ESKİŞEHİR TECHNICAL UNIVERSITY JOURNAL OF SCIENCE AND TECHNOLOGY
A- APPLIED SCIENCES AND ENGINEERING

`2020, Vol: 21, pp. 55-62, DOI: 10.18038/estubtda.820129`

THEORETICAL ANALYSIS OF THE STRUCTURE OF CHIRAL JASMONIC ACID

Nihal KUŞ

Department of Physics, Science Faculty, Eskisehir Technical University, 26470, Eskisehir, Turkey

ABSTRACT

Jasmonic acid, also known as jasmonates, (JA), a molecule formed by the oxygenation of fatty acids, is an organic compound and is found in many plants, especially jasmine. The conformation of this compound is found according to the location in the chiral centers. In this study, the molecular structure of JA (labeled C-4 and C-5 in this study) which has two chiral centers was investigated by DFT and TD-DFT methods. These structures have been found to have RR, RS and SS configurations relative to their chiral centers. Each configuration has *cis* and *trans* conformations depending on the orientation of the chain groups attached to the five atom ring. The minimum energies of each conformation were calculated with DFT/B3LYP/6-311++G(d,p) method and the structures of their stable form were drawn. JA_RR_*trans* conformer was found most stable than the other conformers. Excited state energies were calculated using TD-DFT calculations and also HOMO-LUMO energy gaps were found for all chiral conformers.

Keywords: Jasmonic acid, B3LYP, DFT/ TD-DFT, HOMO-LUMO energy

1. INTRODUCTION

Jasmonic acid (also known as jasmonates -JA), which plays an important role in the regular ripening of fruits, was obtained for the first time from mushroom culture [1]. Jasmonic and methyl jasmonic acid derived from fatty acid synthesized from linolenic acid found in chloroplast membrane [2-4] Gao et al., 2011; Jalalpour et al., 2014). JA plays an effective role such as fruit ripening and aging, sex determination, root elongation, fertility, biotic and abiotic stress tolerance. It also has systemically acquired resistance to healing plant wounds and insect attack. [5-9]. Biosynthetic studies of JA were first described by Vick and Zimmerman [10]. The importance of the centers within responses of chiral-centered JA in plants were studied by Holbrook et al [11]. In our previous study the infrared spectrum of the RS structure of allantoin was studied [12]. It has also chiral center and can exist in R- and S-enantiomeric forms like JA being studied now

In this study, *cis* and *trans* conformations of JA molecule of RR, RS and SS forms were studied by DFT, TD-DFT and NBO methods. For each of the conformations with optimized energies, the interactions between donor and orbitals were examined and the excited state energies were calculated. HOMO-LUMO energy ranges and electrostatic potential regions were determined by calculating B3LYP++G(d,p) level.

2. COMPUTATIONAL METHODS

Calculations have been made using the fundamental laws of quantum mechanics using the computer program Gaussian 09 [13]. Equilibrium geometries at minimum energy of the studied molecule were optimized with DFT approach using the 6-311++G(d,p) fundamental set [14] and the B3LYP function created by Becke, Lee, Yang and Parr [15,16]. Orbital interactions were analyzed by the NBO method.

---

*Corresponding Author: nkus@eskisehir.edu.tr
Received: 30.10.2020 Published: 27.11.2020

Using NBO 3.1 in Gaussian 09 program [17]. Time dependent density functional theory (TD-DFT) was used to obtain low energy excited transitions [18] and also HOMO-LUMO energy gaps were found. In addition, the distribution of electrostatic potential energies was obtained and mapped.

3. RESULTS AND DISCUSSIONS

The 5 carbons of the JA molecule, which has 12 carbon atoms, are in the ring structure. Others are in the chains attached from the 4 and 5 carbons numbered in our study. These chains have 2 different positions depending on the orientation of the chain groups attached to the five atom ring which named *cis* and *trans* for RR, RS and SS forms and shown in. Figure 1 a, b and c.

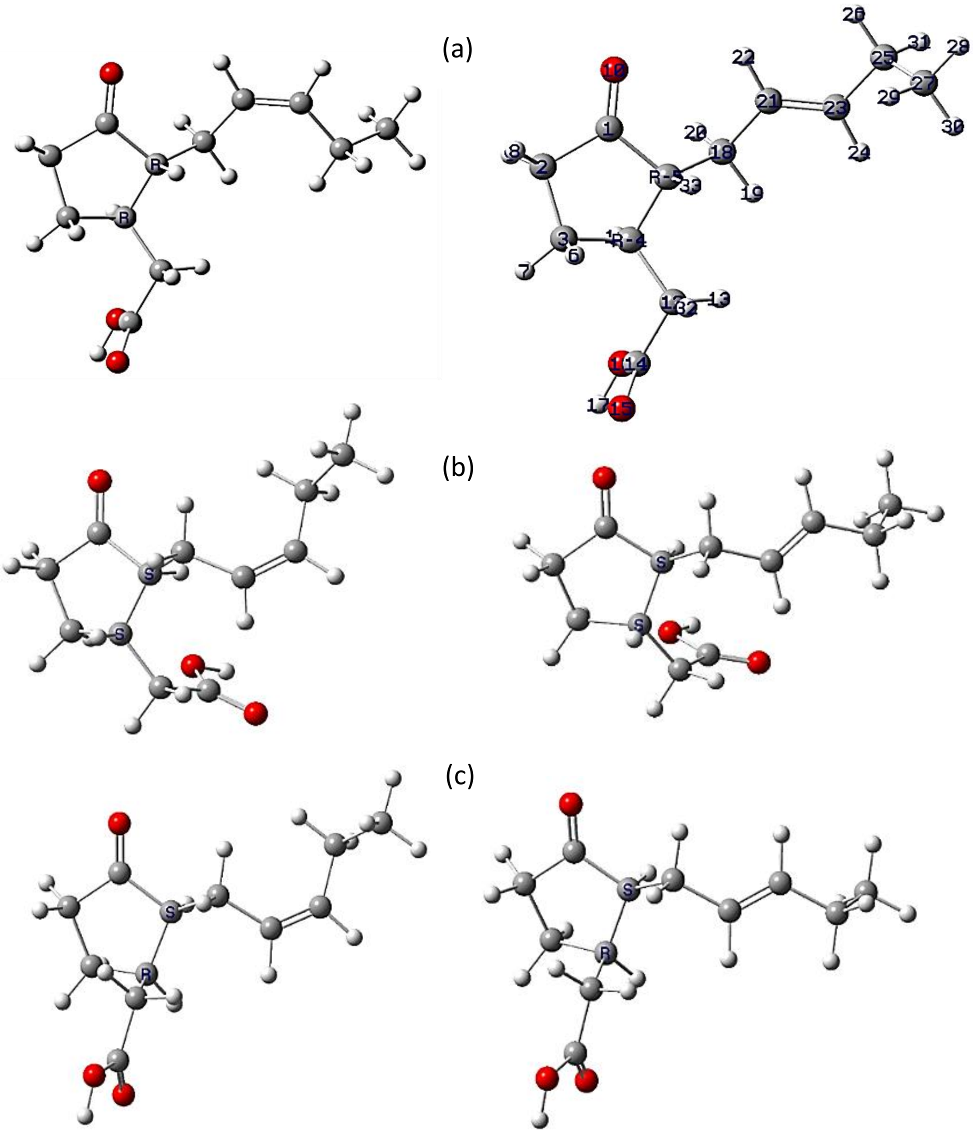
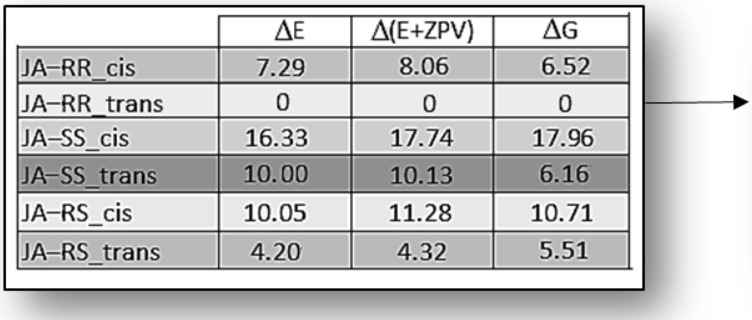


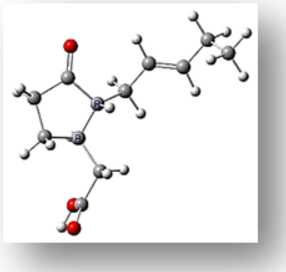
Figure 1. *Cis* and *trans* conformers of RR (a), SS (b), RS (c) isomers of JA calculated by B3LYP(6-311)++G(d,p) level with adopted number .

As can be seen from Table 1, while the RR_*trans* form was calculated in the most stable structure, the SS_*cis* was with the highest relative energy.

Table 1. ΔE(RB3LYP), Δ(E+ZPV) and relative Gibbs (ΔG) energies of JA conformers calculated as kJ mol^{-1}.



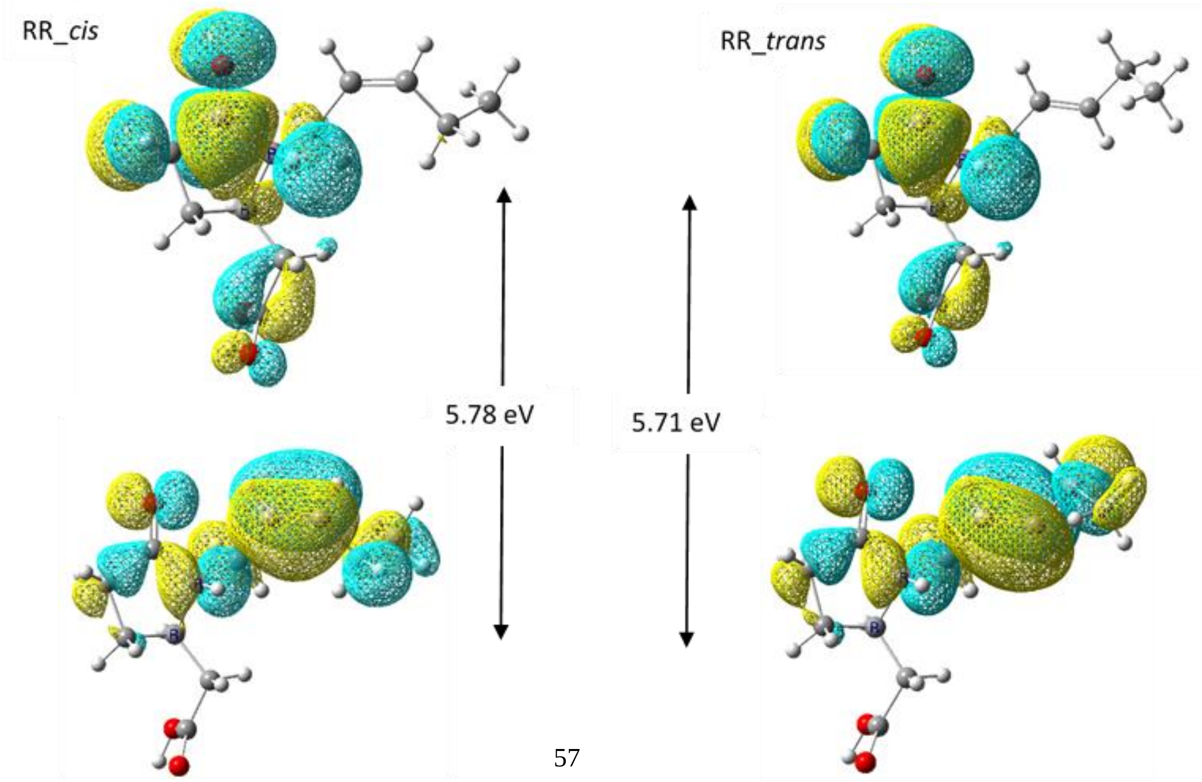
	ΔE	Δ(E+ZPV)	ΔG
JA–RR_cis	7.29	8.06	6.52
JA–RR_trans	0	0	0
JA–SS_cis	16.33	17.74	17.96
JA–SS_trans	10.00	10.13	6.16
JA–RS_cis	10.05	11.28	10.71
JA–RS_trans	4.20	4.32	5.51



The energy difference between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) for JA conformers were drawn in Figure 2. The HOMO−LUMO relative energy for the RR_*trans* conformation was calculated as 5.71 eV, while the RS_*trans* with the highest relative energy was 5.60 eV. As shown in Figure 2, depending on the orbital locations, there is a little change in the difference between the HOMO and LUMO energy values of the molecule.

While LUMO orbitals were observed in 5 rings of the molecule, HOMO orbitals were found to be related to the R and S forms of the molecule.

LUMO orbitals were found to be associated with the R and S forms of the molecule, and the orbital density was concentrated on the C=C double bond in the chain group attached to the ring.



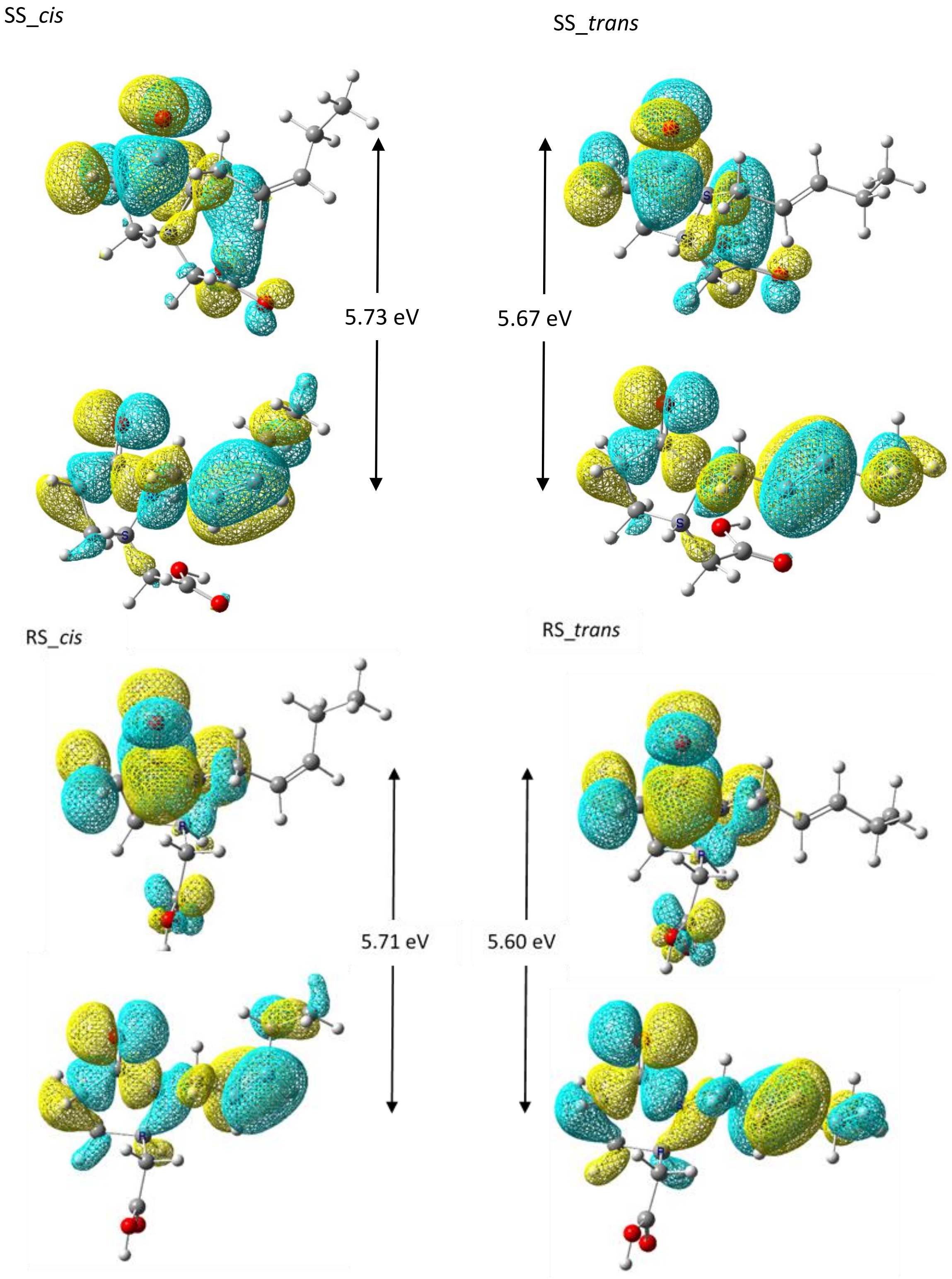


Figure 2. Calculated HOMO and LUMO orbitals for JA_RR_*cis* and *trans*, JA_SS_*cis* and *trans* and JA_RS_*cis* and *trans* conformers using B3LYP/6-311++G(d,p)

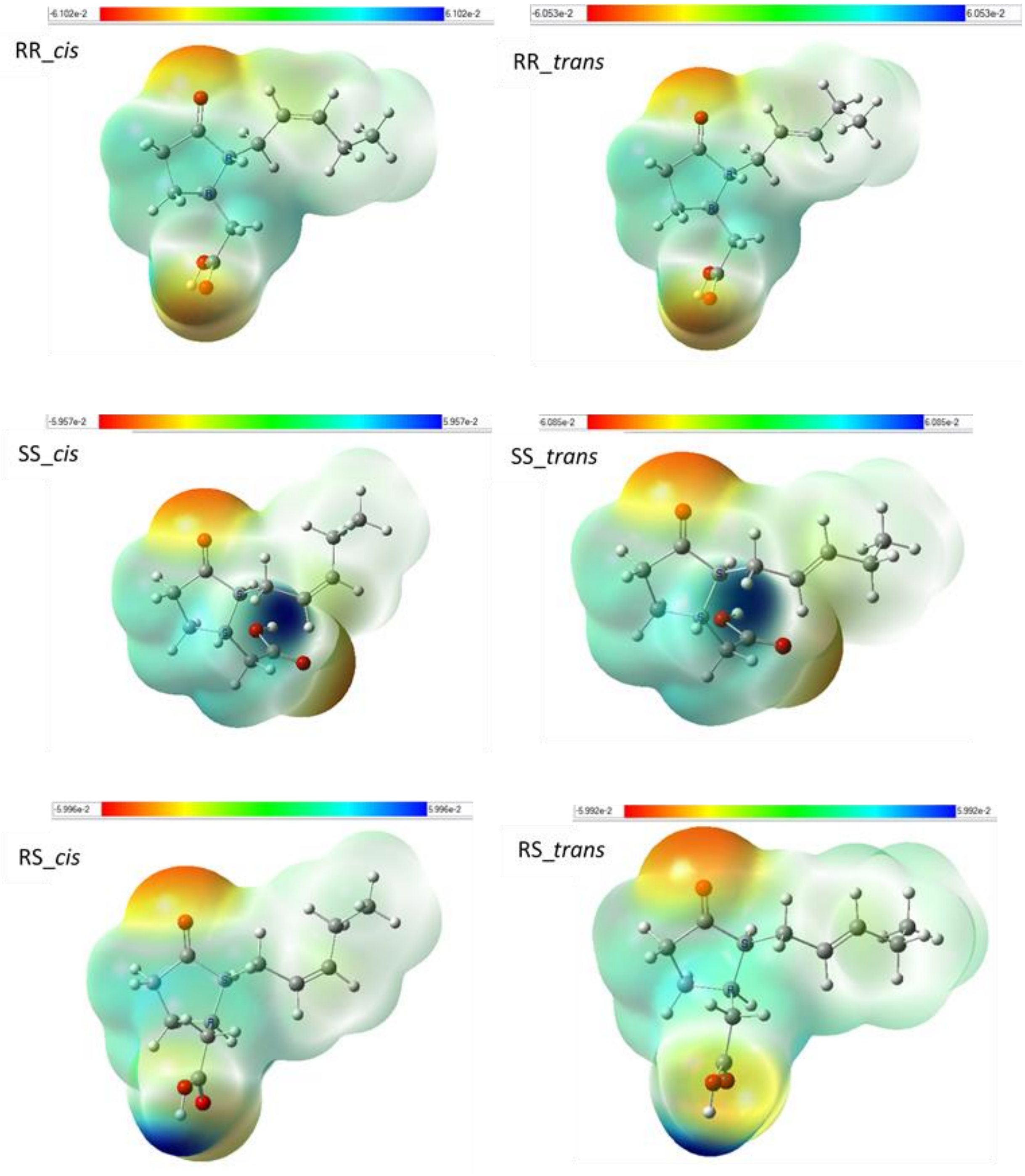


Figure 3. MEP surface for JA conformers calculated using B3LYP/6-311++G(d,p) level.

Surface map of Molecular Electrostatic Potential (MEP) of JA conformers was drawn using Gauss View, and given in Figure 3. The map visualizes charge regions of the molecule. In scale bar, the red and blue colors indicate negative and positive values, respectively. The map of JA showed that the negative electrostatic potentials (red region, electrophilic attack) were intensified around the oxygen which double bonded to chlorine atom.

Table 2. Excited state, excited energy (*E*), wavelength of the vertical absorption (λ), oscillator strength (*f*) and orbital type calculated by the TD-DFT method of JA conformers

	State	*E (eV)*	λ *(nm)*	*f*	*type*
RR_*cis*	S_6	5.8072	213.5	0.0298	HOMO → LUMO+2
RR_*trans*	S_5	5.7953	213.94	0.0083	HOMO-1 → LUMO+1
SS_*cis*	S_3	5.4612	227.03	0.0276	HOMO-1 → -LUMO+1
SS_*trans*	S_3	5.4346	228.14	0.0234	HOMO → -LUMO+1
RS_*cis*	S_4	5.7208	216.73	0.0221	HOMO → LUMO+2
RS_*trans*	S_6	5.8056	213.56	0.0182	HOMO-1 → LUMO+1

The values with high excited energies were found in RR_*cis* (5.8072 eV), RS_*trans* (5.8056 eV) and RR_*trans* (5.7953 eV) forms. The molecule is excited with an efficient energy in the highest state from the ground state and exhibits a significant oscillator strength (Table 2). The load transfer of the RR_*cis* form, which is the highest oscillator strength (0.0298), was found as the transition from HOMO to LUMO+2 level. In this case, it can be considered that the possibility of Transition is higher.

Interaction energies between orbitals, *E(2)*, donor-acceptor NBOs are determined based on the "Second Order Perturbation" theory [17]. In the formula (Eq.1), Fij is the matrix element between the i and j NBO orbitals, qi is the occupancy of the donating orbital, εi and εj are the energies of the acceptor and donor NBOs.

$$E(2) = \Delta E_{ij} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i} \tag{1}$$

As seen in Table 3, for most stable conformer (RR_*trans*), all donors participating in the interaction were lone pairs and the most significant NBO interaction was LP(2)O16→π*(C14–O15). Donor-acceptor orbital interaction energy was calculated about 43.1 kcal mol^{-1} (Figure 4). This interaction can be considered as the main orbital interaction. Stabilization energies were calculated considering values higher than 10%.

Table 3. Donor and acceptor pairs and orbital energies for NBO pairs as calculated by the Fock matrix equation (Equation 1) in the NBO basis for JA_RR_*trans* (atom numbers are given in Figure 1).

Donor NBO *(i)*	Acceptor NBO *(j)*	*E(2)* kcal mol^{-1}	ε_j- ε_i au	F_{ij} au
LP(2)O16	π*(C14 – O15)	43.07	0.35	0.110
LP(2)O15	π*(C14 – O16)	34.22	0.61	0.130
LP(2)O10	π*(C1 – C2)	21.70	0.65	0.107
LP(2)O10	π*(C1 – C5)	21.16	0.65	0.106
LP(1)O10	RY*(1)C1	17.87	1.51	0.147
LP(1)O15	RY*(1)C14	17.49	1.69	0.153
LP(2)O15	π*(C12 – C14)	17.20	0.65	0.097

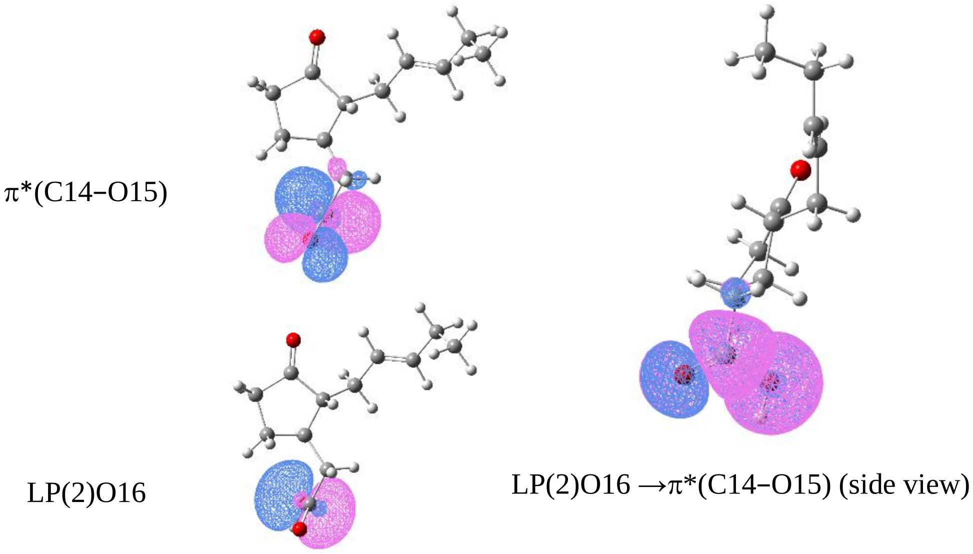


Figure 4. LP(2)O16 →π*(C14−O15) donor-acceptor orbitals interactions for JA_RR_*trans* calculated using NBO method (atom numbers are given in Figure 1).

4. CONCLUSIONS

Optimized energies of the conformation of the RR, RS and SS forms in the chiral state of the JA molecule were found using DFT method with B3LYP/6-311++G(d,p) level. It was calculated that the RR_*trans* form was at the lowest energy and the most stable conformer compared to other conformations. The highest transition energy gap HOMO−LUMO range was found in RR_*cis* form and its value was 5.78 eV. It was seen from the electrostatic potential calculations and drawings that all the conformations have the highest attraction around oxygen bonded to hydrogen by double bond. Excited energy states were determined using TD-DFT calculations and the highest transition energy was calculated as approximately 5.81 eV at RR_*cis* with HOMO→LUMO+2 transition. From the results of NBO calculations, it was found that the donor acceptor interaction with the highest stabilization energy was the interaction of LP (2) O16 →π*(C14−O15) orbitals about 43 kcal mol^{-1}.

REFERENCES

[1] Tsukada K, Takahashi K and Nabeta K. Biosynthesis of jasmonic acid in a plant pathogenic fungus, Lasiodiplodia theobromae. Phytochemistry 2010; 71, 2019–2023.

[2] Kupper FC, Gaquerel E, Cosse A, Adas F, Peters AF, Muller DG et al. Free fatty acids and methyl jasmonate trigger defense reactions in Laminaria digitata. Plant Cell Physiol. 2009; 50, 789–800.

[3] Gao QM, Venugopal S, Navarre D and Kachroo A. Low oleic acid derived repression of jasmonic acid-inducible defense responses requires the WRKY50 and WRKY51 proteins. Plant Physiol. 2011; 155, 464–476.

[4] Jalalpour Z, Shabani L, Afghani L, Sharifi-Tehrani M and Amini S. Stimulatory effect of methyl jasmonate and squalestatin on phenolic metabolism through induction of LOX activity in cell suspension culture of yew. Turk. J. Biol. 2014; 38, 76–82.

[5] Browse J. Jasmonate: preventing the maize tassel from getting in touch with his feminine side. Sci. Signal. 2009; 2, 59, pe9.

[6] Moreno JE, Tao Y, Chory J and Ballare CL. Ecological modulation of plant defense via phytochrome control of jasmonates sensitivity. Proc. Natl. Acad. Sci. U.S.A. 2009; 106, 4935–4940.

[7] Wang J, Song L, Gong X, Xu J and Li M. Functions of Jasmonic Acid in Plant Regulation and Response to Abiotic Stress. Int. J. Mol. Sci. 2020; 21, 1446 (1-17).

[8] Cipollini D. Constitutive expression of methyl jasmonates inducible responses delays reproduction and constrains fitness responses to nutrients in Arabidopsis thaliana. Evol. Ecol. 2010; 24, 59–68.

[9] Nafie E, Hathout T, Al Shyma Al Mokadem. Jasmonic acid elicits oxidative defense and detoxification systems in Cucumis melo L. cells. Braz. J. Plant Physiol. 2011; 23, 161–174.

[10] Vick BA and Zimmerman DC. Biosynthesis of jasmonic acid by several plant species. Plant Physiol. 1984; 75, 458–461.

[11] Holbrook L, Tung P, Ward K, Reid DM, Abrams S, Lamb N, Wilson QJ and Moloney MM. Importance of the Chiral Centers of Jasmonic Acid in the Responses of Plants: Activities and Antagonism between Natural and Synthetic Analogs. Plant. Physiol. 1997; 114, 419-428.

[12] Kus N, Haman BS, Fausto R. Thermal decomposition of allantoin as probed by matrix isolation FTIR spectroscopy. Tetrahedron 2009; 65, 9719–9727.

[13] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA et al. Gaussian 09, Revision A.0.2; Gaussian, Inc.: Wallingford, CT, 2009.

[14] McLean AD, Chandler GS. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms. Z=11−18. J. Chem. Phys. 1980; 72, 5639−5648.

[15] Becke AD. Density Functional Exhange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A: At., Mol., Opt. Phys. 1988; 38, 3098−3100.

[16] Lee CT, Parr R. G. Development of the Colle Salvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B 1988; 37, 785−789.

[17] Weinhold F, Landis CR. Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective. Cambridge University Press: New York, 2005.

[18] Bauernschmitt R, Ahlrichs R. Treatment of Electronic Excitations within the Adiabatic Approximation of Time Dependent Density Functional Theory. Chem. Phys. Lett. 1996, 256, 454−464.