

Understanding the quantitative role of the binding chain (CH₂)_n (n=1,2 and 3) on the physicochemical character in the intramolecular reaction: Case of triene-amide

Abdelilah BENALLOU^{1*}, Hocine GARMES², Habib el alaoui EL ABDALLAOUI¹

¹Team of chemoinformatics research and spectroscopy and quantum chemistry, Department of chemistry, physical and chemistry lab, Faculty of Science.

²Laboratory of bio-organic chemistry, Department of chemistry, Faculty of Science
University Chouaib Doukkali, B. P. 20, 24000 El Jadida, Morocco.

Abstract

In this study, we will be studied quantitatively the binding chain role and understanding the interactions between diene (D) and dienophile (Dp) fragments in the intra-molecule (IM) and identifying the physicochemical variations of these fragments when passing from the isolated fragment (IF) to the linked fragment (LF) at the intra-molecule using the nucleophilic and electrophilic Fukui functions f_k^{\pm} calculated by DFT (density functional theory) method with the B3LYP hybrid and 6-31G(d,p) basis set level. The results found show that the binding chain has a low contribution to the physicochemical character of the intra-molecule and that his principal role focuses on the transfer of the charge between fragments, the quantitative studies we permit to conclude that the nucleophilic Fukui functions of Diene are remains unchanged in the linked fragment than that in diene (D) of isolated fragment (FD_{IF}) as $f_k^{-}(k \in \text{FD}_{\text{IF}}) \approx f_k^{-}(k \in \text{FD}_{\text{LF}})$, and the electrophilic Fukui function of dienophile is divided almost in half in the linked fragment than that in dienophile (Dp) in isolated fragment as $f_k^{+}(k \in \text{FD}_{\text{pIF}}) \approx 2 f_k^{+}(k \in \text{FD}_{\text{pLF}})$.

* Corresponding author:
abdo.benallou@yahoo.fr

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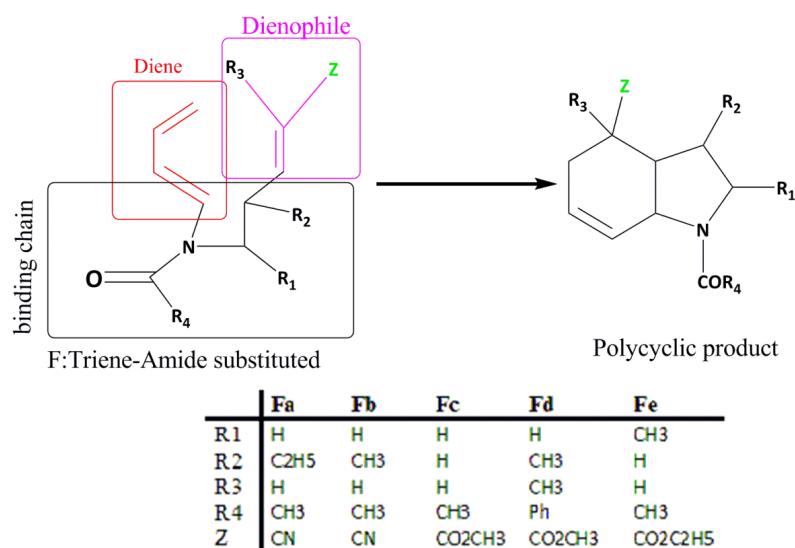
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1. Introduction

Diels Alder (DA) reaction is one of the most useful methods for the construction of six cycles. And attracted a considerable interest of the experimental [1-8] and theoretical scientists [9-14]. There are many variants of the Diels-Alder reaction, by varying the nature of the diene (D) and a dienophile (Dp) many different types of six carboxylic structures can be composed. The intramolecular Diels-Alder (IMDA) reaction is widely used for the construction of the cycles in a single synthetic process [15]. This reaction has been used in the construction of many biological and pharmacological systems and as a highway in the total synthesis of the natural products [16,17]. The distribution of global electronic properties in fragments or in functional groups within a single molecule is a powerful tool to discuss the reactivity of the intramolecular reactions [18,20]. However, the division of combinations or structures are usually arbitrary in nature and they may or may not have a chemical significance. The studies that are carried out on the binding chain role of the intramolecular reaction are much rare, we can particularly mention the work of Tachibana [21] such as these studies is purely qualitative. To understanding the estimable effects of the binding chain on the electrophilicity and nucleophilicity quantities to dienes and dienophiles fragments of the intra-molecule as well to evaluate the possible changes in these quantities in the linked fragment (LF) of intra-molecule compared to that in the isolated fragments (IF) pushed us to make this work. Based on the nucleophilic and electrophilic Fukui functions f^{\mp} , we will try to estimate quantitatively the binding chain $(CH_2)_n$ ($n=1, 2$ to 3) role of IMDA reaction for a single-molecule multi-moiety of triene-amide (Scheme.1). However, this study was conducted using the conceptual DFT in which the descriptors and reactivity indices have naturally found their places.



Scheme 1. Intramolecular cycloaddition Diels-Alder reaction of triene-amide.

2. Computational details

The geometry optimizations were performed at the B3LYP exchange-correlation energy functional [22,23] using the most popular basis sets 6-31G(d,p). All the calculations were performed with GAUSSIAN G09 program package [24] and visualization of the output files are performed using the Gauss-View 5.0.8 software. The global electrophilicity index ω [25] is given by the following expression ($\omega = \mu^2/2\eta$), in terms of the electronic chemical potential μ and the chemical hardness η . Both quantities may be approached in terms of the one-electron energies of the frontier molecular orbital HOMO and LUMO, as ϵ_{HOMO} and ϵ_{LUMO} such as: $\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$ and $\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})$

respectively [26]. The nucleophilicity index N [27] based on the HOMO energies has been obtained within the Kohn-Sham scheme [28] and defined as: $N=(E_{\text{HOMO(Nu)}}-E_{\text{HOMO(TCE)}})$. The nucleophilicity is referred to Tetracyanoethylene (TCE), because it presents the lowest HOMO energy in a large series of molecules already investigated in the context of polar cycloadditions. The local nucleophilicity N_k [29], defined as the product of the global nucleophilic index N and Fukui nucleophilic index f_k^- . Thus $N_k = N f_k^-$ with $N = \sum N_k$. The condensed of Fukui functions in a molecule with N electrons was proposed by Yang and Mortier [30].

$f_k^+ = [q_k(N+1) - q_k(N)]$ for nucleophilic attack

$f_k^- = [q_k(N) - q_k(N-1)]$ for electrophilic attack

$q_k(N)$: Electronic population of the atom k in the neutral molecule.

$q_k(N+1)$: Electronic population of the atom k in the anionic molecule.

$q_k(N-1)$: Electronic population of the atom k in the cationic molecule.

We can determine the electrophilic (ω_F) and nucleophilic (N_F) indices of fragments [31] (F = diene or dienophile) by the below equations:

$$\omega_F = \omega \sum_{k \in F} f_k^+$$

$$N_F = N \sum_{k \in F} f_k^-$$

N and ω are the global nucleophilic and electrophilic indices respectively, the calculation of these functions has been realized by using the natural of populations analysis (NPA) [32]. In our work, we suppose that the intramolecular molecule contains three portions (fragments), such as two fragments are the diene and dienophile and a binder (binding chain) (Figure 1).

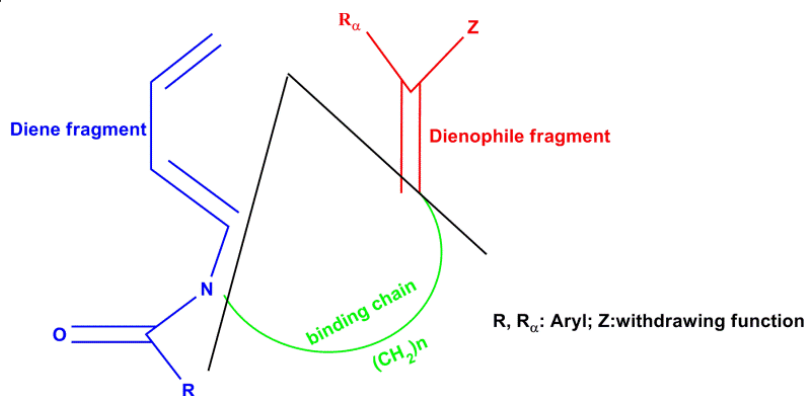


Figure 1. Graphical representation of the three main regions of triene amide molecule.

3. Results and Discussions

3.1. Physicochemical characteristic of triene amide molecules

Before beginning our study, we have tried to display graphically the different molecules used in this work, the graphical representation of compounds Fa, Fb, Fc, Fd and Fe are shown schematically in Table 1, where the dienes fragments are given in the blue colour, as well the dienophiles fragments are given in red and binding chain in black colour. Although the methylene number of the binding chain is ranging from 2 to 3 molecules. The parameters of each molecule as HOMO and LUMO energy, global hardness η , chemical potential μ , electrophilicity ω and nucleophilicity N indices have been determined and summarized in Table 2.

Table 1. Representation of different fragments of triene amide molecules.

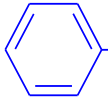
Compounds	Structures
Fa	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH}-\text{CN}$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> COCH_3 </div> <div style="text-align: center;"> C_2H_5 </div> </div>
Fb	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{CH}-\text{CH}=\text{CH}-\text{CN}$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> COCH_3 </div> <div style="text-align: center;"> CH_3 </div> </div>
Fc	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CO}_2\text{CH}_3$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> COCH_3 </div> </div>
Fd	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{C}-\text{CO}_2\text{CH}_3$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  CO </div> <div style="text-align: center;"> CH_3 </div> <div style="text-align: center;"> CH_3 </div> </div>
Fe	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CO}_2\text{C}_2\text{H}_5$ <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> COCH_3 </div> <div style="text-align: center;"> CH_3 </div> </div>

Table 2. HOMO and LUMO energies, chemical potential μ , global hardness η , global electrophilicity ω and nucleophilicity N indices of Fa, Fb, Fc, Fd and Fe compounds.

Compounds	HOMO (a.u.)	LUMO (a.u.)	μ (a.u.)	η (a.u.)	ω (eV)	N (eV)
Fa	-0.21396	-0.04396	-0.129	0.170	1.332	3.299
Fb	-0.21437	-0.04384	-0.129	0.171	1.324	3.288
Fc	-0.20884	-0.03716	-0.123	0.172	1.197	3.438
Fd	-0.20534	-0.04570	-0.125	0.160	1.329	3.533
Fe	-0.20921	-0.03820	-0.124	0.171	1.223	3.428

According to results in Table 2, it is important to note that these compounds have a predominant nucleophilic character such as the calculated values of the nucleophilic character are always higher than those of the electrophilic character. Similarly, the hardness values of these compounds are very closer except to that of Fd compound ($\eta=0.16$) in which has at the amide function the benzene substitution at R_4 position, so this compound can easily lose their electronic charge in interaction with another electrophilic compound. To highlight the binding chain contribution in the HOMO and LUMO energy of the triene-amide molecule, we have tried to study the diene and dienophile fragments independently by adding every time the methylene molecule $(\text{CH}_2)_n$ with $n=1, 2$ and 3 to these fragments. The results are given in Tables 3 and 4. In Tables 3 and 4, we are noted that the change caused by the binding chain to HOMO and LUMO energy of these fragments is too little, such as the HOMO and LUMO energies of different fragments containing the binding chains as (Ba, Bb, Bc, Bd, Be, Ca, 2, 3a, 3b, 3c, 4a, 4b, 4c, 4d, 4f, 4g, 4k, 5a, 5b and 5c) are changed slightly compared to the principal fragments (A, B, C) ; (1, 3, 4, 5) of diene and dienophile respectively, such as the values found of HOMO and LUMO energy for different fragment with or in absence of

binding chain are approximately equal, so this portion of molecule not has major effect of these molecular orbital energies. At this stage and for more exactitude of this result we will be assayed to evaluate the binding chain contributions on the nucleophilicity and electrophilicity of the triene amide molecule. In this end, we will be studied each dienes and dienophiles fragment separately. However, the results found are determined and given in Tables 5 and 6. Table 5 shows for the diene fragment in the isolated state (IS) that the nucleophilic values are greater compared to those of the electrophilic values. Thus, these fragments have more nucleophilicity due to π electron of the unsaturated and conjugated bonds such as the diene fragment hold four π electrons. Consequently the diene has completely preserved their nucleophilic character (donor) despite the amide function is attached to him at the pentane skeleton level. Therefore the dienes are entirely nucleophilic subsequently the dienophiles fragments should be electrophilic in good accordance with the Diels-Alder rule [33].

Table 3. HOMO and LUMO energies of dienes fragments.

Compound	Structures	HOMO (au)	LUMO (au)
D (A)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-0.23002	-0.02566
D (B)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{H}$ COCH_3	-0.20920	-0.03078
D (Ba)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{H}$ COC_2H_5	-0.20803	-0.03250
D (Bb)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{H}$ COC_3H_7	-0.20772	-0.03227
D (Bc)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_3$ COCH_3	-0.20497	-0.02878
D (Bd)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{CH}_3$ COCH_3	-0.20406	-0.02863
D (Be)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{C}_3\text{H}_7$ COCH_3	-0.20315	-0.02811
D (C)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{H}$ $\text{CO}-\text{benzene}$	-0.20867	-0.04868
D (Ca)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{N}-\text{CH}_3$ $\text{CO}-\text{benzene}$	-0.20995	-0.04425

Table 4. HOMO and LUMO energies of dienophiles fragments.

Compounds	Structures	HOMO (au)	LUMO (au)
Dp (1)	$\text{CH}_2=\text{CH}_2$	-0.26540	0.01622
Dp (2)	$\text{CH}_2=\text{CH}-\text{CH}_3$	-0.24848	0.02666
Dp (3)	$\text{N}\equiv\text{C}-\text{CH}=\text{CH}_2$	-0.28956	-0.05699
Dp (3a)	$\text{N}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_3$	-0.27264	-0.04504
Dp (3b)	$\text{N}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	-0.27165	-0.04477
Next table 4			
Dp (3c)	$\text{N}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	-0.27089	-0.04473
Dp (4)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$	-0.27199	-0.04575
Dp (4a)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{CH}_3$	-0.26588	-0.03662
Dp (4b)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	-0.26525	-0.03707
Dp (4c)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}_3\text{H}_7$	-0.26477	-0.03666
Dp (4d)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$	-0.26766	-0.03850
Dp (4f)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_3$	-0.25179	-0.03229
Dp (4g)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-\text{CH}_3$	-0.25149	-0.02956
Dp (4k)	$\text{CH}_3-\text{O}-\text{C}(=\text{O})-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}(\text{CH}_3)_2$	-0.25109	-0.02987
Dp (5)	$\text{CH}_3-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}_2$	-0.26943	-0.04586
Dp (5b)	$\text{CH}_3-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}_2\text{H}_5$	-0.26266	-0.03563
Dp (5c)	$\text{CH}_3-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{CH}=\text{CH}-\text{C}_3\text{H}_7$	-0.26183	-0.03489

Table 5. HOMO and LUMO energies, chemical potential μ , chemical hardness η , global electrophilicity and nucleophilicity indices of dienes fragments.

Fragments	HOMO (a.u.)	LUMO (a.u.)	μ (a.u.)	η (a.u.)	ω (eV)	N (eV)
(A)	-0.23002	-0.02566	-0.12784	0.20436	1.087	2.861
(B)	-0.20920	-0.03078	-0.11999	0.17842	1.097	3.427
(Ba)	-0.20803	-0.03250	-0.12026	0.17553	1.121	3.459
(Bb)	-0.20772	-0.03227	-0.11999	0.17545	1.116	3.467
(Bc)	-0.20497	-0.02878	-0.11692	0.17619	1.055	3.542
(Bd)	-0.20406	-0.02863	-0.11634	0.17543	1.049	3.567
(Be)	-0.20315	-0.02811	-0.11563	0.17504	1.039	3.591
(C)	-0.20867	-0.04868	-0.12646	0.15999	1.359	3.441
(Ca)	-0.20995	-0.04425	-0.12710	0.16570	1.326	3.406

Table 6. HOMO and LUMO energies, chemical potential μ , chemical hardness η , global electrophilicity and nucleophilicity indices of dienophiles fragments.

Fragments	HOMO (a.u.)	LUMO (a.u.)	μ (a.u.)	η (a.u.)	ω (eV)	N (eV)
(1)	-0.26540	0.01622	-0.12459	0.28162	0.750	1.898
(2)	-0.24848	0.02666	-0.11091	0.27514	0.608	2.358
(3)	-0.28956	-0.05699	-0.173275	0.23257	1.756	1.241
(3a)	-0.27264	-0.04504	-0.15884	0.22760	1.508	1.701
(3b)	-0.27165	-0.04477	-0.15821	0.22680	1.501	1.728
(3c)	-0.27089	-0.04473	-0.15781	0.22616	1.497	1.749
(4)	-0.27199	-0.04575	-0.15887	0.22624	1.517	1.719
(4a)	-0.26588	-0.03662	-0.15125	0.22926	1.357	1.885
(4b)	-0.26525	-0.03707	-0.15116	0.22818	1.362	1.902
(4c)	-0.26477	-0.03666	-0.15216	0.22811	1.380	1.915
(4d)	-0.26766	-0.03850	-0.15308	0.22916	1.391	1.837
(4f)	-0.25179	-0.03229	-0.14204	0.21950	1.250	2.268
(4g)	-0.25149	-0.02956	-0.14054	0.22193	1.210	2.277
(4k)	-0.25109	-0.02987	-0.14048	0.22122	1.213	2.287

Table 6 shows that these dienophile fragments in isolated state (IS) have a predominant nucleophilic character because containing an unsaturated bond of two π electrons (fragment 1), Then when we will add an electron withdrawing substituent (CN, CO₂R) to the Z position of these fragments (Figure.1) we remark that the nucleophilicity has been diminished and afterward these fragments becomes most electrophilic. Therefore, following to results noted in tables 5 and 6 the addition of methylene chains to these dienophiles and dienes fragments does not have more effect on the nucleophilic and electrophilic characters.

3.2. Local nucleophilic and electrophilic descriptors of Fukui functions quantities

To enhance accuracy of results founds previously, we will attempt to make a comparison by the electrophilic and nucleophilic quantities between the independent fragments (isolated state) and those constitute one molecule (fragments+binding chain), in this goal we will be tried to calculate the local nucleophilic and electrophilic of Fukui functions of the most attractive atoms in the triene amide molecule such as C1 and C4 (diene) as well C7 and C8 (dienophile) by using the natural population analysis (NPA) of such these quantities are given in Tables 7 and 8.

Table 7. Local nucleophilic Fukui function f_k^- of active centres of linked and isolated diene and dienophile fragment.

Entry	f_{C1}^- (Diene)		f_{C4}^- (Diene)		f_{C7}^- (Dienophile)		f_{C8}^- (Dienophile)	
	LF	IS	LF	IS	LF	IS	LF	IS
Fa	0.1813	0.1953	0.0701	0.0795	-0.0357	0.2142	0.0328	0.2069
Fb	0.1828	0.1953	0.0713	0.0795	-0.0377	0.2319	0.0337	0.2113
Fc	0.1805	0.1953	0.0693	0.0795	-0.0347	0.2181	0.0346	0.3009
Fd	0.1393	0.1878	0.0646	0.0806	-0.0073	0.2336	0.0483	0.2596
Fe	0.1779	0.1908	0.0724	0.0742	-0.0318	0.2034	0.0244	0.2753

LF: Linked fragment; IS: Isolated fragment.

We are noted from to results in Table 7 that the local nucleophilic Fukui functions of active centres (C1 and C4) in diene fragment is almost equal in two cases (in the linked and in the isolated fragment) as: f_k^- of the diene in linked fragment of intra-molecule (IM) $\approx f_k^-$ of the diene in isolated fragment (IS), in which meant that the binding chain does not influence widely the nucleophilic characters of these reactive atoms in the linked fragment of intra-molecule compared to the diene in isolated fragment. In addition, these active centres of dienes fragments are fully preserved their chemical characters (donor of the electron) in the fragments-binding chain molecule (IM). In contrary, the results founds for the active centres (C7 and C8) of dienophile fragment are diverse of both cases in which the local nucleophilic Fukui functions verified that f_k^- of the dienophile in the linked fragment of intra-molecule $\neq f_k^-$ of the dienophile in isolated fragment, these remarks allows us to confirm the results found previously in which the diene is purely nucleophilic. As results to this paragraph, the binding chain has a negligible contribution in the nucleophilicity of triene amide molecule.

Table 8. Local electrophilic Fukui function f_k^+ of active centres of linked and isolated diene and dienophile fragments.

Entry	f_{C1}^+ (Diene)		f_{C4}^+ (Diene)		f_{C7}^+ (Dienophile)		f_{C8}^+ (Dienophile)	
	LF	IS	LF	IS	LF	IS	LF	IS
Fa	0.1100	0.1786	0.0698	0.1485	0.1281	0.2823	0.0826	0.1679
Fb	0.1122	0.1786	0.0718	0.1485	0.1217	0.2774	0.0819	0.1681
Fc	0.11080	0.1786	0.0715	0.1485	0.1081	0.2508	0.0499	0.1000
Fd	0.0747	0.1002	0.0354	0.0298	0.0586	0.2513	0.0322	0.0915
Fe	0.1015	0.1772	0.0684	0.1498	0.1211	0.2492	0.0547	0.1000

Following to results in Table 8 we remark that the local electrophilic Fukui functions of (C7,C8) and (C1,C2) atoms in isolated fragments are greater to about twice than those dienophile and diene in the linked fragments of intra-molecule as: f_k^+ of dienophile in isolated fragment (IF) $\approx 2f_k^+$ of dienophile in the linked fragments of intra-molecule and f_k^+ of diene in isolated fragment (IF) $\approx 2f_k^+$ of diene in the linked fragments of intra-molecule as (f_{c1}^+ (Dp_{IF}) $\approx 2f_{c1}^+$ (Dp_{LF}), f_{c4}^+ (Dp_{IF}) $\approx 2f_{c4}^+$ (Dp_{LF}), f_{c7}^+ (Dp_{IF}) $\approx 2f_{c7}^+$ (Dp_{LF}) and f_{c8}^+ (Dp_{IF}) $\approx 2f_{c8}^+$ (Dp_{LF})). Thereby, the electrophilicity character of linked fragment in the intra-molecule is reduced almost twice than that in isolated fragment (IF), this remark can be explained that into triene amide molecule a dienophile fragment has a bond contains two π electron and a diene fragment has a conjugates and unsaturated bond of four π electrons attached by a binding chains ($4\pi(\text{diene})+2\pi(\text{dienophile})$) in which decrease the high electrophilicity. Subsequently following these results the binding chain play a role of charge transfer between fragments and has an insufficient contribution in the electrophilicity and nucleophilicity of triene amide molecule.

3.3. Regional nucleophilic and electrophilic descriptors of Fukui functions quantities

To make into account the consequences established in above we thought to calculate the regional nucleophilic and electrophilic Fukui functions of linked fragments in the intra-molecules (LF) as well to those fragments in the isolated fragment (IF), the results are given in Table 9.

Table 9. Regional of nucleophilic and electrophilic Fukui functions

Entry	$\sum f_k^-(D)$		$\sum f_k^+(D)$		$\sum f_k^-(Dp)$		$\sum f_k^+(Dp)$	
	F(IS)	F(LF)	F(IS)	F(LF)	F(IS)	F(LF)	F(IS)	F(LF)
Fa(3c+Bc)	0.9679	0.9042	0.9799	0.5447	0.9570	0.0958	0.9689	0.4553
g(3b+Bc)	0.9679	0.9042	0.9799	0.5447	0.9506	0.0905	0.9385	0.4437
Fc(4a+Bc)	0.9679	0.9042	0.9799	0.5447	0.9214	0.0966	0.9245	0.4459
Fd(4k+Ca)	0.9653	0.8228	0.9771	0.7081	0.9550	0.1772	0.9527	0.2919
Fe(5a+Bd)	0.9635	0.9320	1.0594	0.5300	0.9266	0.0769	0.9341	0.4699

Next to results in Table 9, we have confirmed the same finding discussed earlier in which stipulates that the dienes and dienophiles fragments in the isolated fragment are retained their initial characters (attractor and/or donor) in compared to those fragments in the linked fragment of intra-molecule (LF). Consequently, the dienes and dienophiles in the independent fragments are preserved completely their nucleophilic Fukui functions as $\sum f_k^-(D_{IF}) \approx \sum f_k^-(D_{LF})$ and lost almost half in their electrophilic Fukui functions as $\sum f_k^+(D_{pIF}) \approx 2 \sum f_k^+(D_{pLF})$ compared than those linked fragments

in the intra-molecule respectively. It is important to note that in case of electrophilic Fukui functions, diene and dienophile have a great values, additionally the diene fragment has a major nucleophilicity so this is anomaly of IMDA reaction, such as in DA reaction both fragments must be a different character and diene cannot has two different characters in same time, as a result the diene is nucleophile (donor) per consequent the dienophile is electrophile (attractor). However, all atoms belonging to the diene and dienophiles fragments in both cases have been verified the observed characteristics such as: For nucleophilic characters of diene fragment:

$$\sum_{k \in FD(IF)} f_k^- \approx \sum_{k \in FD(LF)} f_k^- ; \quad k = 1, 2, \dots, n.$$

Such as $f_1^- + f_2^- + \dots + f_n^- = f_1^- + f_2^- + \dots + f_n^-$

and $f_1^- = f_1^-; f_2^- = f_2^-$ then $f_n^- = f_n^-$

Consequently: $f_k^- (k \in FD(IF)) = f_k^- (k \in FD(LF))$

Consequently, the binding chain did not influence widely the nucleophilic characters of the diene fragment within the triene amide molecule.

- For electrophilic characters of dienophile fragment:

$$\sum_{k \in FDP(IF)} f_k^+ \approx 2 \sum_{k \in FDP(LF)} f_k^+ \quad k = 1, 2, \dots, n.$$

$$f_1^+ + f_2^+ + \dots + f_n^+ = 2(f_1^+ + f_2^+ + \dots + f_n^+)$$

$$f_1^+ + f_2^+ + \dots + f_n^+ = 2f_1^+ + 2f_2^+ + \dots + 2f_n^+$$

$$f_1^+ = 2f_1^+; f_2^+ = 2f_2^+ \text{ and } f_n^+ = 2f_n^+$$

f_k^+ of linked fragment in the intra-molecule = $1/2 f_k^+$ of isolated fragment

f_k^+ of dienophile in the isolated fragment (IS) $\approx 2f_k^+$ of dienophile in the linked fragment (LF).

Subsequently, following the above results the binding chain plays a role of charge and heat transfer and at the same time plays a perturbing role between fragments ($\mu_D \neq \mu_{DP}$). However, the binding chain didn't have sufficient electrophilic and nucleophilic characters contribution in the intra-molecule of triene-amide.

4. Conclusion

In this work, we have tried to assess the likely role of the binding chain in the triene amide molecule including in same time two fragments of diene and dienophile and a binding chain linked them, we are used in our study the local and regional electrophilic/and nucleophilic Fukui functions combined with a DFT theoretical methods, we have seen quantitatively in this study that these fragments preserve their physicochemical characters in the linked fragment of intra-molecule as in the isolated fragment. In addition we are found that the nucleophilicity of the diene has been unchanged in the linked fragment of intra-molecule than that in isolated fragment such as $f_k^- (k \in FD_{IF}) \approx f_k^- (k \in FD_{LF})$ as well the electrophilicity of dienophile is divided almost half in the linked fragment of intra-molecule than that in isolated fragment as $f_k^+ (k \in FDP_{IF}) \approx 2f_k^+ (k \in FDP_{LF})$. Therefore, the binding chain has a very little contribution of the physicochemical quantities of the triene amide molecule.

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