A QUANTUM CHEMICAL STUDY ON ELUCIDATION OF MOLECULAR STRUCTURE, ELECTRIC MOMENTS AND VIBRATIONAL ANALYSES OF BETA-DAMASCENONE AND ITS ISOMER- A COMPARATIVE STUDY

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Abstract:
A comparative, quantum chemical study on of energies, dipole moment and vibrational wavenumbers of trans- beta-Damascenone and cis-beta-Damascenone was carried out by using B3LYP methods with 6-311+G(d,p) and 6-311++G(d,p) basis sets. A complete vibrational analysis of both the compounds has been performed and assignments are made on the basis of potential energy distribution. The frontier orbitals and molecular electrostatic potential surface study has also been employed to understand the active sites of title compounds. The calculation of the IR spectra is not only important in order to confirm the validity of the simulations but it also allows additional insight into the molecular level of the system not accessible from experiment. Therefore, simulated IR and Raman spectra of the title compounds are also presented in this study. The structure activity relationship based on the study of frontier orbital gap, dipole moment data along with the molecular electrostatic potential map of the title compounds have been used to understand the active sites of the molecules.

Keywords: Density Functional Theory; Frontier Orbital Energy Gap; Isomers; Damascenone.

Cite This Article: Amarendra Kumar. (2017). “A QUANTUM CHEMICAL STUDY ON ELUCIDATION OF MOLECULAR STRUCTURE, ELECTRIC MOMENTS AND VIBRATIONAL ANALYSES OF BETA-DAMASCENONE AND ITS ISOMER- A COMPARATIVE STUDY.” International Journal of Engineering Technologies and Management Research, 4(10), 123-136. DOI: 10.5281/zenodo.1051048.
aroma which has been described as reminiscent of exotic flowers with fruit and berry undertones (Ohloff, 1978; Naiker & Allen, 1996), and also as sweet, raisin-like (Simpson & Millar, 1984), honey-like, iononelike and cooked quince-like (Kotseridis et al., 1999). Damascenone was first identified in grapes and wine by Schreier & Drawert (1974) and mechanisms for its formation from the carotenoid neoxanthin were proposed by Skouroumounis & Sefton (2001). Damascenone occurs in Pinotage, Shiraz and Cabernet Sauvignon wines well above the threshold values reported by most researchers [5-8].

The aim of the present communication is to investigate the molecular structural, vibrational and energetic data analysis of the molecules under study, in gas phase, due to their biological and industrial importance. The structure and the ground state energy of the molecules under investigation has been analyzed employing DFT/B3LYP level. In order to obtain a more complete description of molecular motion, vibrational frequency calculations have been carried out at the DFT level. The vibrational analysis also yields the detailed information about the intra molecular vibrations in the molecular fingerprint region. The reported geometries, molecular properties such as equilibrium energy, dipole moment and vibrational frequencies along with the electrostatic potential maps, have also been used to understand the activity of the molecules.

2. Computational Methods

The DFT calculations [9] of the title molecules under investigation have been performed by employing Becke’s three parameter hybrid exchange functionals [10] with Lee–Yang–Parr functional (B3LYP) [11,12] method using the Gaussian 03 program [13]. The vibrational frequencies are also calculated and scaled down by the appropriate factor [14]. The vibrational frequency assignments have been carried out by combining the results of the Gaussview 5.0.8 program [15], symmetry considerations and the VEDA 4 program [16].

3. Result and Discussion

3.1. Molecular Geometry Optimization and Energies

The structure of trans β-damascenone and cis-β-damascenone has been investigated in order to assess the difference and similarities in the properties of these two isomers. The equilibrium geometry optimization for both the molecules has been achieved by energy minimization, using DFT at the B3LYP level, employing the basis set 6-311++G (d, p). The optimized geometry of both molecules under study are confirmed to be located at the local true minima on potential energy surface, as the calculated vibrational spectra has no imaginary frequency. The optimized molecular structures thus obtained together with the numbering scheme of the atoms are shown in Fig. 1. The optimized geometrical parameters of trans-β-damascenone and cis-β-damascenone have been given in Table1 and Table 2 respectively. In case of both the compounds, two C-C double bonds of six membered ring have values 1.338 and 1.3567 Å/ 1.33782 and 1.35723 Å respectively; and other C-C bond lengths of six membered ring are calculated between the range (1.468 Å -1.547 Å). The C=O bond length in both the molecules equal to 1.22 Å are also consistent with the standard C=O bond length (1.22 Å) [17, 18]. The six membered ring endocyclic C=C–C angles in trans-β-damascenone/cis-β-damascenone are found to be varying in
the range (108.9-121.5)/ (109.0-121.5) degree. The skeleton of both the molecules is not strictly planar, the carbonyl groups deviate from the plane of five membered rings.

Figure 1: 3D optimized structures along with numbering scheme of (a) trans- β-damascenone (b) cis- β-damascenone

Figure 2: Patterns of the principle highest occupied and lowest unoccupied molecular orbitals of (a) trans- β-damascenone and (b) cis- β-damascenone obtained with B3LYP/6-311++G(d,p)

Figure 3: MESP surface of (a) trans- β-damascenone and (b) cis- β-damascenone obtained with B3LYP/6-311++G(d,p)
Table 1: Optimized parameters of trans- and cis-β-damascenone at DFT/B3LYP/6311++G (d, p)

| Parameter                          | trans-β-damascenone | cis-β-damascenone |
|------------------------------------|---------------------|-------------------|
| ZPE (kcal mol⁻¹)                   | 172.729             | 172.902           |
| E (kcal mol⁻¹)                     | 182.352             | 182.498           |
| Cᵥ (cal mol⁻¹ K⁻¹)                 | 58.047              | 57.830            |
| S (cal mol⁻¹ K⁻¹)                  | 122.083             | 122.482           |
| G (kcal mol⁻¹)                     | 146.544             | 146.571           |
| H (kcal mol⁻¹)                     | 157.416             | 175.559           |
| Energy Gap (eV)                    | 4.0758              | 4.056             |
| Electric Dipole Moment (Debye)     | 2.9105              | 2.4711            |

3.2. Electronic Properties

The most important orbitals in a molecules are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [19]. The lower value for frontier orbital gap in case of cis conformer of damascenone than trans conformer of damascenone makes it more reactive and less stable (refer to Table 1). The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor. The 3D plots of the frontier orbitals HOMO and LUMO and the molecular electrostatic potential (MESP) map for both molecules are shown in Fig. 2 and Fig.3 respectively. It can be seen from the figure that, the HOMO is distributed uniformly in both the compounds over six membered ring and carbonyl group and the LUMO is found to spread over entire molecule except the atom C (10) in both the molecules. All the HOMO and LUMO have nodes. The nodes in each HOMO and LUMO are placed symmetrically. The MESP which is a plot of electrostatic potential mapped onto the constant electron density surface is shown in Fig. 3. The resulting surface simultaneously displays electrostatic potential value over the molecular shape and size. The MESP map for both the isomers clearly suggests that the carbonyl oxygen atoms (dark red) have maximum negative and probable site for nucleophillic attack, and the hydrogen atoms attached to the six membered ring and that attached to the carbon chain bear the most positive charge (blue region).The dipole moment in a molecule is another important electronic property that results from non-uniform distribution of charges on the various atoms in a molecule. It is mainly used to study the intermolecular interactions involving the van der Waal type dipole–dipole forces, etc., because larger the dipole moment, stronger will be the intermolecular interactions. Here large value of dipole moment in cis- isomer in comparison to trans isomer makes cis-β-damascenone more polar than trans-β-damascenone molecule. The calculated frontier orbital gap, dipole moment values for both the molecules are also given in Table 1.
Table 2: The optimized geometric parameters of trans-β-damascenone, bond lengths in angstrom (Å), bond angles and selected dihedral angles (in degrees)

| Parameter   | Theoretical Value | Parameter   | Theoretical Value |
|-------------|-------------------|-------------|-------------------|
| C1-C6       | 1.5484            | C6-C12      | 1.5475            |
| C1-H25      | 1.0949            | C6-C13      | 1.5417            |
| C1-H26      | 1.1015            | C7-C8       | 1.489             |
| C2-C3       | 1.3378            | C7-O10      | 1.2264            |
| C2-H24      | 1.0855            | C8-C9       | 1.3444            |
| C3-C4       | 1.4691            | C8-H19      | 1.085             |
| C3-H23      | 1.0859            | C9-C14      | 1.4955            |
| C4-C5       | 1.3572            | C6-C12      | 1.5475            |
| C2-C1-C3    | 113.3857          | C3-C7-C8    | 117.131           |
| C2-C1-H15   | 108.2863          | C5-C7-C8    | 121.943           |
| C2-C1-H16   | 110.8118          | C7-C8-C11   | 117.9045          |
| C3-C1-H15   | 109.2369          | C7-C8-C12   | 120.6967          |
| C3-C1-H16   | 108.8613          | C3-C9-H22   | 110.0564          |
| H15-C1-H16  | 105.9842          | C3-C9-H23   | 110.1925          |
| C1-C2-C4    | 119.827           | C3-C9-H24   | 111.2987          |
| C1-C2-H17   | 119.3578          | H22-C9-23   | 108.5944          |
| C4-C2-H17   | 120.7655          | H22-C9-24   | 108.1384          |
| C1-C3-C7    | 108.9993          | H23-C9-24   | 108.4863          |
| C1-C3-C9    | 110.1104          | C3-C10-H25  | 111.6605          |
| C1-C3-C10   | 107.7047          | C3-C10-H26  | 111.3117          |
| C7-C3-C9    | 108.7887          | C3-C10-H27  | 109.6579          |
| C7-C3-C10   | 112.2938          | H25-C10-H26 | 108.4208          |
| C9-C3-C10   | 108.9325          | H25-C10-H27 | 107.953           |
| C2-C4-C5    | 121.5417          | H26-C10-H27 | 107.6965          |
| C2-C4-H18   | 120.6764          | C8-C11-C13  | 121.6043          |
| C5-C4-H18   | 117.7568          | C8-C11-H28  | 117.6593          |
| C4-C5-C6    | 114.7331          | C13-C11-H28 | 120.6919          |
| C4-C5-C7    | 119.8657          | C11-C13-C14 | 125.4881          |
| C6-C5-C7    | 125.3005          | C11-C13-H29 | 117.2008          |
| C5-C6-H19   | 113.7845          | C14-C13-H29 | 117.3106          |
| C5-C6-H20   | 110.8046          | C13-C14-H30 | 110.5715          |
| C5-C6-H21   | 109.3213          | C13-C14-H31 | 112.1866          |
| H19-C6-H20  | 108.4883          | C13-C14-H32 | 110.594           |
| H19-C6-H21  | 107.5759          | H30-C14-H31 | 108.4995          |
| H20-C6-H21  | 106.5696          | H30-C14-H32 | 106.2517          |
| C3-C7-C5    | 120.5009          | H31-C14-H32 | 108.5273          |
| C3-C1-C2-C4 | 30.9339           | C1-C3-C9-H22| 61.3344           |
| C3-C1-C2-H17| -151.6101         | C1-C3-C9-H23| -178.933          |
| H15-C1-C2-C4| -90.4624          | C1-C3-C9-H24| -58.5359          |
| H15-C1-C2-H17| 86.9935        | C7-C3-C9-C22| -179.274          |
| H16-C1-C2-C4| 153.6971          | C7-C3-C9-C23| -59.5413          |
Table 3: The optimized geometric parameters of cis-β-damascenone, bond lengths in angstrom (Å), bond angles and selected dihedral angles (in degrees)

| Parameter     | Theoretical Value | Parameter     | Theoretical Value |
|---------------|-------------------|---------------|-------------------|
| C1-C2         | 1.4995            | C8-C9         | 1.3444            |
| C1-C6         | 1.5484            | C8-H19        | 1.085             |
| C1-H25        | 1.0949            | C9-C14        | 1.4955            |
| C1-H26        | 1.1015            | C9-H18        | 1.0894            |
| C2-C3         | 1.3378            | C11-H20       | 1.0961            |
| C2-H24        | 1.0855            | C11-H21       | 1.0956            |
| C3-C4         | 1.4691            | C11-H22       | 1.0875            |
| C3-H23        | 1.0859            | C12-H30       | 1.0927            |
| C4-C5         | 1.3572            | C12-H31       | 1.0904            |
| C4-C11        | 1.5109            | C12-H32       | 1.0958            |
| C5-C6         | 1.5462            | C13-H27       | 1.09               |
| C5-C7         | 1.5024            | C13-H28       | 1.0944            |
| C6-C12        | 1.5475            | C13-H29       | 1.0946            |
| C6-C13        | 1.5417            | C14-H15       | 1.0953            |
| C7-C8         | 1.489             | C14-H16       | 1.0864            |
| C7-O10        | 1.2264            | C14-H17       | 1.0975            |
| C2-C1-C6      | 113.3852          | C6-C12-H32    | 110.0234          |
| C2-C1-H25     | 110.8013          | H30-C12-H31   | 108.5207          |
| C2-C1-H26     | 108.2737          | H30-C12-H32   | 108.1446          |
| C6-C1-H25     | 108.8644          | H31-C12-H32   | 108.6057          |
3.3. Vibrational Analysis

The optimized molecular structure belongs to the C1 point group as it does not display any special symmetry. The calculated IR spectra of both the compounds have been given in Fig. 4. The overestimation of the vibrational wavenumbers in ab-initio and DFT methods are corrected either by computing anharmonic correlations explicitly or by introducing a scaled field [20], even directly scaling the calculated wavenumbers with proper factor. The vibrational wavenumbers are calibrated accordingly with the scaling factor of 0.9679 for DFT at B3LYP.
The vibrational assignments have been done on the basis of relative intensities, line shape, the VEDA 4 program and the animation option of Gaussview 5. The calculated and scaled wavenumber of trans β-damascenone and cis-β-damascenone are given in Table 5 and Table respectively. The calculated vibrational spectra of both the molecules have been divided in two regions; a low wavenumber fingerprint region (<2000 cm\(^{-1}\)) and a high wavenumber functional group region (4000- 2000 cm\(^{-1}\)). A total of 90 (3\(N-6\)) normal modes of vibrations have been calculated for for trans-β-damascenone and cis-β-damascenone and given alongwith potential energy distribution in table 4 and Table 5 respectively.

![Theoretical IR of Damascenone](image1)

**Figure 4: Theoretical FTIR Spectra of trans- β-damascenone and cis- β-damascenone**

**Table 4: Vibrational analysis of prominent modes of trans-β-Damascenone at the B3LYP/6-11++G (d, p) level**

| IR frequency (in cm\(^{-1}\)) | Scaled Frequency (in cm\(^{-1}\)) | Assignment |
|-------------------------------|-----------------------------------|------------|
| 3168.09                       | 3063                              | \(\nu_s[(C2-H17)(64) + (C4-H18)(34)]\) |
| 3161.58                       | 3057                              | \(\nu(C11-H28)(96)\) |
| 3145.20                       | 3041                              | \(\nu_s[(C2-H17)(35) + (C4-H18)(65)]\) |
| 3142.20                       | 3038                              | \(\nu(C13-H29)(93)\) |
| 3135.13                       | 3031                              | \(\nu[(C6-H19)(90)]\) |
| 3121.68                       | 3018                              | \(\nu_s[(C9-H22)(41) + (C10-H25)(43)]\) |
| 3118.08                       | 3015                              | \(\nu_s[(C9-H23)(38) + (C10-H25)(44)]\) |
| 3098.76                       | 2996                              | \(\nu[(C14-H31)(79)]\) |
| 3084.15                       | 2982                              | \(\nu_s[(C9-H22)(29) + (C10-H24)(60)]\) |
| 3077.67                       | 2976                              | \(\nu_s[(C10-H26)(43) + (C10-H27)(53)]\) |
| 3055.92                       | 2955                              | \(\nu_s[(C6-H20)(40) + (C6-H21)(60)]\) |
| 3054.96                       | 2954                              | \(\nu_s[(C14-H30)(51) + (C14-H32)(49)]\) |
| 3045.29                       | 2945                              | \(\nu[(C1-H16)(95)]\) |
| 3023.22                       | 2923                              | \(\nu_s[(C10-H26)(44) + (C10-H27)(35)]\) |
| 3016.44                       | 2917                              | \(\nu_s[(C9-H22)(61) + (C9-H24)(17)]\) |
| 3014.83                       | 2915                              | \(\nu_s[(C6-H20)(55) + (C6-H21)(35)]\) |
| 3012.78                       | 2913                              | \(\nu_s[(C14-H30)(40) + (C14-H31)(17) + (C14-H32)(42)]\) |
| 2966.10                       | 2868                              | \(\nu[(C1-H15)(96)]\) |
\[ V_{as}(O12-C8)(45) + (C13-C11)(32) \]

\[ V_{l}(C2-C4)(23) \]

\[ V_{d}(O12-C8)(44) + (C13-C11)(35) \]

\[ V_{l}(C2-C4)(40) + \sigma(C3-C7-C5)(17) \]

\[ \sigma(H25-C10-H27)(17)+ (H24-C9-H23)(16) + (H26-C10-H25)(33) \]

\[ \sigma(H25-C10-H27)(28)+ (H27-C10-H26)(21) \]

\[ \sigma(H23-C9-H22)(31)+ \tau (H24-C9-H23)(16) \]

\[ \sigma(H19-C6-H21)(54)+ (H21-C6-H20)(20) + \tau (H21-C6-C5-C7)(15) \]

\[ \sigma(H22-C9-H24)(28)+ (H27-C10-H26)(16) \]

\[ \sigma(H20-C6-H10)(48)+ (H21-C6-H20)(11) \]

\[ \sigma(H30-C14-H32)(30) + \tau (H31-C14-H30)(22) + (H32-C14-H31)(15) \]

\[ \sigma(H31-C14-H30)(37)+ (H32-C14-H31)(43) \]

\[ \sigma(H16-C1-H15)(77) \]

\[ \sigma(H17-C2-C4)(34)+ (H18-C4-C2)(41) \]

\[ \omega(H21-C6-H20)(25) \]

\[ \omega(H21-C6-H20)(24) \]

\[ \omega(H30-C14-H32)(47)+ (H31-C14-H30)(22) + (H32-C14-H31)(23) \]

\[ \omega(H22-C9-H24)(28)+ (H27-C10-H26)(21) + (H24-C9-H23)(24) \]

\[ \tau_1 (H15-C1-C2-C4)(24)+ (H16-C1-C2-C4)(33) \]

\[ \sigma(H28-C11-C13)(51) \]

\[ \sigma(H29-C13-C14)(61) \]

\[ \tau (H15-C1-C2)(13) \]

\[ \sigma(H15-C1-C2)(23) \]

\[ \sigma(H18-C4-C2)(25) \]

\[ \omega(H21-C6-H20)(24) \]

\[ \sigma(H17-C2-C4)(26) \]

\[ \sigma(H15-C1-C2)(32) \]

\[ \sigma(H17-C2-C4)(29) \]

\[ \tau_1 (H29-C13-C11-C8)(28)+ (H31-C14-C13-C11)(41) \]

\[ \omega(H19-C6-H21)(32)+ \omega (H19-C6-C5-C7)(47) \]

\[ \tau_1 (H24-C9-C3-C1)(19)+ (H26-C10-C3-C1)(21) \]

\[ \tau_1 (H28-C11-C13-C14)(49)+ (H29-C11-C11-C8)(26) \]

\[ \tau_1 (H28-C11-C13-C14)(49)+ (H29-C11-C11-C8)(26) \]

\[ \sigma(C11-C8)(20) \]

\[ \tau_1 (H17-C2-C4-C5)(32)+ (H18-C4-C2-C1) \]

\[ \tau_1 (H23-C9-C3-C1)(16) \]

\[ \tau_1 (H23-C9-C3-C1)(16) \]

\[ \tau_0 (H28-C11-C13-C14)(28) \]

\[ \tau_0 (H28-C11-C13-C14)(28) \]

\[ \tau_1 (H17-C2-C4-C5)(32) \]

\[ \tau_0 (O12-C7-C11-C8)(24) \]

\[ \sigma(C2-C4-C5)(61) \]

\[ \sigma(C6-C5-C4)(21) \]

\[ \sigma(C14-C13-C11)(33) \]
Table 5: Vibrational analysis of prominent modes of cis-β-Damascenone at the B3LYP/6-11++G (d, p) level

| IR frequency (in cm\(^{-1}\)) | Scaled IR Frequency (in cm\(^{-1}\)) | Assignment |
|-------------------------------|---------------------------------------|------------|
| 3168.50                       | 3064                                  | Vs[(C2-H24)(61) + (C3-H23)(38)] |
| 3166.51                       | 3062                                  | Vs[(C8-H19)(77)] |
| 3161.82                       | 3057                                  | Vs[(C8-H19)(17)+ (C14-H16)(76)] |
| 3146.06                       | 3042                                  | Vs[(C2-H24)(37) + (C3-H23)(60)] |
| 3141.17                       | 3037                                  | Vs[(C11-H22)(91)] |
| 3123.58                       | 3020                                  | Vs[(C12-H31)(60)+ (C13-H27)(24)] |
| 3120.30                       | 3017                                  | Vs[(C12-H31)(22)+ (C13-H27)(63)] |
| 3111.40                       | 3009                                  | Vs[(C31-H18)(92)] |
| 3084.15                       | 2982                                  | Vs[(C12-H30)(62)+ (C12-H32)(29)] |
| 3076.66                       | 2975                                  | Vs[(C13-H28)(52)+ (C13-H29)(44)] |
| 3055.95                       | 2955                                  | Vs[(C11-H20)(41)+ (C11-H21)(58)] |
| 3052.46                       | 2952                                  | Vs[(C14-H15)(68)+ (C14-H17)(30)] |
| 3045.25                       | 2945                                  | Vs[(C1-H25)(95)] |
| 3023.07                       | 2923                                  | Vs[(C13-H28)(34)+ (C13-H29)(41)] |
| 3017.07                       | 2917                                  | Vs[(C12-H30)(17)+ (C12-H32)(58)] |
| 3015.39                       | 2916                                  | Vs[(C11-H20)(54)+ (C11-H21)(38)] |
| 3012.00                       | 2912                                  | Vs[(C14-H15)(27)+ (C14-H17)(68)] |
| 2966.28                       | 2868                                  | Vs[(C1-H26)(96)] |
| 1707.77                       | 1651                                  | Vs[(O10-C7)(50)+ (C9-C8)(50)] |
| 1692.85                       | 1637                                  | Vs[(C2-C3)(38)+ (C5-C4)(24)] |
| 1645.87                       | 1591                                  | Vs[(O10-C7)(37)+ (C9-C8)(40)] |
| 1612.73                       | 1559                                  | Vs[(C2-C3)(27)] |
| 1520.59                       | 1470                                  | σ[(C31-C12-H30)(21)+ (H27-C13-H29)(28)]+ σ[(H28-C13-H27)(15)] |

**Note:** The data provided in the table represents selected vibrational frequencies and their corresponding scaled frequencies along with the assignments.
| 1506.47 | 1457 | $\sigma[(H31-C12-H30)(18)+ (H28-C13-H27)(31)] + \tau [(H29-C13-H28)(12)]$ |
| 1500.40 | 1451 | $\sigma[(H32-C12-H31)(29)+ (H29-C13-H28)(18)]$ |
| 1490.57 | 1441 | $\sigma[(H22-C11-H21)(57)+ (H21-C11-H20)(18)]$ |
| 1489.54 | 1440 | $\rho [(H16-C14-H15)(20)] + \sigma [(H17-C14-H16)(52)]$ |
| 1485.99 | 1437 | $\sigma[(H20-C11-H22)(55)] + \rho [(H21-C11-H20)(12)]$ |
| 1485.50 | 1436 | $\rho [(H30-C12-H32)(28)] + \sigma [(H29-C13-H28)(19)]$ |
| 1468.25 | 1420 | $\sigma[(H16-C14-H15)(38)+ (H15-C14-H17)(23)]$ |
| 1465.07 | 1417 | $\sigma[(H26-C1-H25)(76)]$ |
| 1440.58 | 1393 | $\sigma[(H19-C8-C9)(34)+ (H18-C9-H8)(26)]$ |
| 1427.19 | 1380 | $\sigma[(H24-C2-C1)(25)+ (H23-C3-H2)(38)]$ |
| 1416.32 | 1369 | $\sigma[(H21-C11-H20)(22)]$ |
| 1413.04 | 1366 | $\sigma[(H21-C11-H20)(25)]$ |
| 1398.77 | 1352 | $\omega[(H16-C14-H15)(21)+ (H15-C14-H17)(38)] + (H17-C14-H16)(24)]$ |
| 1392.78 | 1347 | $\omega[(H31-C12-H30)(22)+ (H30-C12-H32)(19)] + (H32-C12-H31)(21)]$ |
| 1352.97 | 1308 | $\tau_1 [(H25-C1-C2-C3)(28)+ (H26-C1-C2-C3)(27)]$ |
| 1302.94 | 1260 | $\sigma[(C6-C5-C4)(10)]$ |
| 1280.70 | 1238 | $\sigma[(H19-C8-C9)(31)+ (H18-C9-C8)(33)]$ |
| 1265.14 | 1223 | $\sigma[(H25-C1-C2)(16)] + \tau_1 [(H26-C1-C2-C3)(20)]$ |
| 1226.60 | 1186 | $\sigma[(H23-C3-C2)(28)]$ |
| 1213.84 | 1174 | $V_1[(C13-C6)(17)] + \tau_1 [(H32-C12-C6-C1)(18)]$ |
| 1175.28 | 1136 | $V_1[(C7-C5)(16)] + \sigma[(H24-C2-C1)(23)]$ |
| 1144.27 | 1106 | $\sigma [(H25-C1-C2)(25)]$ |
| 1114.94 | 1078 | $\tau_1 [(H15-C14-C9-C8)(15)] + \tau_0 [(H17-C14-C9-C8)(17)]$ |
| 1072.66 | 1037 | $\tau_0 [(H18-C9-C8-C7)(15)] + (H16-C14-C9-C8)(27)]$ |
| 1071.35 | 1036 | $\tau_1 [(H16-C14-C9-C8)(27)]$ |
| 1053.49 | 1019 | $\tau_0 [(H22-C11-C4-C3)(23)] + \tau_1 [(H21-C11-C4-C3)(27)]$ |
| 1036.43 | 1002 | $\tau_1 [(H30-C12-C6-C1)(20)] + (H29-C13-C6-C1)(20)]$ |
| 1016.73 | 983 | $V_{as}[(C1-C2)(35)]$ |
| 1014.66 | 981 | $\tau_0 [(H19-C8-C9-C14)(46)] + (H18-C9-C8-C7)(16)]$ |
| 992.00 | 959 | $\tau_0 [(H24-C2-C3-C4)(32)] + (H23-C2-C3-C1)(43)]$ |
| 985.73 | 953 | $\sigma[(C2-C3-C4)(11)]$ |
| 971.02 | 939 | $V_{as}[(C8-C7)(16)] + V_{as}[(C14-C9)(15)]$ |
| 949.52 | 918 | $V_{as}[(C13-C6)(17)] + \tau_1 [(H31-C12-C6-C1)(15)]$ |
| 901.27 | 871 | $V_{as}[(C14-C9)(42)]$ |
| 898.94 | 869 | $V_{as}[(C12-C6)(16)]$ |
| 849.08 | 821 | $V_{as}[(C12-C6)(16)] + \tau_0 [(H010-C8-C5-C7)(18)]$ |
| 831.10 | 803 | $\sigma[(O10-C7-C8)(24)]$ |
| 800.59 | 774 | $\tau_1 [(H18-C9-C8-C7)(18)] + \tau_0 [(O10-C8-C5-C7)(16)]$ |
| 748.14 | 723 | $\tau_1 [(H24-C2-C3-C4)(26)]$ |
3.3.1. C-C and C-H Vibrations

C-C stretching wavenumbers are observed as mixed modes in the range 1500 cm⁻¹ to 1100 cm⁻¹ and agree well with the general appearance of C-H and C-C stretching modes. C-C stretches are calculated to be (1490-1078) cm⁻¹ trans-β-damascenone and (1518-1296) cm⁻¹ for cis-β-damascenone. The C-H stretching vibrations for both the compounds are calculated in the range 3000 cm⁻¹ -3200 cm⁻¹.

3.3.2. Ring Vibrations

The six membered ring spectral region predominantly involves the C–H, C–C and C=C stretching, and C–C–C as well as H–C–C-bending vibrations. The bands due to the ring C–H-stretching vibrations were observed as a group of partially overlapping absorptions in the region 3110–3069 cm⁻¹ with more than 90% potential energy contribution. Vibrations involving C–H in-plane bending are found in the region 1600–825 cm⁻¹. The computed wavenumbers at 1017 cm⁻¹ are identified as the trigonal ring bending and 1022 cm⁻¹ as ring breathing modes respectively.

4. Conclusions

The present study on trans β-damascenone and cis-β-damascenone, comprised of equilibrium geometries optimization and the calculation of molecular ground state properties at DFT/6-311++G (d, p) level. In general, a slight change in the calculated optimized parameters in cis
isomer has been observed. Theoretical IR spectra and normal mode analysis of title compounds has also been done and compared. The lower value of frontier orbital gap makes cis-β-damascenone more polarizable hence more reactive than trans β-damascenone. The structure activity relationship based on the study of frontier orbital gap, dipole moment data along with the molecular electrostatic potential map of trans β-damascenone and cis-β-damascenone, have been used to understand the active sites of the molecules under study.

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