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Natural Bond Orbital Population Analysis of α -trans-himachalene.

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ABSTRACT

The molecular structure and the chemical reactivity descriptors of α -trans-himachalene was calculated by the B3LYP density functional model with 6-311G(d,p) basis set by Gaussian 09 program. The active sites for nucleophilic and electrophilic attacks have been chosen by relating them to the Fukui function indices and the dual descriptor. This descriptor is capable of simultaneously explaining the nucleophilicity and electrophilicity of the given atomic sites in the molecule. Sites of the six membered ring double bond are amenable to electrophilic attack, while the sites of the exocyclic double bond are susceptible of nucleophilic attack. The calculated descriptors are in agreement with the known experimental facts about the chemical reactivity of the α -trans-himachalene molecule presented in the literature.

Keywords: DFT; frontier molecular orbital theory; reactivity index; dual descriptor.

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INTRODUCTION

This work is the part of our ongoing program concerning the valorisation of essential oil of the Atlas Cedar *cedrus atlantica* [1-3]. It is one of the raw materials in perfume industry. This oil has been the object of various important studies which focused on the isolation, identification, and reactivity of its constituents [4–7]. The essential oil of the Atlas Cedar is primarily constituted (75%) of three sesquiterpenic bicyclic hydrocarbons: α -cis-himachalene, α -himachalene and γ -cis-himachalene. Its treatment with hydrochloric acid in acetic acid followed by a dehydrohalogenation in basic medium leads to the formation of α -trans-himachalene. The reactivity of these sesquiterpenes has been extensively studied [8, 9]. Indeed, our group has studied himachalenes reactivity (hemisynthesis) in order to obtain new compounds with interesting olfactory properties in perfumery [10, 11].

The objective of the present work is to investigate the nature of bonding in an α -trans-himachalene (Figure 1), by using natural bond orbital (NBO) analysis. We have shown that the results from NBO calculations can provide the detailed insight into the electronic structure of molecule.

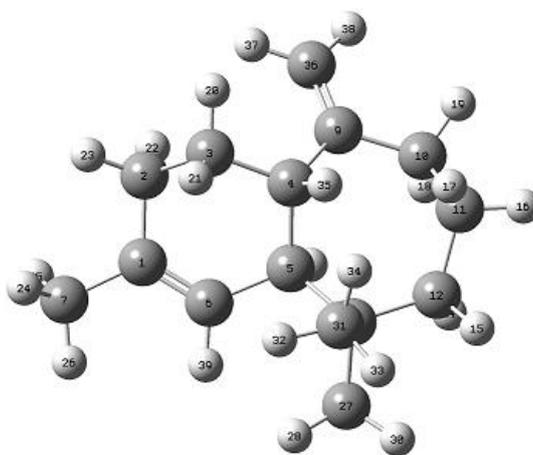


Fig 1: The optimized equilibrium structure of α -trans-himachalene

The knowledge of reactivity on a molecule is an essential concept; it is of a crucial interest because it allows understanding interactions that are operating during a reaction mechanism. In particular electrostatic interactions have been successfully explained by the use of the molecular electrostatic potential [12, 13].

On the other hand, there is no a unique tool to quantify and rationalize covalent interactions, however since 2005 a descriptor of local reactivity whose name is simply dual descriptor, [14,15] has allowed to rationalize reaction mechanisms in terms of overlapping nucleophilic regions with electrophilic regions in order to get a maximum stabilization thus leading to final products or intermediates; all those favorable nucleophilic–electrophilic interactions have been explained as a manifestation of the Principle of Maximum Hardness [16] in addition, chemical reactions have been understood in terms of the Hard and Soft Acids and Bases Principle [17,18], principle that has been used even with the aim of replacing the use of the Molecular Orbital Theory to understand the whole chemistry [19]. In fact the present work is a good chance to test the capability of the most recent reactivity descriptors coming from the Conceptual DFT [20-23].

Theory and computational details

Fukui Function (FF) [24-26] is one of the widely used local density functional descriptors to model chemical reactivity and site selectivity and is defined as the derivative of the electron density $\rho(r)$ with respect to the total number of electrons N in the system, at constant external potential $v(r)$ acting on an electron due to all the nuclei in the system

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)} \right)_N \quad (1)$$

The condensed FF is calculated using the procedure proposed by Yang and Mortier [27], based on a finite difference method.

$$f_k^+(N) = \rho_K(N+1) - \rho_K(N) \quad \text{for nucleophilic attack} \quad (2)$$

$$f_k^-(N) = \rho_K(N) - \rho_K(N-1) \quad \text{for electrophilic attack} \quad (3)$$

$$f_k^0(N) = \frac{1}{2}(\rho_K(N+1) - \rho_K(N-1)) \quad \text{for radical attack} \quad (4)$$

Where $\rho_K(N)$; $\rho_K(N-1)$ and $\rho_K(N+1)$ are the gross electronic populations of the site k in neutral, cationic, and anionic systems, respectively.

The condensed dual descriptor DD has been defined as $f^{(2)}(r) = \Delta f(r)$. In spite of having been discovered several years ago, a solid physical interpretation was not provided in such a moment [28]. They used the notation $\Delta f(r)$, but currently it has been replaced by the modern notation $f^{(2)}(r)$ in order to highlight that this is a Fukui function of second order. Its physical meaning is to reveal nucleophilic and electrophilic sites on a molecular system at the same time. Mathematically it is defined in terms of the derivative of the Fukui function, $f(r)$ [22], with respect to the number of electrons, N. The local reactivity descriptor (LRD) may be interpreted as the variation of η (the molecular hardness which measures the resistance to charge transfer) with respect to $v(r)$, the external potential. The definition of $f_k^{(2)}(r)$ is shown as indicated by Morell et al. [20, 29]:

$$f^{(2)}(r) = \left(\frac{\partial f(r)}{\partial N} \right)_{v(r)} = \left(\frac{\partial \eta}{\partial v(r)} \right)_N \quad (5)$$

As mentioned above, DD allows one to obtain simultaneously the preferably sites for nucleophilic attacks ($f^{(2)}(r) > 0$) and the preferably sites for electrophilic attacks ($f^{(2)}(r) < 0$) into the system at point r. DD has demonstrated to be a robust tool to predict specific sites of nucleophilic and electrophilic attacks in a much more efficient way than the Fukui function by itself because dual descriptor is able to distinguish those sites of true nucleophilic and electrophilic behavior, in consequence some works have been published with the aim of remarking the powerfulness of $f^{(2)}(r)$ and all those Local Reactivity Descriptors LRDs depending on DD [24,30-33].

The general working equation to obtain DD is given by the difference between nucleophilic and electrophilic Fukui function [30]. A well-known first level of approximation implies the use of finite difference method where to the sum of electronic densities of the system with one more electron and one less electron is subtracted by the double of the total electronic density of the original system. Since this level of approximation implies a time-demanding computing, a second level of approximation has been used for some years where the densities of FMOs provide an easier-to-compute working equation:

$$f^{(2)}(r) = f^+(r) - f^-(r) \cong \rho_L(r) - \rho_H(r) \quad (6)$$

Where densities of LUMO and HOMO are represented by $\rho_L(r)$ and $\rho_H(r)$, respectively.

Hence, when an interaction between two species is well described through the use of this LRD, it is said the reaction is controlled by frontier molecular orbitals (or frontier-controlled) under the assumption that remaining molecular orbitals do not participate during the reaction.

Settings and computational methods

The understanding of chemical reactivity and site selectivity of the molecular systems has been effectively handled by the conceptual density functional theory (DFT). Chemical potential, global hardness, global softness, electronegativity and electrophilicity are global reactivity descriptors, highly successful in predicting global chemical reactivity trends. The formal definitions of all these descriptors and working equations for their computation have been described. Various applications of both global and local reactivity descriptors in the context of chemical reactivity and site selectivity have been reviewed in detail.

Popular qualitative chemical concepts such as electronegativity (χ) [34] and hardness (η) [35,36] have been provided with rigorous definitions within the purview of conceptual DFT. Electronegativity is the negative of chemical potential defined [37] as follows for an N-electron system with total energy E and external potential $v(r)$,

$$\mu = -\chi = \left(\frac{\partial E}{\partial N} \right)_{v(r)} \quad (7)$$

Where (μ) is the Lagrange multiplier associated with the normalization constraint of DFT [38; 39] Hardness (η) is defined [40] as the corresponding second derivative,

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)} \right)_N \quad (8)$$

Using a finite difference method, working equations for the calculation of (μ) and (η) may be given as [35]:

$$\mu = -\left(\frac{I + A}{2} \right) \quad (9)$$

$$\eta = I - A \quad (10)$$

Where I and A are the ionization potential and electron affinity, respectively. If $\mathcal{E}_{\text{homo}}$ and $\mathcal{E}_{\text{lumo}}$ are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively, then the above equations can be rewritten [41], using Koopmans' theorem [42], as

$$\mu = \left(\frac{\mathcal{E}_{\text{homo}} + \mathcal{E}_{\text{lumo}}}{2} \right) \quad (11)$$

$$\eta = \mathcal{E}_{\text{lumo}} - \mathcal{E}_{\text{homo}} \quad (12)$$

In this work, (μ) and (η) are calculated using "Eqs. (12) and (13)". The electrophilicity index ω represents the stabilization energy of the systems when it gets saturated by electrons coming from the surrounding:

$$\omega = \left(\frac{\mu^2}{2\eta} \right) \quad (13)$$

This quantity can be considered as a measure of the electrophilic power of a system. All calculations were carried out with the Gaussian 09 package [43]. Geometry optimization was performed utilizing Becker's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [44]. The population analysis has also been performed by the natural bond orbital method [45] at B3LYP/6-311G(d,p) level of theory using natural bond orbital (NBO) program [46] under Gaussian 09 program package.

NBO analysis stresses the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. For each donor NBO(i) and acceptor NBO(j), the stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as

$$E^{(2)} = q_i \left(\frac{(F_{i,j})^2}{\epsilon_j - \epsilon_i} \right) \quad (14)$$

Where q_i is the orbital occupancy, ϵ_i and ϵ_j are diagonal elements and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

RESULTS AND DISCUSSION

Molecular geometry

The optimized molecular structure along with the numbering of atoms of α -trans-himachalene is as shown in Fig.1. The global minimum energy obtained by the DFT structure of α -trans-himachalene is -586.1680 u.a. The Distance matrix (angstroms) is presented in Table 1.

Table 1: Distance matrix in Å of α -trans-himachalene obtained by B3LYP/6-311G.**

	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₂₇	C ₃₁	C ₃₆
	0,00														
C ₁	0														
	1,50	0,00													
C ₂	9	0													
	2,48	1,53	0,00												
C ₃	4	0	0												
	2,97	2,57	1,53	0,00											
C ₄	5	6	9	0											
	2,53	2,96	2,61	1,58	0,00										
C ₅	4	9	2	0	0										
	1,33	2,46	2,79	2,58	1,51	0,00									
C ₆	6	4	9	5	5	0									
	1,50	2,57	3,80	4,47	3,92	2,49	0,00								
C ₇	5	5	5	5	3	4	0								
	4,05	3,42	2,59	1,51	2,54	3,71	5,52	0,00							
C ₉	3	4	0	8	6	9	4	0							
	5,14	4,80	3,95	2,57	3,03	4,47	6,60	1,52	0,00						
C ₁₀	2	2	9	0	7	1	9	5	0						
	5,53	5,44	4,40	2,91	3,10	4,61	6,99	2,60	1,54	0,00					
C ₁₁	2	1	9	7	4	3	0	7	1	0					
	5,08	5,41	4,63	3,15	2,56	3,92	6,41	3,37	2,60	1,54	0,00				
C ₁₂	6	9	1	8	8	0	1	9	0	0	0				
	3,82	4,41	3,81	2,62	1,57	2,59	5,05	3,48	3,37	2,69	1,55	0,00			
C ₁₃	7	9	3	3	1	3	6	2	3	3	7	0			

C ₂	4,28	5,26	5,01	3,98	2,56	2,95	5,18	4,78	4,57	3,92	2,46	1,54	0,00		
7	4	8	6	1	2	3	5	8	3	5	9	6	0		
C ₃	4,27	4,77	3,92	3,08	2,57	3,24	5,40	4,23	4,30	3,37	2,55	1,54	2,49	0,00	
1	2	6	3	2	9	5	8	8	9	1	1	2	1	0	
C ₃	4,52	3,55	2,96	2,52	3,64	4,53	5,87	1,33	2,47	3,79	4,68	4,76	6,01	5,49	0,00
6	6	1	5	8	2	7	8	4	7	7	3	9	0	3	0

Electronic Properties

Quantum chemical methods are important to obtain information about molecular structure and electrochemical behaviour. According to Figure. 2, the HOMO orbital is localized mainly on the most substituted double bond whereas LUMO orbital is localized mainly on the exocyclic double bond.

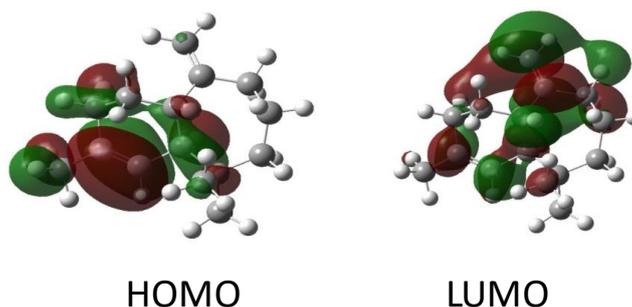


Fig 2: Isodensity representation of HOMO and LUMO orbitals for the most stable conformer of α -trans-himachalene.

Figure 3 shows the results of the frontier molecular orbitals (FMO) analysis calculated for molecule α -trans-himachalene with B3LYP/6-311G**. The calculated values are -6.5593 , -6.2801 , 0.4057 , 0.5635 and 6.6858 eV for $E_{\text{HOMO}-1}$, E_{HOMO} , E_{LUMO} , $E_{\text{LUMO}+1}$ and the HOMO–LUMO gap (ΔE), respectively. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. The HOMO–LUMO gap (ΔE), is 6.6858 eV and such a large energy gap implies high stability for the molecule [45, 47, 48]

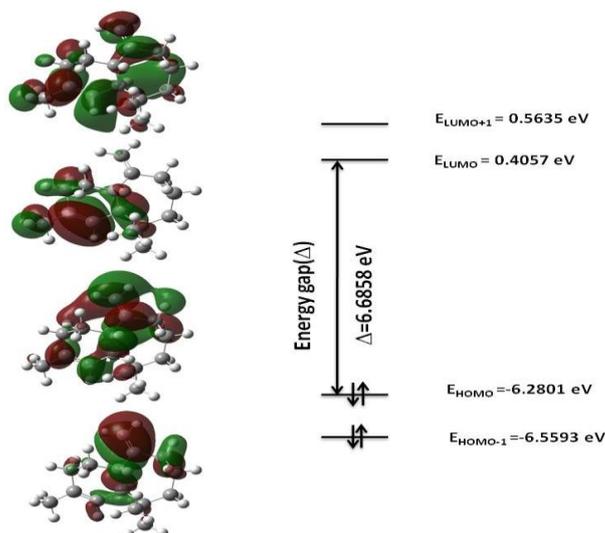


Fig 3: Calculated Frontier molecular orbitals of α -trans-himachalene (Δ : energy gap between LUMO and HOMO - B3LYP/6-311G**).

Fukui functions

DFT is one of the important tools of quantum chemistry to understand popular chemical concepts such as electronegativity, electron affinity, chemical potential, and ionization potential. In order to solve the

negative Fukui function problem, different attempts have been made by various groups [49]. Kolandaivel et al. [50] introduced the atomic descriptor to determine the local reactive sites of the molecular system. In the present study, the optimized molecular geometry was utilized in single-point energy calculations, which have been performed at the DFT for the anions and cations of the title compound using the ground state with doublet multiplicity. The individual atomic charges calculated by natural population analysis (NPA) have been used to calculate the Fukui function.

Table 2: Condensed Fukui functions FF and Descriptor Dual DD calculated by B3LYP/ 6-311G**

Atoms	The FF and DD calculated by B3LYP/6-311G** from the NPA			
	f^+	f^-	f°	$f^{(2)}$
C ₁	0,1004	0,1808	0,1406	-0,0804
C ₂	-0,0095	-0,0317	-0,0206	0,0221
C ₃	-0,0078	-0,0034	-0,0056	-0,0044
C ₄	-0,0103	-0,0176	-0,0139	0,0073
C ₅	-0,0019	-0,0269	-0,0144	0,0251
C ₆	0,1245	0,1671	0,1458	-0,0426
C ₇	-0,0096	-0,0392	-0,0244	0,0296
C ₉	0,0935	0,0612	0,0773	0,0324
C ₁₀	-0,0149	-0,0138	-0,0143	-0,0011
C ₁₁	-0,0046	-0,0047	-0,0046	0,0000
C ₁₂	0,0042	-0,0165	-0,0061	0,0207
C ₁₃	-0,0089	0,0191	0,0051	-0,0280
C ₂₇	-0,0036	-0,0103	-0,0069	0,0067
C ₃₁	0,0074	0,0022	0,0048	0,0052
C ₃₆	0,1484	0,1214	0,1349	0,0271

The electrophilic f_k^+ and nucleophilic f_k^- condensed Fukui functions and $f_k^{(2)}$ over the atoms of the α -trans-himachalene molecule calculated with the B3LYP/ 6-311G** basis set are shown in Table 2. It can be concluded from the analysis of the results on Table.2 that the B3LYP/6-311G** method for NPA derived charges display a large negative value of the condensed dual descriptor $f_k^{(2)}$ over the most substituted double bond C₁ and C₆, implying that this will be the preferred sites for the electrophilic attack. While, the exocyclic double bond C₉ and C₃₆ atom will be the preferred sites for nucleophilic attack.

NBO Analysis

Natural bond orbital analysis is an important method for studying intra- and inter-molecular bonding and interaction between bonds. The results of natural bond orbital (NBO) analysis and the polarization coefficient values of atoms for molecule α -trans-himachalene are listed in Table 3. The σ (C₁-C₆) bond is formed from an SP^{1.61} hybrid on C₁(s(38.22%) p(61.73%) d(0.04%)) and an SP^{1.49} on C₆ s(40.13%) p(59.83%) d(0.04%). The polarization coefficients of C₁ = 0,707 and C₆ = 0,708 suggest that C₆ is relatively more electron-rich than the C₁ atom. The calculated natural charge (NBO) of the C₁ atom is positive (0.018^e) whereas C₆ has a negative value (-0.215^e). The bonding orbital for the C₉-C₃₆ bond is $\sigma = 0,713$ SP^{1.62} + 0,701 SP^{1.38}. The calculated natural charge (NBO) of the C₉ atom is positive (0.027^e) whereas C₃₆ has a negative value (-0.406^e). In C-H bonds, the hydrogen atoms have almost 0% of p character. On contrary, almost 100% p-character was observed in both the atoms of all the π bonding and antibonding. The π (C₁-C₆) bond is $\pi = 0,697$ SP^{99.99} + 0,717 SP^{99.99} and The π (C₉-C₃₆) bond is $\pi = 0,689$ SP¹⁰⁰ + 0,725 SP¹⁰⁰.

Table 3: Occupancy, energy, polarization coefficient and hybrid for α -trans-himachalene

σ and π bonding (C _A -C _B)	Occupancy	Energy (u.a)	Polarization coefficient of atom A	Hybrid of atom A	Polarization coefficient of atom B	Hybrid of atom B
σ (C ₁ -C ₂)	1,970	-0,600	0,703	SP ^{2,28}	0,711	SP ^{2,41}
σ (C ₁ -C ₆)	1,977	-0,716	0,707	SP ^{1,61}	0,708	SP ^{1,49}
π (C ₁ -C ₆)	1,936	-0,254	0,697	SP ^{99,99}	0,717	SP ^{99,99}
σ (C ₁ -C ₇)	1,977	-0,615	0,706	SP ^{2,23}	0,708	SP ^{2,12}
σ (C ₂ -C ₃)	1,977	-0,585	0,710	SP ^{2,58}	0,704	SP ^{2,58}
σ (C ₃ -C ₄)	1,976	-0,583	0,701	SP ^{2,46}	0,713	SP ^{2,65}
σ (C ₄ -C ₅)	1,958	-0,555	0,707	SP ^{2,89}	0,707	SP ^{2,85}
σ (C ₄ -C ₉)	1,966	-0,599	0,713	SP ^{2,59}	0,701	SP ^{2,14}
σ (C ₅ -C ₆)	1,971	-0,597	0,716	SP ^{2,64}	0,699	SP ^{2,03}
σ (C ₅ -C ₁₃)	1,959	-0,567	0,711	SP ^{2,59}	0,703	SP ^{2,84}
σ (C ₉ -C ₁₀)	1,971	-0,598	0,704	SP ^{2,35}	0,710	SP ^{2,35}
σ (C ₉ -C ₃₆)	1,982	-0,729	0,713	SP ^{1,62}	0,701	SP ^{1,38}
π (C ₉ -C ₃₆)	1,966	-0,257	0,689	SP ¹⁰⁰	0,725	SP ¹⁰⁰
σ (C ₁₀ -C ₁₁)	1,980	-0,588	0,709	SP ^{2,52}	0,705	SP ^{2,53}
σ (C ₁₁ -C ₁₂)	1,982	-0,591	0,706	SP ^{2,46}	0,708	SP ^{2,50}
σ (C ₁₂ -C ₁₃)	1,965	-0,576	0,706	SP ^{2,28}	0,708	SP ^{2,99}
σ (C ₁₃ -C ₂₇)	1,966	-0,583	0,710	SP ^{3,16}	0,704	SP ^{2,13}
σ (C ₁₃ -C ₃₁)	1,971	-0,587	0,708	SP ^{3,02}	0,706	SP ^{2,13}

Another useful aspect of NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and inter molecular interactions. The second order Fock matrix is carried out to evaluate the donor-acceptor interactions in the NBO analysis.

Table 4 lists the selected values of the calculated second order interaction energy $E^{(2)}$ between donor-acceptor orbitals in α -trans-himachalene. According to the results of the NBO analysis for molecule α -trans-himachalene, the π (C₁-C₆) participates as donor and the anti-bonding σ^* (C₂-C₃) and σ^* (C₅-C₁₃) orbital act as acceptor, while, the π (C₉-C₃₆) participates as donor and the anti-bonding σ^* (C₄-C₅) and σ^* (C₁₀-C₁₁) orbital act as acceptor. The stabilization energies $E^{(2)}$ for the transfer of electron density are 0,69 ; 1,51 ; 2,65 and 0,78, respectively. These values indicate small charge transfer from the bonding orbital for π (C₁-C₆) to the anti-bonding orbital for σ^* (C₂-C₃) and σ^* (C₅-C₁₃) and from π (C₉-C₃₆) to σ^* (C₄-C₅) and σ^* (C₁₀-C₁₁).

Table 4: Second order perturbation theory analysis of fock matrix in NBO basis

Donor(i)	ED(i)	Acceptor (j)	ED (j)	$E^{(2)a}$ (Kj/mol)	$E(j)-E(i)^b$ (a.u)	$F(i,j)^c$ (a.u)
σ (C ₁ -C ₆)	1.9767	σ^* (C ₁ -C ₂)	0.0296	3,16	1,16	0,054
		σ^* (C ₁ -C ₇)	0.0194	3,07	1,16	0,053
		σ^* (C ₅ -C ₆)	0.0236	3,74	1,16	0,059
		σ^* (C ₅ -C ₁₃)	0.0398	1,12	1,09	0,031
π (C ₁ -C ₆)	1.9365	σ^* (C ₂ -C ₃)	0.0149	0,69	0,65	0,019
		σ^* (C ₅ -C ₁₃)	0.0398	1,51	0,63	0,028
σ (C ₁ -C ₇)	1.9769	σ^* (C ₁ -C ₆)	0.0223	3,88	1,32	0,064
		σ^* (C ₅ -C ₆)	0.0236	4,63	1,06	0,063
σ (C ₂ -C ₃)	1.9768	Π^* (C ₁ -C ₆)	0.0921	0,98	0,67	0,023
σ (C ₄ -C ₅)	1.9581	σ^* (C ₉ -C ₃₆)	0.0162	1,91	1,24	0,044
		Π^* (C ₉ -C ₃₆)	0.0624	2,24	0,62	0,034
σ (C ₄ -C ₉)	1.9665	σ^* (C ₉ -C ₃₆)	0.0162	3,61	1,28	0,061
σ (C ₅ -C ₆)	1.9711	σ^* (C ₁ -C ₇)	0.0194	4,55	1,04	0,061
		σ^* (C ₁ -C ₆)	0.0223	4,43	1,30	0,068

$\sigma(C_5-C_{13})$	1.9590	$\sigma^*(C_1-C_6)$	0.0223	1,67	1,27	0,041
		$\Pi^*(C_1-C_6)$	0.0921	0,60	0,65	0,018
$\sigma(C_9-C_{10})$	1.9710	$\sigma^*(C_9-C_{36})$	0.0162	2,81	1,28	0,054
		$\sigma^*(C_4-C_5)$	0.0338	0,81	1,09	0,027
$\sigma(C_9-C_{36})$	1.9661	$\sigma^*(C_4-C_9)$	0.0364	3,69	1,18	0,059
		$\sigma^*(C_9-C_{10})$	0.0228	2,77	1,16	0,051
		$\sigma^*(C_{10}-C_{11})$	0.0156	1,27	1,12	0,034
		$\sigma^*(C_4-C_5)$	0.0338	2,65	0,62	0,036
$\pi(C_9-C_{36})$	1.9661	$\sigma^*(C_{10}-C_{11})$	0.0156	0,78	0,65	0,020
		$\sigma^*(C_9-C_{36})$	0.162	2,39	1,27	0,049
$\sigma(C_{10}-C_{11})$	1.9802					

^aE⁽²⁾ means energy of hyper conjugative interactions

^bEnergy difference between donor and acceptor i and j NBO orbitals

^cF(i,j) is the Fock matrix element between i and j NBO orbitals

CONCLUSION

Based on a combined study of DFT with NBO method and from the whole of the results presented in this contribution it has been clearly demonstrated that the sites of interaction of the α -trans-himachalene molecule can be predicted by using DFT-based reactivity descriptors such as the hardness, Fukui function, and descriptor dual calculations. These descriptors were used in the characterization and successfully description of the preferred reactive sites and provide a firm explanation for the reactivity of the α -trans-himachalene molecule.

The Natural Bond Orbital (NBO) analysis has provided the detailed insight into the type of hybridization and the nature of bonding in α -trans-himachalene. Analysis of the polarization coefficients suggests that C₆ and C₃₆ are relatively more electron-rich than the C₁ and C₉ respectively. The HOMO–LUMO measured energy gap (ΔE) for α -trans-himachalene was 6.6858 eV.

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