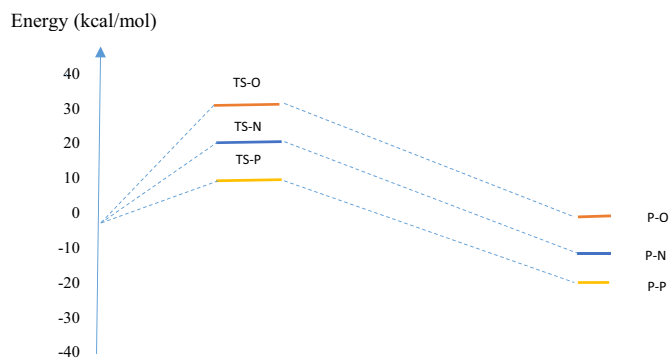


Figure 4. Energy profiles, in kcal/mol, for the Diels-Alder reaction of 1,3-butadiene and hetero-dienophile.

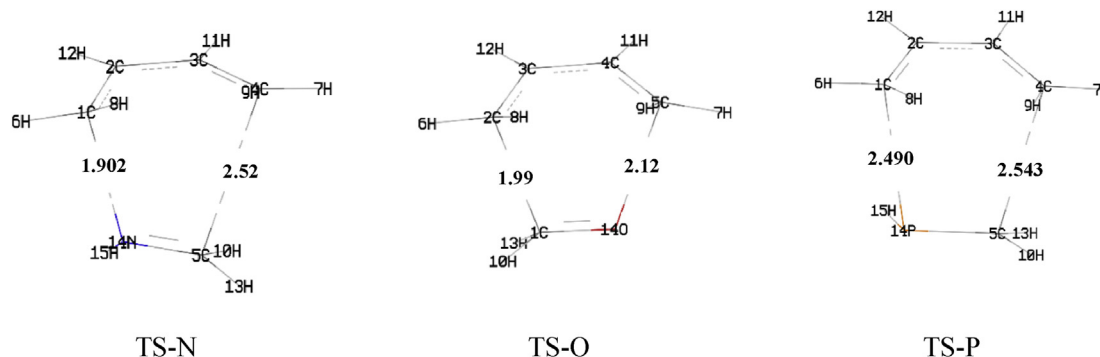


Figure 2. Transitions states for reactions 1, 2 and 3.

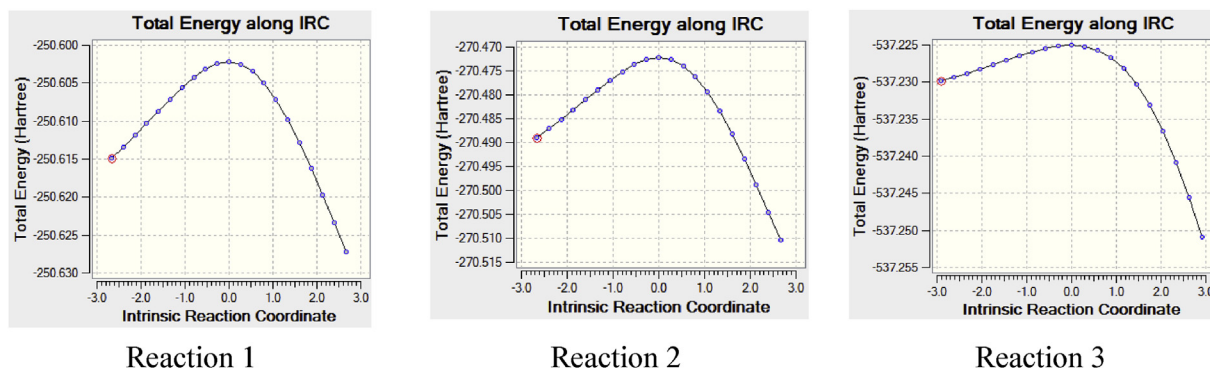


Figure 5. B3LYP/cc-pVDZ IRC plots for the Diels-Alder reaction for the 1,3-butadiene and hetero-dienophile with Z = (NH, O, PH).

Table 2. Stabilization energies E_{ij} (kcal/mol) of major interactions in the transition structures TS-N, TS-O and TS-P obtained from NBO analysis.

Interactions	TS-N	TS-O	TS-P
$\pi_{C1-C2} \rightarrow \pi^*_{C3-C4}$	25.290	—	—
$\pi_{C3-C4} \rightarrow \pi^*_{C1-C2}$	11.720	—	—
$\pi_{C1-C2} \rightarrow \pi^*_{C5-N14}$	33.330	—	—
$\pi_{C5-N14} \rightarrow \pi^*_{C1-C2}$	23.390	—	—
$\pi_{N14} \rightarrow \pi^*_{C1-C2}$	37.100	—	—
$\pi^*_{C5-N14} \rightarrow \pi^*_{C1-C2}$	50.670	—	—
$\pi^*_{C1-O14} \rightarrow \pi^*_{C2-C3}$	—	148.780	—
$\pi_{C2-C3} \rightarrow \pi^*_{C1-O14}$	—	61.070	—
$\pi^*_{C1-C2} \rightarrow \pi^*_{C3-C4}$	—	—	112.640
$\pi_{C1-C2} \rightarrow \pi^*_{C1-P14}$	—	—	18.070

Table 3. Difference between the two possible HOMO/LUMO combinations for 1,3-butadiene diene and dienophile [Z = NH, O, PH] (Energies in eV).

Z	$ E_{HOMO}^{Diene} - E_{LUMO}^{Dienophile} $	$ E_{HOMO}^{Dienophile} - E_{LUMO}^{Diene} $
N	5.920	6.470
O	5.030	6.480
P	4.480	6.530

corresponding dienes behave as nucleophiles while the dienophiles behave as electrophiles.

The value of the gap for 1,3-butadiene-Dienophile (Z = NH) is 5.920 and for Dienophile-1,3-butadiene is 6.470; therefore 1,3-butadiene is a nucleophile while the ethylene behaves as electrophiles.

The value of the gap by intervening phosphorus (Z = PH) 4.480 is low compared to nitrogen 5.920 and oxygen 5.030 (Z = O).

On the other hand, we notice that all these heteroatoms favor the Diels-Alder reaction, whose magnitude depends on the heteroatom, and this is confirmed by the values of the activation energies found in Table 2. We note here that the substitution of phosphorus for the dienophile's carbon considerably reduces the activation energy, and therefore accelerates the reaction more than oxygen and nitrogen.

4. QT-AIM analysis

Topology analysis of electron density is a main ingredient of Bader's [27] atoms in molecules (AIM) theory [28]. In this example, we will perform this kind of transition state geometries.

The results of the electronic density and Laplacian of the intermolecular interactions between 1,3-butadiene and hetero-dienophile in the structure of the transition state as shown in Figure 6 are given in Table 4, an Atoms in Molecules (AIM) analysis was undertaken from the Quantum Theory of Atoms in Molecules (QTAIM). Developed by Richard Bader, the AIM analysis (Table 4) for the TS-N, TS-O and TS-P structure showed that these molecules are stabilized through interaction between two reactants evidenced by the dashed bond paths (BP's).

Figure 6 shows the existence of critical points BCP (3,-1) in the three transitions states for the links C1-N14, C4-C5, C5-O14, C1-C2, C1-P14, C4-C5, the electron density values are positive as well as the Laplacian values are almost all positive except C1-N14 and C1-C2.

5. Conclusion

The reaction mechanism and topology of transition states geometries of Diels-Alder reaction between 1,3-butadiene and hetero-dienophile (Z = NH, O, PH) have been studied using density functional theory (DFT) methods at the B3LYP/cc-pVDZ level. The analysis of stationary points of

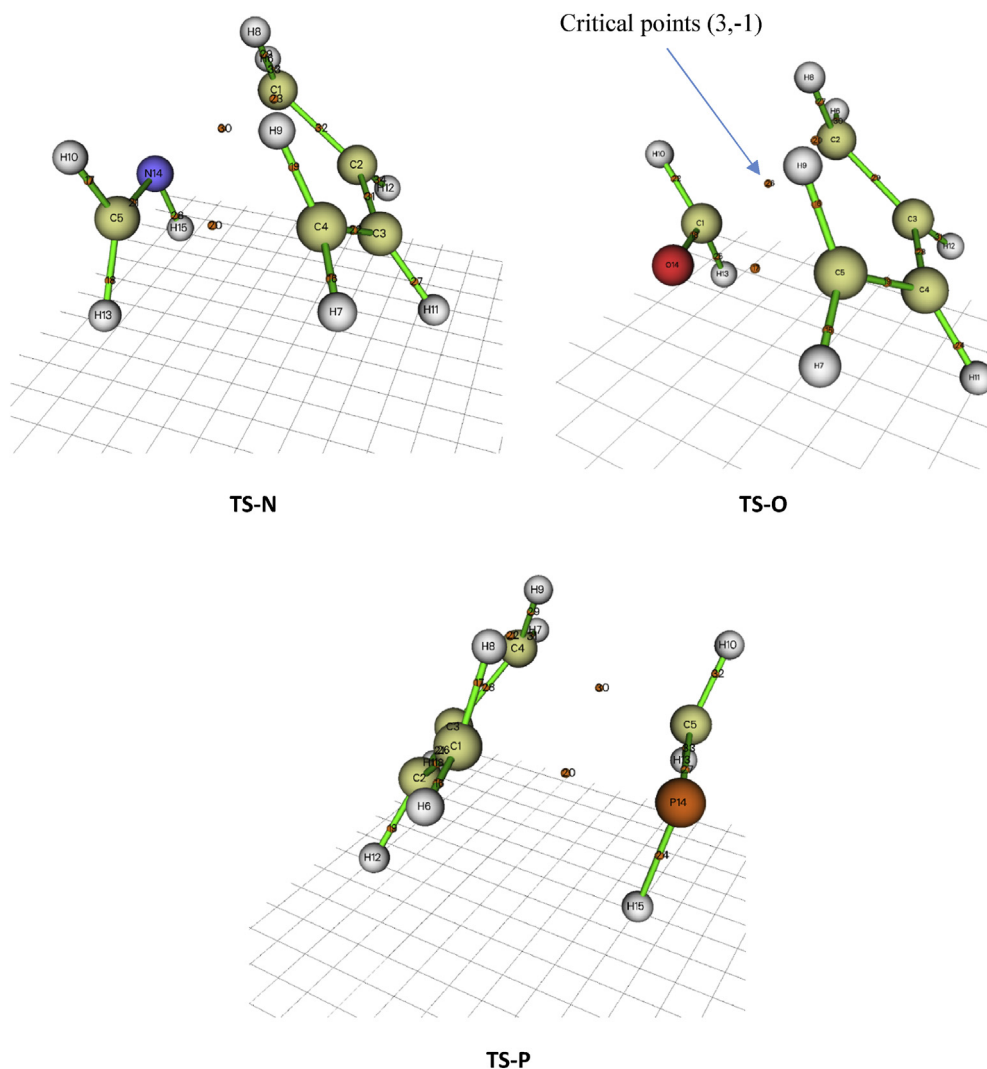


Figure 6. Schematic structure of AIM analysis of transitions states of TS-N, TS-O and TS-P.

Table 4. AIM properties of the main bonds for the transitions states TS-N, TS-O and TS-P.

TS	$\rho(\text{e}/\text{a}^3)$	$\nabla^2\rho(\text{e}/\text{a}^5)$
TS-N(C1–N14)	0.294	-0.695
TS-N(C4–C5)	0.298	0.055
TS-O(C5–O14)	0.052	0.125
TS-O(C1–C2)	0.085	-0.010
TS-P(C1–P14)	0.046	0.035
TS-P(C4–C5)	0.029	0.052

Electronic density (ρ) and Laplacian ($\nabla^2\rho$).

the potential energy surfaces schemes (PESs), the intrinsic reaction coordinate (IRC) calculations and the calculated bond lengths and bond orbitals (BOs) shows that these cycloadditions take place through a highly asynchronous concerted process. Quantum theory of atoms in molecules (QTAIM) analysis shows critical points in the structure of the transition state, with positive density values and the Laplacian that explains the formation of new bonds to obtain the Diels-Alder adduct.

Declarations

Author contribution statement

Imad Hammoudan, Samir Chtita: Analyzed and interpreted the data; Wrote the paper.

Driss Riffi-Temsamani: Contributed analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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