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A COMPUTATIONAL STUDY ON REGIOSELECTIVITY OF 1,3-DIPOLAR CYCLOADDITION REACTIONS OF 3-AZIDOPROPANE-1,2-DIOL WITH DIACETYLENE DERIVATIVES

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Abstract: The reactivity and regioselectivity of 1,3-dipolar cycloadditionreactions of 3-azidopropane-1,2-diol (**1**) with diacetylene derivatives (**2a, 2b and 2c**) have been investigated by using density functional theory (DFT) -based on reactivity indices and activation energy calculations at B3LYP/6-31G(d) level of theory in the gasphase. The potential energy surface analyses for both reactions are in agreement with the experimental observations. Moreover, our calculations on the geometries, bond orders (BOs) and charge transfers (CTs) at the transition state (TS) structures shows which these 1,3-DC reactions occur via an synchronous concerted mechanism, and unfavorable TSs are more asynchronous than the favorable ones.

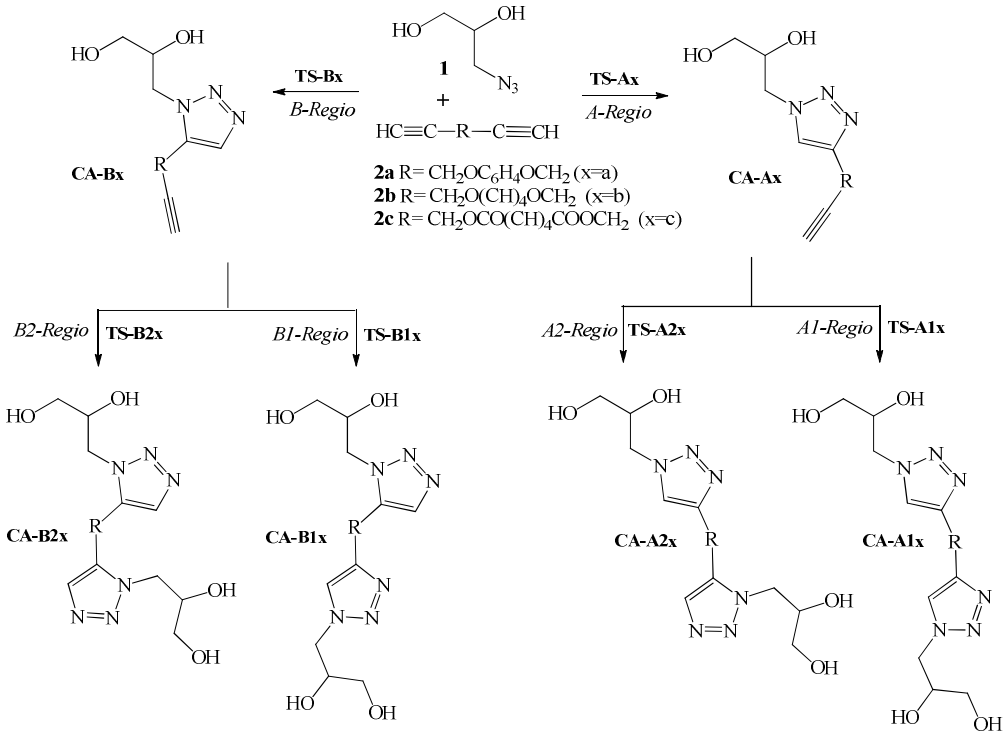
Keywords: Regioselectivity, 1,3-dipolar cycloaddition,click chemistry, DFT reactivity indices.

Introduction

Since the 1,3-dipolar cycloaddition(1,3-DC) of azides with alkynes was investigated by Huisgen et al,[I-III] it has attracted much attention because of theoretical interest of the reaction [IV] and the synthetic importance of the aromatic and nonaromatic five-membered [1,2,3]-triazoleheterocycles. The regioselectivity of this kind of 1,3-DC reaction mainly depends on the electronic and steric effects.[V]The alkyne-azide 1,3-DC reactions have been extensively applied in almost every area of chemistry, including materials chemistry, drug discovery, development of sensors, polymer chemistry, chemical biology, and organic synthesis.[VI-XII]
Themechanism of 1,3-DC reactions have traditionally been studied by using the frontier molecular orbital (FMO) theory and transition state theory (TST). Although TST remains the most widely used and the most rigorous approach for the study of the mechanism and the regiochemistry of these reactions, the localization of transition states is not always easier. Furthermore, transition-state calculations are often very time-consuming when bulky substituents are present in reactive systems. The reactivity indices, as defined by the conceptual density functional theory,[XIII]such as Fukui and Parr indices, local softnesses and local electrophilicity and nucleophilicity have been used to rationalise the reactivity and regiochemistry of cycloaddition reactions.[XIV-XVII]

Recently, Houk and et al have reported theoretical studies on the reactivity and regioselectivity of metal free of 1,3-DC reactions of different azides as a dipole with variousalkynes as a dipolarophilebased on transition states, activation barriers and reactivity indexes.[XVIII-XX]They observed that the reaction mainly depends on the electronic and steric effects of substituents.

In the past decades, in addition to the selectivity behavior, the understanding of the underlying principles in pericyclic reactions has grown from a fruitful interplay between theory and experiment and continues to present a real challenge.[XXI-XXIII]The study on mechanism of metal-free 1,3-DC reactions of different azides with various alkynes has been the main challenge in order to synthesis of polymeric compounds.[XXIV-XXVI] Thus, in the present work, in continuation of our previous works on the theoretical investigation of 1,3-DC reactions,[XXVII-XXXI] a theoretical study on the observed differences in reactivity and regioselectivity of the 1,3-DC reactions of 3-azidopropane-1,2-diol (**1**) with diacetylene derivatives (**2a-c**) based on activation energy calculations and DFT-based reactivity indiceswas performed, in order to achieve a deeper insight to these 1,3-DC reactions (Scheme 1).



Scheme 1. Regioisomeric pathway for the investigated 1,3-DC reactions.

Computational details

All calculations were carried out with GAUSSIAN03 program suite.[XXXII]Geometry optimization of the reactants was carried out using DFT methods at the B3LYP/6-31G(d) level of theory.[XXXIII]The transition states (TSs) for the 1,3-DC reactions have been localized at the B3LYP/6-31G(d) level of theory. Frequency calculations characterized the stationary points to verify that the TSs had one and only one imaginary frequency. The intrinsic reaction coordinates (IRC) [XXXIV]calculation was performed in forward and backward path to identify that each saddle point connects to the two associated minima using the second-order González–Schlegel integration method.[XXXV]

The atomic electronic populations were evaluated with Mullikenanalysis.[XXXV-XL]The electronic chemical potential μ was evaluated in terms of the one electron energies of the HOMO and LUMO, using Eq. (1)[XLI]:$\mu=(\varepsilon_H+\varepsilon_L)/2$ (1)

The global electrophilicityω for dipoles and dipolarophile was evaluated using Eq. (2) [XLII]:$\omega=\mu^2/2(\varepsilon_L-\varepsilon_H)$(2)

Results and discussion

Our obtained results are presented in three sections. In the first section, we concentrate our attention on the energetic aspects of the 1,3-DC reactions. In the second section, we investigate the bond lengths, bond orders and charge transfers in the transition structures. Finally, the last section is directed towards DFT-based reactivity indices.

Analysis based on energetic aspects

In the present work, the transition states are located through vibrational frequency analysis. Each such transition state is characterized by a single imaginary frequency. For the different structures of the approaching reactants, transition states and the products, a convenient naming system has been employed. In these reactions, the 1,3-DC reactions dipole **1**with dipolarophiles**2a-c**carry out from tworegioisomeric pathways (*A-regio* and *B-regio*) leading tothe formation of the corresponding transition states (**TS-Ax**, **TS-Bx**) and cycloadducts (**CA-Ax**, **CA-Bx**),where x=**a-c**is$CH_2OC_6H_4OCH_2$, $CH_2O(CH)_4OCH_2$ and $CH_2OCO(CH)_4CO_2CH_2$ respectively(see Scheme 1), and also thecorresponding transition states (**TS-A1x**, **TS-A2x, TS-B1x, TS-B2x**) and cycloadducts (**CA-A1x**, **CA-A2x, CA-B1x, CA-B2x**) are formed via the reaction of**CA-Ax** and **CA-Bx**with another dipole **1**.

Total energies (in a.u.) for the all species and relative energies (in kcal/mol) for the TSs and products are summarized in Table 1. The alltransition state structures for the reaction of **1**+**2a**, **1**+**2b** and **1**+**2c**are given in Figure 1 to3 respectively. All the reactions progressed exothermically with large ΔH values (Table 1). According to Hammond's postulate, the TSs should then be closer to the reactants. As shown inTable 1, the relative Gibbs free energy values, ΔG, for the TSs corresponding to the two regioisomeric pathway are: 28.44(**TS-Aa**), 30.31 (**TS-Ba**) kcal mol^{-1} for the 1,3-DC reaction of dipole**1** with dipolarophile**2a** and after the reaction with another dipole **1** are:28.88 (**TS-A1a**), 29.87 (**TS-A2a**), 28.11 (**TS-B1a**), 30.57 (**TS-B2a**)kcal mol^{-1},for the 1,3-DC reaction of dipole**1** with dipolarophile**2b** and then reaction with another dipole **1** are: 29.70 (**TS-Ab**), 31.99 (**TS-Bb**), 29.13 (**TS-A1b**), 30.37 (**TS-A2b**), 30.10 (**TS-B1b**), 31.28 (**TS-B2b**) kcal $mol^{-1}$and finally for the 1,3-DC reaction of dipole **1** with dipolarophile **2c** and then reaction with another dipole **1** are: 27.95 (**TS-Ac**), 29.40 (**TS-Bc**), 31.06 (**TS-A1c**), 32.80 (**TS-A2c**), 34.10 (**TS-B1c**), 35.81 (**TS-B2c**) kcal mol^{-1}.We can conclude whichin the all reaction, the formation of cycloadducts**CA-Ax** is more favorable than the **CA-Bx** ones by about 2 kcal mol^{-1}, the formation of cycloadducts**CA-A1x** is more favorable than the **CA-A2x** ones by about 1 to 1.5 kcal mol^{-1} and the also the formation of cycloadducts**CA-B1x** is more favorable than the **CA-B2x** ones by about 1 to 2 kcal mol^{-1} (Table 1 and Figure 1 to 3).

Analysis of bond lengths, bond orders and charge transfers in the transition states

The geometries of the allTSs, related charge transfers (CT), the lengths of the C–N forming bonds and their Wiberg bond order values involved in these 1,3-DC reactions are shown inFigure 1(for reaction of **1**+**2a**), Figure 2 (for reaction of **1**+**2b**) and Figure 3 (for reaction of **1**+**2c**). An analysis of the lengths of the two C–N forming bonds in the TSs shows that they are formed in the same extent, although,difference in unfavorable TSs is more than favorable ones. The extent of bond formation along a reaction pathway is provided by the concept of bond order (BO).[XLIII]The BO (Wiberg indices) values of the two C–N forming bonds at TSs are shown in brackets inFigure 1 to 3. For all three reaction, these values are almost equal (0.26, 0.27) in favorable TSs (**TS-Ax**, **TS-A1x**, **TS-B1x**). Nodifferences of BO for two

forming bonds at the favorable TSs indicatesynchronous concerted mechanism for these 1,3-DC reaction. While, for unfavorable ones (**TS-Bx**, **TS-A2x**, **TS-B2x**), there are little differences. These values are within the range of 0.22 to 0.34. These results show that the unfavorable TSs in these reactionsare more asynchronous than the favorable TSs.

The electronic nature of these 1,3-DC reactions is evaluated by analyzing the charge transfer (CT) at the TSs along the cycloaddition process. The natural atomic charges are shared between the dipole**1** and dipolarophiles**2a-c** and these data are shown in Figure 1to 3. In the gas phase, the CT at the TSs, which passes from the dipolarophileto the dipole moiety, are in the range 0.048 to 0.071 efor the favorableTSs and 0.054 to 0.101 e for the unfavorable ones indicating nearly low-polar character for these 1,3-DC reactions. Moreover, the CT calculations show an inverse electron demand (IED) character for these reactions. These low and inverse charge transfer can be related to the electron-rich character of the diacetylene derivatives **2a-c**as a dipolarophile.

Table 1. Total Gibbs free energies, *G* (a.u) of reactants (**1**, **2a-c**), transition states (TSs) and cycloadducts (CAs), relative Gibbs free energies (ΔG, in kcal mol^{-1}) computed at 298.15 K and 1 atm in the gas phase for the transition states (TSs) and cycloadducts (CAs) involved in the 1,3-DC reactions of **1** with **2a-c**.[a]

System	*G*	ΔG	System	*G*	ΔG
1	-433.0566		**TS-B1c**	-1632.4312	34.10
2a	-613.4162		**TS-B2c**	-1632.4285	35.81
2b	-539.5803		**CA-Aa**	-1046.5644	-57.45
2c	-766.2827		**CA-Ba**	-1046.5562	-52.27
TS-Aa	-1046.4275	28.44	**CA-A1a**	-1479.7121	-57.15
TS-Ba	-1046.4245	30.31	**CA-A2a**	-1479.7074	-54.19
TS-A1a	-1479.5750	28.88	**CA-B1a**	-1479.7074	-59.37
TS-A2a	-1479.5734	29.87	**CA-B2a**	-1479.7012	-55.49
TS-B1a	-1479.5680	28.11	**CA-Ab**	-972.7237	-54.46
TS-B2a	-1479.5641	30.57	**CA-Bb**	-972.72148	-53.04
TS-Ab	-972.5896	29.70	**CA-A1b**	-1405.8723	-57.65
TS-Bb	-972.5860	31.99	**CA-A2b**	-1405.8674	-54.60
TS-A1b	-1405.7340	29.13	**CA-B1b**	-1405.8674	-56.03
TS-A2b	-1405.7320	30.37	**CA-B2b**	-1405.86	-53.95
TS-B1b	-1405.7301	30.10	**CA-Ac**	-1199.4312	-57.68
TS-B2b	-1405.7283	31.28	**CA-Bc**	-1199.4289	-56.20
TS-Ac	-1199.2948	27.95	**CA-A1c**	-1632.5764	-55.54
TS-Bc	-1199.2925	29.40	**CA-A2c**	-1632.5690	-50.90
TS-A1c	-1632.4384	31.06	**CA-B1c**	-1632.5690	-52.38
TS-A2c	-1632.4356	32.80	**CA-B2c**	-1632.5623	-48.17

[a]Computed at6-31G(d)

IRC calculations were carried out for all studied reactions and presented only for the reaction pathway leading to **CA-Aa (**Figure 4). This figure shows saddle point clearly and demonstrates that the TS connect to the associated minima in the concerted mechanism.

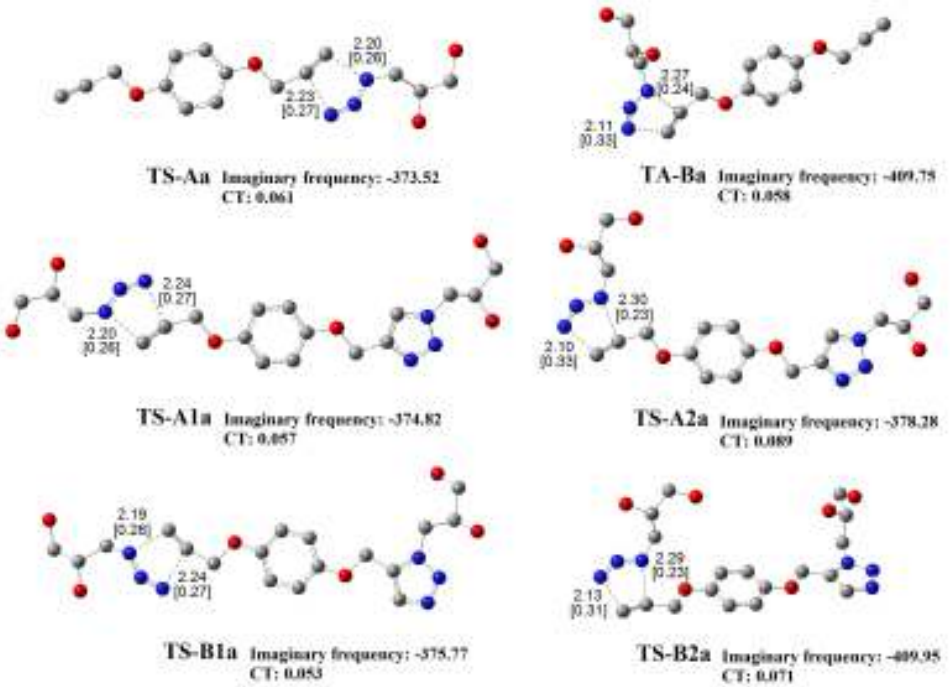


Figure 1. Optimized geometries for the favorable TS structures in the reaction of **1+2a** at the B3LYP/6-31G(d) level of theory. Hydrogen atoms have been omitted for clarity. Distances of forming bonds are given in angstroms. The bond orders are given in square brackets.

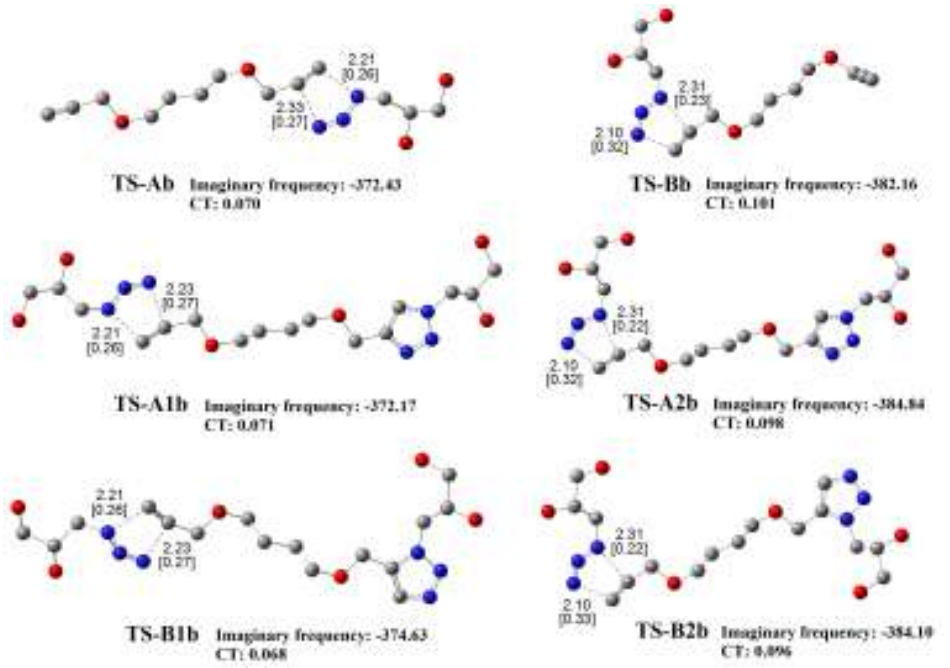


Figure 2. Optimized geometries for the favorable TS structures in the reaction of **1+2b** at the B3LYP/6-31G(d) level of theory. Hydrogen atoms have been omitted for clarity. Distances of forming bonds are given in angstroms. The bond orders are given in square brackets.

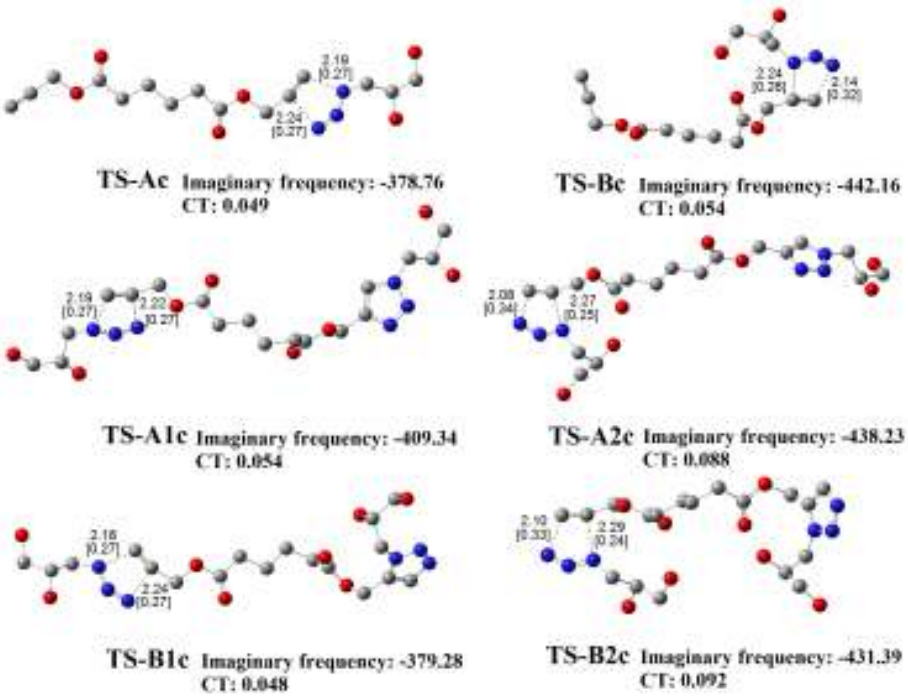


Figure3. Optimized geometries for the all TS structures in the reaction of **1+2c** at the B3LYP/6-31G(d) level of theory. Hydrogen atoms have been omitted for clarity. Distances of forming bonds are given in angstroms. The bond orders are given in square brackets.

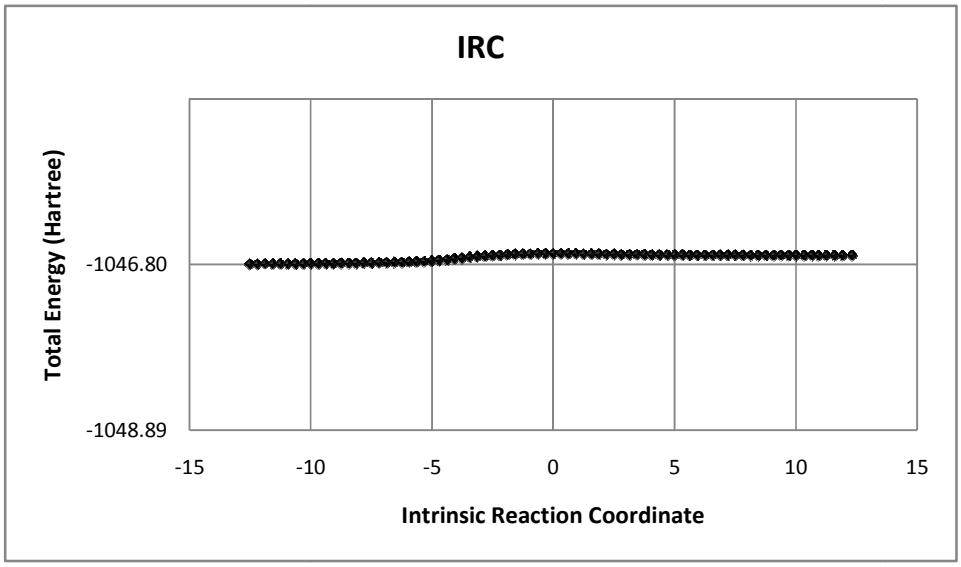


Figure4. B3LYP/6-31G (d) IRC plot for the reaction pathway leading to CA-Aa.

DFT-based reactivity indices

HOMO and LUMO energies, electronic chemical potential μ, chemical hardness η, global electrophilicityω and global nucleophilicity$N$ of the dipole**1**and dipolarophiles**2a-c**, are given in Table 2.

Table 2.HOMO and LUMO energies in a.u., electronic chemical potential (μ in a.u.), chemical hardness (η in a.u.), global electrophilicity (ω, in eV) and global nucleophilicity (N, in eV) for reactants **1** and **2a-c**.

Reactants	ε_{HOMO}	ε_{LUMO}	μ	η	ω	N^a
1	-0.2638	-0.0364	-0.1501	0.2274	1.3480	1.9429
2a	-0.2035	-0.0068	-0.1051	0.1967	0.7648	3.5834
2b	-0.2564	-0.0310	-0.1437	0.2254	1.2465	2.1443
2c	-0.2714	-0.0064	-0.1389	0.2650	0.9906	1.7361

[a] HOMO energy of tetracyanoethylene is -0.3351 a.u. at the same level of theory.

As it can be seen inTable 2, the electronic chemical potential (μ) of dipolarophiles**2a**(-0.1051)**2b** (-0.1437) and **2c**(-0.1389) are greater than dipole **1**(-0.1501), which shows the charge transfer is taking place from dipolarophiles**2a-c**to dipole**1**.Consequently, the dipole**1** can act as electerophileand dipolarophiles**2a-c** as nucleophile in these 1,3-DC reactions. Moreover, our obtained results show which these 1,3-DC reactions are IED and in agreement with CT calculations at the TSs. The difference in electrophilicity for the dipole/dipolarophile pair, $\Delta\omega$, was found to be a measure of the high- or low-polar character of the cycloaddition reactions.[XLIV]The small $\Delta\omega$ between dipole **1** with dipolarophiles**2a-c** are 0.585, 0.102 and0.357eV, respectively, show a low-polar character for these 1,3-DC reactions.

Conclusion

Mechanism and regiochemistry for the 1,3-DC reactions of 3-azidopropane-1,2-diol (**1**) with diacetylene derivatives (**2a-c**) have been investigated using activation energy calculations and DFT-based reactivity indexes at the B3LYP/6-31G (d) level of theory. The results obtained in this study allow us to conclude that activation energy calculations clearly predict the regiochemistry of these 1,3-DC reactions. In addition, the calculation on TS structures show that these 1,3-DC reactions occur via an synchronous concerted mechanism.

Acknowledgments

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