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Comparative Stability of 1-Methylcyclopropene and Methylenecyclopropane Tautomers: Ab initio and DFT Study

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Abstract

The geometric optimizations, relative stabilities, and infrared spectroscopy **analyses** of the 1-methylcyclopropene and methylenecyclopropane tautomers were all accomplished using a combination of CCSD and DFT methods. Data that demonstrate the relative stability of the endo-en and exo-en forms were examined. The thermodynamic results showed that methylenecyclopropane is the more stable isomer at the B3LYP / aug-cc-PVDZ level of theory, with enthalpy (H=12.4kcal/mol and Gibbs energy (G=11.7kcal/mol) lower than that for 1-methylcyclopropene. These results and those from the preceding experiments are in perfect agreement. The vibrational frequencies and geometrical factors that were discovered in earlier studies also show strong consistency. Additionally, the CCSD/ aug-cc-PVDZ level of theory was used to calculate molecular orbitals such as natural bond orbitals (NBOs), HOMO-LUMO energy gaps, and electrostatic potential (ESP) surfaces. It was explained how crucial it is to choose the most stable tautomer while manufacturing 1-methylcyclopropene (1-MCP), which is used to control fruit quality in the post-harvest environment.

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Introduction

A single chemical molecule can exist in two or more forms that can be switched out by replacing one or more atoms, a phenomenon known as tautomerism (Moradi *et al*., 2012). Understanding the factors affecting the migration of tautomeric groups or atoms between distinct tautomers is essential when studying the processes of isomeric reaction (Antonov, 2013; Michael, 2007). This may have an impact on the outcome through a number of intermediate structural isomers. The operation of tautomerism is influenced by the reaction conditions, such as pressure, temperature, and catalysis. For instance, 1-methylcyclopropene (endo-en) to methylenecyclopropane (exo-en) exhibits a tautomerism with an actively high upward convergence, and the two isomers show no signs of environmental rearrangement.

It has been noted that the production of methylenecyclopropane can be produced more quickly when a potassium t-butoxide catalyst is present (Krull, 1969). The 1,3-acyl migration photochemical rearrangement is a frequent rearrangement for β, γ-unsaturated ketones. For example, the hydrogen shift inside the 10,11-dimethyltricyclo[4.3.2.0] undec-10-en-2-one. The primary photo-rearranged isomer of undec-10-en-2-one is 10-methyl-11-methylenetricyclo[4.3.2.0]undecan-2-one (Peet *et al*., 1973). Studies on the structure and tautomerism of 1-methylcyclopropene to methylenecyclopropane (**Scheme 1**) have been published in a few publications (Hehre *et al*., 1975; Al-Mazaideh *et al*., 2016; Al-Mazaideh *et al*., 2018; Goumans *et al*., 2003; Kemp; Willis, 1967; Laurie *et al*., 1970). The more stable isomer, methylenecyclopropane, has been found to have an enthalpy of 10.2kcal/mol experimentally, 6.8kcal/mol, and 11.2-11.4kcal/mol theoretically (Wiberg *et al*., 1969; Baird *et al*., 1967; Bach *et al*., 2004). There haven't been many thermodynamic studies done yet on the tautomerism of 1-methylcyclopropene to methylenecyclopropane. According to our research on this subject, none of the isomers' theoretical or experimentally determined Gibbs free energy (ΔG^o) or heat of formation (ΔH_f^o) have been documented.

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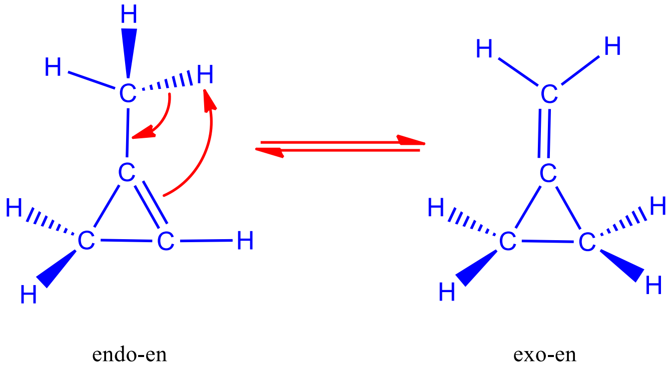

Scheme 1 1-Methylcyclopropene (endo-en) isomerizing into Methylenecyclopropane (exo-en).

The only thermochemical information for both isomers is the heat of hydrogenation (Wiberg *et al*., 1969; Bach *et al*., 2004). Due to a lack of information, it is decided to research the thermodynamics, structure, and stability of 1-methylcyclopropene in comparison to methylenecyclopropane. It is employed a transition state complex that links the two isomers along the tautomerism pathway to fully comprehend the reaction mechanism and to determine the rate constants (k_f, and k_r) for the forward and backward reactions, respectively. The equilibrium constant was determined (K_{eq}), which assisted in calculating the relative availability of the two isomers, utilizing the Gibbs free energy gap between the two tautomers.

The fact that 1-MCP and methylenecyclopropane are organic molecules that bind with the ethylene receptor and disperse free after various times makes it important to examine the tautmerization of these chemicals. Methylenecyclopropane is an agonist, whereas 1-MCP is an antagonist for ethylene. By inhibiting the receptor, 1-MCP has shown promise in scientific research and commercial protection against ethylene (Sisler *et al*., 1999; Blankenship *et al*., 2003). 1-MCP has given the plant science research community a useful instrument to study the biology of ethylene (Jiang *et al*., 2000; Sisler *et al*., 1997). The pattern of climacteric fruit ripening is also modified by ethylene action suppression (Watkins, 2006).

1 Materials and Methods

Utilizing the Gaussian-09 software (Frisch *et al*., 2009, the optimal geometries of the tautomers (minima) and the transition state have both been found computationally (with the Minnesota 06 [M06] functional and hybrid exchange-correlation B3LYP). These calculations were performed using the polarized basis sets 6-31+G(d), aug-cc-PVTZ, and aug-cc-PVDZ. Thermodynamic data and vibrational frequency were both calculated using frequencies. It was optimized using both QST2 (Ayala *et al*., 1997) and the Berny methods (Dillet *et al*., 1994) to get the thermodynamic data of the transition state. When there is just one imaginary eigenvalue with the transition state, all estimated vibrational frequencies for the minimal state have zero imaginary eigenvalues.

The following equations (1 and 2) (McQuarrie *et al*., 1999) were used to compute the comparative isomerization enthalpies and Gibbs free energies:

$$\Delta H_{com} = (E_0 + H_{cor})_{(endo)} - (E^0 + H_{cor})_{(exo)} \tag{1}$$

$$\Delta G_{com} = (E_0 + G_{cor})_{(endo)} - (E^0 + G_{cor})_{(exo)} \tag{2}$$

(E_o+H_{cor}) and (E_o+G_{cor}) are the corrected electronic energies where E_o is the zero point energy, H_{cor} is the thermal correction of the enthalpy, and G_{cor} is the thermal correction of the Gibbs free energy. Equation 3 (McQuarrie *et al*., 1999) was used to get the forward operation (k_f) and backward operation (k_r) rate constants for the isomerization reaction (Scheme 1).

$$k(T) = \frac{k_B T}{hc^\circ} e^{-\Delta G^\#/TR} \tag{3}$$

Where T=298.15 K for temperature and c°=1, for the concentration. k_B, R, and h are the Boltzmann, universal gas and Planck constants, respectively. In addition, using the CCSD/aug-cc-PVDZ level of theory, the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were predicted to interpret the orbital overlapping and the potential for charge transfer inside the two tautomers. To clarify the intramolecular, hybridization, and delocalization of electron density inside the investigated tautomer, NBO analysis has been carried out on the molecule at the CCSD/ aug-cc-PVDZ level of theory. The results are shown in **Table 5**. To have a thorough investigation of intra and intermolecular interactions, natural bond orbital (NBO) (MacKerell *et al*., 1998; Markova *et al*., 2015) analysis provides information about interactions in both filled and virtual orbital regions. In the NBO analysis, the second-order Fock matrix was used to assess the donor-acceptor interactions (Zhurko, 2009). The stabilizing energy connected to the i-j delocalization can be calculated as follows (equation 4) for each donor NBO(i) and acceptor NBO(j):

$$E^{(2)} = \Delta E_{ij} = q_i = \frac{F(i,j)^2}{\varepsilon_i \varepsilon_j} \tag{4}$$

where *F(i,j)* is the off-diagonal NBO Fock matrix element, q_i is the donor orbital occupancy, εi, εj are diagonal elements (orbital energies). The overlapping of orbitals between bonding and anti-bonding, which results in an intramolecular charge transfer, is what causes a molecular system to become stable (ICT). The electrostatic potential (ESP) surface was examined using CCSD/aug-cc-PVDZ level theory to forecast the reactive behaviour of both tautomers.

2 Results and Discussion

2.1 Geometry

Figure 1 depicts the optimized structures of the transition state as well as the minimum tautomers (1-methylcyclopropene and methylenecyclopropane). **Table 1** shows the associated geometrical parameters at the M06 and CCSD levels of theory. As seen, there is a good agreement between the bond lengths, angles, and dihedral angles of the two levels of theory. The two minima's C-C and C=C bond lengths differ by 0.04 Å. Bond angle discrepancies also range from 0-1.0°. The C2-C3-C4-C1 dihedral angle has the most variation, which is 0.1°.

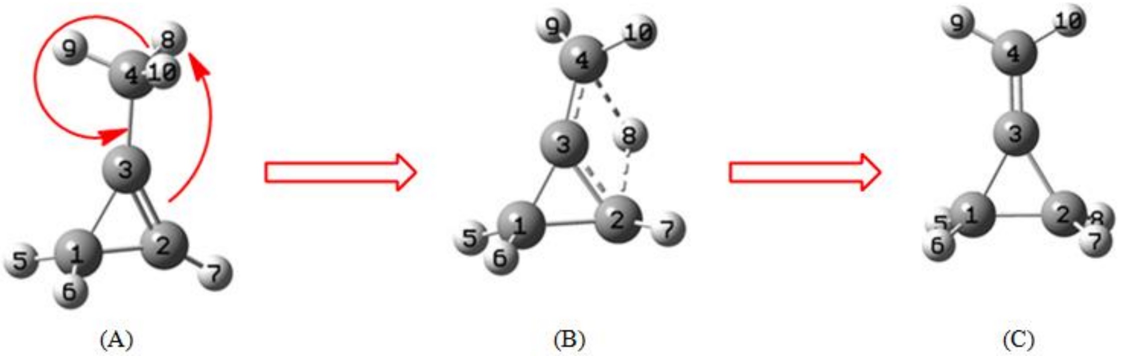

Fig. 1 The optimized geometries of (A) 1-methylcyclopropene, (B) the transition state and (C) methylenecyclopropane.

Table 1 Selected bond lengths (Å), angles (º), and dihedral angles (º) of the optimized tautomers (endo- en and exo-en), as well as the transition state (TS) geometries, at the theoretical levels of CCSD /6-31+G (d); aug-cc-PVDZ and M06/ aug-cc/PVDZ; PVTZ.

Structure	Bond (**Å**)	Expt[a]	CCSD/6-31+G(d)	CCSD/aug-cc-PVDZ	M06/aug-cc-PVDZ	M06/aug-cc-PVTZ	M06/aug-cc-Angles (º)	Expt[a]	CCSD/6-31+G(d)	CCSD/aug-cc-PVDZ	M06/aug-cc-PVDZ	M06/aug-cc-PVTZ
endo-en	C1–C2	1.515	1.515	1.528	1.501	1.490	C1–C2–C3		64.4	64.4	64.4	64.5
	C2=C3	1.300	1.302	1.313	1.297	1.284	C2–C3–C1		64.7	64.7	64.4	64.4
	C1–C3		1.511	1.524	1.501	1.492	C2–C1–C3	50.0	51.0	51.0	51.2	51.0
	C3–C4	1.476	1.484	1.492	1.469	1.464	C2–C3–C4	152.0	151.7	151.6	152.4	152.6
	C4–H8	1.098	1.096	1.102	1.098	1.090	C2–C3–C4–C1		180.0	180.0	179.9	180
exo-en	C1–C2	1.542	1.543	1.556	1.531	1.522	C1–C2–C3		58.4	58.4	58.4	58.5
	C2–C3	1.457	1.472	1.483	1.461	1.455	C2–C3–C1	63.0	63.3	63.3	63.2	63.1
	C1–C3	1.457	1.472	1.483	1.461	1.455	C2–C1–C3		58.4	58.4	58.4	58.5
	C3=C4	1.332	1.330	1.338	1.323	1.311	C2–C3–C4		148.4	148.4	148.4	148.5
	C2–H8	1.090	1.090	1.095	1.093	1.083	C2–C3–C4–C1		179.8	179.8	179.9	179.9
TS	C1–C2		1.496	1.509	1.470	1.458	C1–C2–C3		63.1	62.9	63.8	64.1
	C2–C3		1.389	1.410	1.398	1.387	C2–C3–C1		61.9	61.7	60.4	60.2
	C1–C3		1.513	1.524	1.517	1.511	C2–C1–C3		55.0	55.4	55.8	55.7
	C3–C4		1.446	1.443	1.412	1.404	C2–C3–C4		160.0	158.9	164.4	164.5
	C2–H8		2.113	2.080	2.044	2.013	C2–C3–C4–C1		47.9	36.2	33.7	34
	C4–H8		1.638	1.641	1.606	1.611						

[a] For endo-en and exo-en, respectively, the experimental bond lengths and angles were taken from References (2003; Kemp, 1967; Laurie *et al.*, 1970).

The two levels of the theory's parameters are in good accord, as can be seen. It was discovered that the two minima's C=C and C-C bond length differences were 0.02Å apart. The bond lengths between M06/aug-cc-PVDZ and M06/aug-cc-PVTZ are longer, as indicated in **Table 1**. Bond lengths typically increase when the basis set shrinks and when the core correlation is applied (Helgaker *et al.*, 1997; Helgaker *et al.*, 2000). Additionally, it is seen that utilizing the identical basis set, the bond lengths of CCSD/ aug-cc-PVDZ are longer than those of M06. This can be a reference to the M06 (Zhao *et al.*, 2008) exchange-correlation functional. On the other hand, the dihedral angle differences are 0.1°, while the C-C-C bond angle differences of the minima vary from 0 to 0.9°. In experiments, it was discovered that the endo-en C1-C2, C2=C3, C3-C4, and C4-H8 bond lengths were 1.515, 1.300, 1.476, and 1.098Å, respectively, while the C2-C1-C3 and C2-C3-C4 bond angles were 50.0° and 152.0°, respectively (Kemp, 1967). These results closely match those from calculations. Table 1 makes it abundantly evident that the experimental exo-en bond lengths are identical to or very close to one of those found in this work. C1–C2, C2–C3, C1–C3, C3=C4 and C2–H8 of exo-en are, respectively, 1.542, 1.457, 1.332, and 1.090Å, which are in good accord with my findings.

The C2-C3-C1 bond angle was discovered to be 63.0°, which is extremely similar to current findings. The C2-C3-C4-C1 dihedral angle in both isomers is close to 180°, as illustrated in Table 1. At a different theoretical level, the endo-en ring of cyclopropene (endo-en) is flatter than the exo-en ring of cyclopropane (in very little value). The cyclopropene ring in the endo-en isomer has a trapezoid geometry and a C2=C3 bond length of ~1.30Å, but the lengths of the remaining C-C bonds range from 1.49 to 1.53Å. The C-C single bonds in the exo-en isomer have two values: 1.455 and 1.556Å.

2.2 The comparative stability, thermodynamic and kinetic results

Table 2 lists the comparative stabilities of the endo-en tautomer and the TS at various theoretical levels, as measured by their enthalpies (ΔH_{com}) and Gibbs free energies (ΔG_{com}) with respect to the most stable exo-en tautomer. Also included is the calculated equilibrium constant K_{eq}. Due to the large energy gap of the transition state, the computed rate constants for the forward (k_f) and backward (k_r) operations using Eq. (3) have exponents smaller than 10^{-36}, indicating that they are equal to zero. The values of comparative energy (ΔH_{com}) for the endo-entautomer and transition states (comparative to the exo-entautomer) using M06 functionals are the same as Wiberg's reported experimental finding (10.2kcal/mol). The exo-en tautomer (methylenecyclopropane) is the most stable, according to both theoretical calculations (using CCSD, B3LYP, and M06) and experimental results. The least stable tautomer (endo-en) has a heavily substituted C=C link because the cyclopropene ring has two sp2 hybridized carbon atoms and is assumed to be more strained than the cyclopropane ring (Wiberg *et al*., 1969). This is due to the weak C-H bond that exists in cyclopropane (Johnson *et al*., 1997).

Endo-en tautomer's theoretical heat of hydrogenation is approximately 11.3kcal/mol higher than exo-en (Bach *et al*., 2004). Strain energy difference (ΔSE=12.1kcal/mol (Turner *et al*., 1968), and 7.9kcal/mol (Baird *et al*., 1967)) between 1-methylcyclopropene and methylenecyclopropane. The values of comparative energy (ΔH_{com}) of the endo-en tautomer found by this study are comparable to those of heat of hydrogenation and strain energy difference.

The tautomerism operation does not appear to occur under ambient circumstances due to the high value of the Gibbs free energy of activation ($\Delta G^{\#}$ the energy gap between the exo-en and the transition state, Table 2). In reality, a catalyst can be used to provide a quantitative yield of the required methylenecyclopropane, as suggested by Krull and Arnold (Krull, 1969). Methylenecyclopropane has been isomerized from 1-methylcyclopropene using a potassium t-butoxide catalyst. Results of calculations utilizing the polar solvent (DMSO) and the (a non-polar solvent) chloroform are shown in Table 2. Neither the energy gap in the TS nor the energy gap between exo-en and endo-en tautomers is significantly impacted by solvents.

2.3 Vibrational frequencies

2.3.1 Methylenecyclopropane

A nonlinear molecule with 10 atoms typically has 24 different vibrational modes. There are 17 in-plane (symmetrical) and 7 out-of-plane (asymmetrical) vibrational modes for the C_2v-symmetric compound methylenecyclopropane (Loewenstein, 1954). All the vibrational frequencies are displayed in **Table 3**. One of the ring puckering frequencies according to my calculation utilizing the CCSD/aug-cc-PVDZ level of theory is at ~273cm^{-1}. Experimentally, it was discovered that this rocking vibration mode's wavelength was 290cm^{-1} (Mitchell, 1971). In good agreement with the identical mode (wagging) discovered at 360cm^{-1} utilizing the IR and Raman spectrum, another fundamental ring puckering is observed at 349cm^{-1}. Experimentally, the theoretical location of the C=C stretching at 1842cm^{-1} is seen at 1743cm^{-1}. The =CH_2 rocking, wagging, twisting, scissoring, symmetric stretching, and asymmetric stretching are placed at 911, 921, 1089, 1490, 3151, and 3244cm^{-1}, respectively, according to the CCSD/aug-cc-PVDZ level of theory. These vibrational modes have experimental values of 792, 889, 1144, 1437, 3010, and 3086cm^{-1}, respectively. The same system was examined by (Al-Mazaideh *et al*., 2016) utilizing the DFT/B3LYP functional and the 6-311G basis set. Their findings indicate that endo-en is 18.518 kJ/mol, more stable than exo-en, which contradicts the current results, and experimental findings and overstates the energy value. This could be explained by the use of simplistic theory.

2.3.2 1-Methylcyclopropene

The 1-methylcyclobutene -Cs symmetry molecule- comprises 24 vibrational modes, each of which has an Asymmetry. Each vibrational mode is included in **Table 4**. At the CCSD/aug-cc-PVDZ level of theory, the C=C stretching is assigned to the absorption band at 1851cm^{-1}. According to experimental findings, this band has a medium IR peak at 1788cm^{-1} (Mitchell, 1969). There is a puckering vibration that rings at 275cm^{-1}. Experimental observation of this puckering mode (CH_3-C out-of-plane bend) at 283cm^{-1} has been made. Another fundamental ring puckering (CH_3-C in-plane bend) is located at 319cm^{-1} and is wellconcordant with the same mode found at 331cm^{-1} using the IR and Raman spectrum. At 1520 and 3132cm^{-1}, respectively, the -CH$_2$ scissoring and asymmetric stretching take place. Experimental values for these vibrational modes are 1487 and 3071cm^{-1}, respectively. Comparable results from experimental measurement of C-H stretching at 3133cm^{-1} were obtained in this study.

Table 2 The equilibrium constant K_{eq}, the rate constants k_f and k_r of the forward and backward of the tautomerism operation, and the comparative energies ΔH_{com} and ΔG_{com} with respect to the most stable tautomer exo-en (Scheme 1).

Geometry	Method	Basis set	ΔH_{com}^{a,b}	ΔG_{com}^{a,b}	K_{eq}($\times 10^{-7}$)	k_f (s^{-1})	k_r (s^{-1})
endo-en	CCSD	6-31+G(d)	11.94	11.19	0.063		
		aug-cc-PVDZ	11.95	11.26	0.056		
	M06	6-31+G(d)	10.22	9.49	1.106		
		aug-cc-PVDZ	10.56	9.90	0.554		
		aug-cc-PVTZ	9.77	9.04	2.364		
		aug-cc-PVDZ (DMSO)^{b}	10.33	9.66	0.830		
		aug-cc-PVDZ (chloroform)^{b}	10.27	9.54	1.017		
	B3LYP	6-31+G(d)	11.87	11.15	0.067		
		aug-cc-PVDZ	12.40	11.71	0.026		
TS^{b}	CCSD	6-31+G(d)	89.87	89.68		1.82×10^{-45}	1.15×10^{-53}
		aug-cc-PVDZ	85.79	85.62		1.94×10^{-42}	1.08×10^{-50}
	M06	6-31+G(d)	81.42	81.31		1.41×10^{-40}	1.56×10^{-47}
		aug-cc-PVDZ	78.09	77.96		8.06×10^{-38}	4.46×10^{-45}
		aug-cc-PVTZ	79.58	79.41		1.63×10^{-39}	3.86×10^{-46}
		aug-cc-PVDZ (DMSO)^{c}	75.07	75.02		7.68×10^{-36}	6.38×10^{-43}
		aug-cc-PVDZ (chloroform)^{c}	76.31	76.22		8.27×10^{-37}	8.42×10^{-44}
	B3LYP	6-31+G(d)	84.09	83.97		2.61×10^{-41}	1.76×10^{-49}
		aug-cc-PVDZ	80.96	80.84		1.32×10^{-38}	3.46×10^{-47}

[a] Each energy is expressed in kcal/mol.

[b] For the TS: $\Delta H_{com} = \Delta H^{\#}$ and $\Delta G_{com} = \Delta G^{\#}$.

[c] DMSO and chloroform as solvents.

Table 3 Calculated methylenecyclopropane (exo-en) vibrational frequencies (cm^{-1}).

CCSD		M06		
Vibration (cm^{-1}) /aug-cc-PVDZ	IR intensity	Vibration (cm^{-1}) /aug-cc-PVTZ	Scaled^{b}	Experimental^{a} Vibration (cm^{-1})
272.5	4.7	307.7	294.8	290 (m)
349.1	0.2	339.4	325.2	360 (m)
608.1	0.0	605.9	580.5	616 (vw)
737.9	6.0	737.2	706.2	723 (s)
746.5	1.2	764.3	732.2	748 (w)
911.0	14.5	901.3	863.4	792 (w)
921.1	39.0	907.6	869.5	889 (vs)
944.9	0.0	945.6	905.9	937 (vw)
1035.8	2.75	1021.1	978.2	1002 (m)
1062.0	2.97	1066.0	1021.2	1036 (s)
1064.2	0.6	1082.6	1037.1	1125 (m)
1088.6	3.9	1086.8	1041.1	1144 (vw)
1148.2	5.2	1126.4	1079.1	1174 (s)
1163.0	0.0	1155.9	1107.3	1072 (m)
1445.9	0.2	1411.4	1352.2	1353 (m)
1448.8	1.3	1417.7	1358.1	1410 (m)
1490.1	0.5	1453.0	1391.9	1437 (m)
1841.5	3.0	1850.4	1772.7	1743 (m)
3131.5	14.4	3102.7	2972.3	2999 (s)
3136.7	10.9	3103.3	2972.9	3002 (s)
3151.4	13.3	3110.5	2979.9	3010 (s)
3216.5	0.0	3178.6	3045.1	3051 (m)
3228.5	14.8	3189.8	3055.9	3071 (m)
3244.2	10.8	3191.2	3057.2	3086 (m)

[a] Reference (Mitchell, 1971).

[b] Scaling coefficient = 0.958, Reference (Alecu *et al*., 2010).

The experimental intensities are: vs:very strong, s:strong, m:medium, w:weak.

Table 4 Calculated 1- methylcyclopropene (endo-en) vibrational frequencies (cm^{-1}).

CCSD		M06		
Vibration (cm^{-1})		Vibration (cm^{-1})		Experimental[a]
/aug-cc-PVDZ	IR intensity	/aug-cc-PVTZ	Scaled[b]	Vibration (cm^{-1})
160.97	0.3000	143.37	137.4	
275.08	12.4605	300.67	288.0	283 (m)
318.81	1.4226	318.11	304.8	331 (vw)
673.54	0.6498	705.00	675.4	665 (w)
679.17	33.4499	727.40	696.9	696 (s)
939.17	11.9482	927.80	888.8	919 (s)
984.08	6.6938	978.26	937.2	950 (vw)
987.86	1.4570	986.89	945.4	964 (w)
1039.37	0.0012	1046.67	1002.7	1032 (s)
1062.60	25.6835	1067.12	1022.3	1059 (w)
1085.48	6.3931	1089.38	1043.6	1097 (w)
1104.56	2.0195	1112.79	1066.1	1168 (w)
1201.86	3.4371	1198.36	1148.0	1308 (vw)
1401.49	0.1973	1389.51	1331.2	1390 (m)
1473.13	6.7772	1454.91	1393.8	1400 (vw)
1477.67	7.5558	1458.22	1397.0	1450 (m)
1520.42	4.7861	1501.61	1438.5	1487 (m)
1850.61	13.8669	1886.16	1806.9	1788 (m)
3039.29	26.6660	3011.79	2885.3	2895 (vs)
3061.23	69.8837	3017.07	2890.4	2929 (w)
3109.54	16.8448	3072.23	2943.2	2973 (vs)
3129.59	18.2207	3080.00	2950.6	3049 (w)
3131.70	43.5044	3104.02	2973.7	3071 (vw)
3294.24	0.1074	3243.54	3107.3	3133 (s)

[a] Reference (Mitchell, 1969).

[b] Scaling coefficient =0.958, Reference (Alecu *et al*., 2010).

The experimental intensities are vs:very strong, s:strong, m:medium, w:weak.

2.4 Frontier molecular orbitals

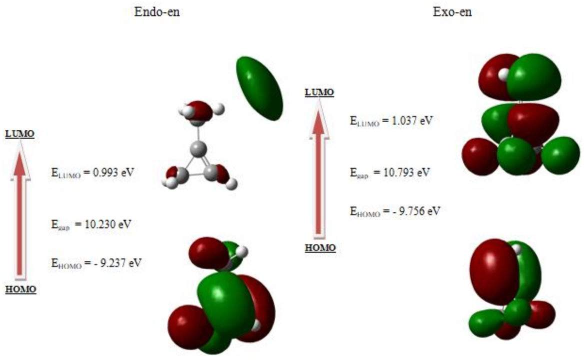

Fig. 2 Frontier molecular orbital of 1-methylcyclopropene (endo-en) and Methylenecyclopropane (exo-en) tautomers .

The frontier molecular orbitals (FMOs) of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of chemical species (using CCSD/aug-cc-PVDZ) are essential pointers for chemical reactivity together with the stability of compounds (**Figure 2**). The results revealed that the methylenecyclopropane tautomer showed higher LUMO and *HOMO* values, including their corresponding energy gap (E_{HOMO}=-9.756eV, E_{LUMO}=1.037eV, and E_{gap}=10.793eV). This implies superior stability and lower chemical reactivity compared to its 1-methylcyclopropene counterpart. The chemical potential (μ)=0.5 * (E_{LUMO}+E_{HOMO}); showed negative values for the methylenecyclopropane (-4.359eV) and 1-methylcyclopropene (-4.122eV) tautomes. The red and green colours indicate different lobes' phases. The red and green colours stand for the positive and negative signs of the molecular orbital wave function, respectively. The HOMO and LUM*O* spatial locations of the methylenecyclopropane and 1-methylcyclopropene are different. Using HOMO and LUMO orbital energies, the hardness η=0.5*(E_{LUMO}–E_{HOMO}) is as follows; methylenecyclopropane =5.397eV and 1-methylcyclopropene =5.115eV. The softness *S*=1/η; methylenecyclopropane =0.185eV and 1-methylcyclopropene =0.196eV. The chemical hardness implies a useful pointer for predicting chemical stability. The molecule with a small energy gap has a higher softness value. Global electrophilicity index $\omega=\mu^2/2\eta$ for methylenecyclopropane is more electrophilic than another tautomer with the highest electrophilicity index of 1.760eV. A good electrophile is the predictor of a high softness value and a low hardness value from the result's electrophilicity index.

2.5 Natural bond orbital (NBO) analysis

In **Tables 5** and **6** the perturbation energies of significant donor–acceptor interactions are comparatively presented for endo-en and exo-en tautomers. The larger the E^2 value, the more intense the interaction between electron donors and electron acceptors, *i.e.* the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system (Sebastian *et al.*, 2010).

Table 5 Second order perturbation energy ($E^{(2)}$) in NBO basis for 1-methylcyclopropene using CCSD/aug-cc-PVDZ basis set.

Donor(*i*)	ED/e	Acceptor(*j*)	ED/e	$E^{(2)}$ kcal/mol	E(*j*)-E(*i*) (a.u)	F(*i.j*(a.u)
σ(C1-C2)	1.94242	σ*(C3 - C4)	0.03520	36.21	1.34	0.198
σ(C1-C3)	1.93822	σ*(C2- H7)	0.03257	32.77	1.36	0.190
π(C2-C3)	1.92379	σ*(C1 - H5)	0.03164	17.32	1.05	0.122
π(C2-C3)	1.92379	σ*(C1- H6)	0.03164	17.32	1.05	0.122
σ(C1-C2)	1.94242	σ*(C1- C3)	0.03372	14.05	1.23	0.118
σ(C1-C3)	1.93822	σ*(C1-C2)	0.02267	13.88	1.23	0.118
σ(C4-H8)	1.98590	σ*(C1-C3)	0.03372	08.62	1.26	0.094
σ(C1-C2)	1.94242	σ*(C2-C3)	0.02065	08.25	01.6	0.103
σ(C1-C3)	1.93822	σ*(C2-C3)	0.02065	07.53	1.62	0.100
σ(C2-C3)	1.97039	σ*(C3-C4)	0.03520	06.87	1.61	0.094
σ(C4-H9)	1.98079	π*(C2-C3)	0.02646	06.01	0.93	0.067
σ(C4-H10)	1.98081	π*(C2-3)	0.02646	06.00	0.93	0.067
σ(C3-C4)	1.99286	σ*(C2-C3)	0.02065	04.79	1.82	0.084
σ(C2-C3)	1.97039	σ*(C2-H7)	0.03257	04.56	1.61	0.077
σ(C2-C3)	1.97039	σ*(C1-C3)	0.03372	04.26	01.5	0.071
σ(C4-H9)	1.98079	σ*(C2-C3)	0.02065	04.19	1.63	0.074
σ(C4-H10)	1.98081	σ*(C2-C3)	0.02065	04.19	1.63	0.074
σ(C2-C3)	1.97039	σ*(C1-C2)	0.02267	04.12	1.48	0.070
σ(C2-C3)	1.97039	σ*(C1-H5)	0.03164	03.56	1.61	0.068
σ(C2-C3)	1.97039	σ*(C1-H6)	0.03164	03.56	1.61	0.068

NBO analysis was performed to calculate the σ(C–C), σ(C–H) and π(C–C) bonding and antibonding orbital occupancies and also the stabilization energies (E^2) associated with σ(C–C) to σ*(C–C), to σ*(C–H) and to π*(C–C); σ(C–H) to σ*(C–C) and to π*(C–C); and π(C–C)→σ*(C–H) delocalizations (see Tables 5 and 6). 1-methylcyclopropene has nine σ (C–C)→σ*(C–C); the higher stabilization energy for the intramolecular interaction is formed by the orbital overlap between σ(C1-C2) and σ*(C3-C4); σ(C1-C3) and σ*(C1-C2); and σ(C2-C3) and σ*(C3-C4) with stabilization energy of about 36.21, 13.88 and 6.87kcal/mol, respectively. For methylenecyclopropane which has ten σ(C–C)→σ*(C–C), the higher stabilization energy for σ(C1-C2) and σ*(C3-C4); σ(C1-C3) and σ*(C1-C2) and σ(C2-C3) and σ*(C1-C2) with stabilization energy of about 28.64, 7.17 and 7.17kcal/mol, respectively, (Tables 5 and 6), which result into intermolecular charge transfer (ICT) causing stabilization of the two forms. The NBO results show that six sigma C−H bonds in methylenecyclopropane more than in 1-methylcyclopropene (five sigma C–H). From Tables 5 and 6, it is noted that the maximum occupancies are 1.99286, 1.98590, 1.98081 and 1.98079 are obtained for σ(C3 -C4), σ(C4-H8), σ(C4-H10), and σ(C4-H9) for 1-methylcyclopropene, respectively. the maximum occupancies for methylenecyclopropane are 1.99031, 1.98502, 1.98502, 1.98502, 1.98501, 1.98296 and 1.98296 are obtained for σ(C3-C4), σ(C1-H5), σ(C1-H6), σ(C2-H8), σ(C2 H7), σ(C4-H9) and σ(C4-H10) for methylenecyclopropane, respectively.

2.6 Electrostatic surface potential (ESP)

ESP parameters can be used to illustrate the electron-attracting and withdrawing power of substituents (Remya *et al.*, 2016). The red colour correlated the most negative electrostatic potential region, and the blue correlated with the most positive electrostatic potential region (**Figure 3**). ESP at the CCSD/aug-cc-PVDZ optimized geometry was calculated. The ESP colour outline is as follows: red for electron-rich, partly negative charge; blue for electron-deficient, partly positive charge; light blue for the slightly electron-deficient region; yellow for the slightly electron-rich region and green denotes neutral.

Besides, the maximum positive region favoured nucleophilic attack (blue colour), whereas the maximum negative region favoured electrophilic attack (red colour). The electron-rich area for both tautomers is located on the double bond. By comparison, the electrostatic potential (ESP) surface for the two tautomers revealed that the negative potentials (red colour) were spread over the electronegative double bond; meanwhile, the deep blue was detected on the hydrogen atoms. The green colour explained the neutral electrostatic potential surface for the compounds.

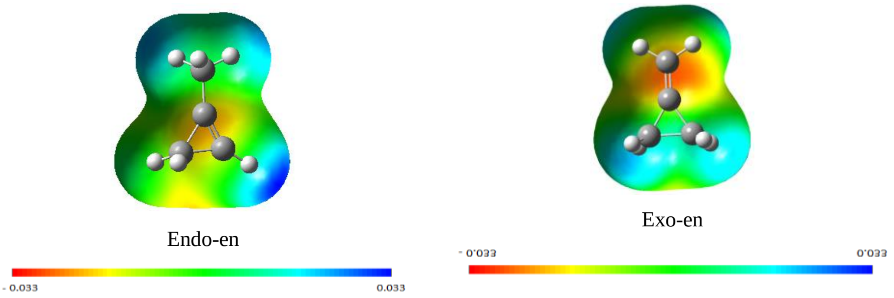

Fig. 3 Electrostatic surface potential of 1-methylcyclopropene (endo-en), and Methylenecyclopropane (exo-en) tautomers.

Table 6 Second order perturbation energy ($E^{(2)}$) in NBO basis for methylenecyclopropane using CCSD/aug-cc-PVDZ basis set.

Donor(*i*)	ED/e	Acceptor(*j*)	ED/e	$E^{(2)}$ kcal/mol	$E(j)$-$E(i)$ (a.u)	$F(i.j)$(a.u)
σ(C1-C2)	1.95408	σ*(C3- C4)	0.02800	28.64	1.62	0.193
σ(C4-H9)	1.98296	σ*(C2-C3)	0.02874	11.54	1.34	0.111
σ(C4-H10)	1.98296	σ*(C1-3)	0.02874	11.54	1.34	0.111
σ(C1-C2)	1.95408	σ*(C1-C3)	0.02874	09.76	1.30	0.101
σ(C1-C2)	1.95408	σ*(C2-C3)	0.02874	09.76	1.30	0.101
σ(C1-C3)	1.96180	σ*(C1-C2)	0.02150	07.17	1.28	0.086
σ(C2-C3)	1.96180	σ*(C1-C2)	0.02150	07.17	1.28	0.086
σ(C1-C3)	1.96180	σ*(C3-C4)	0.02800	05.77	1.72	0.089
σ(C2-C3)	1.96180	σ*(C3-C4)	0.02800	05.77	1.72	0.089
σ(C3-C4)	1.99031	σ*(C1-C3)	0.02874	03.99	1.65	0.073
σ(C3-C4)	1.99031	σ*(C2-C3)	0.02874	03.99	1.65	0.073
σ(C1-C3)	1.96180	σ*(C2-H8)	0.01179	03.86	1.44	0.067
σ(C1-H5)	1.98502	π*(C3-C4)	0.03400	03.86	0.94	0.054
σ(C1-H6)	1.98502	π*(C3-C4)	0.03400	03.86	0.94	0.054
σ(C2-C3)	1.96180	σ*(C1-H5)	0.01179	03.86	1.44	0.067
σ(C2-H7)	1.98501	π*(C3-C4)	0.03400	03.86	0.94	0.054
σ(C2-H8)	1.98502	π*(C3-C4)	0.03400	03.86	0.94	0.054
σ(C1-C3)	1.96180	σ*(C2-H7)	0.01179	03.85	1.44	0.067
σ(C2-C3)	1.96180	σ*(C1-H6)	0.01179	03.85	1.44	0.067
σ(C1-C3)	1.96180	σ*(C2-C3)	0.02874	03.24	1.41	0.060

Conclusions

The geometry and relative stability of the two tautomers, 1-methylcyclopropene (endo-en) and methylenecyclopropane, has been calculated theoretically using two DFT functionals (B3LYP and M06) and ab initio with 6-31+*G(d)*, aug-cc-PVTZ and aug-cc-PVDZ polarized basis sets. Exo-en is the most stable isomer, according to recent study findings, which are in line with the existing experimental data. Additionally, the outcomes of the geometrical optimizations are in strong accord with earlier findings that have been reported in the literature. Additionally, the tautomerism operation contained the geometry of the transition state connecting the two isomers. It can be inferred that the process is vigorous and unlikely to happen at room temperature without a catalyst. The outcomes are well-aligned with the data discovered both with and without the use of the scaling coefficient. The two isomers' vibrational modes were then calculated and compared to earlier experimental values reported in the literature. Additionally, this conformation has a wider HOMO-LUMO gap of 10.793eV, which further attests to its notable stability. The NBO analysis has shown that the strongest stability for both tautomers is provided by the σ C-C and C-H bonding and σ*C-C and C-H antibonding interactions. The ESP map reveals that the positive potential sites are located near the hydrogen atoms, whereas the negative potential sites are on doubly bonded structures. These websites might offer details on potential reaction zones for the term tautomers. The study of factors that can control the predominant tautomerization direction of the two compounds such as temperature, pressure, volume or catalysts represents a new tool for storage operators for the management of fruit quality in the post-harvest environment.

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Nomenclature

B3LYP	=Becke, 3-parameter, Lee–Yang–Parr	[-]
c°	=Concentration	[mol/l]
CCSD	=Coupled-Cluster with Singles and Doubles	[-]
cc-PVDZ	=Correlation consistent-Plarized Valence Double Zeta	[-]
cc-PVTZ	=Correlation consistent-Plarized Valence Triple Zeta	[-]
DFT	=Density Functional Theory	[-]
DMSO	=Dimethylsulfoxide	[-]
E_o	=The zero point energy	[kcal/mol]
E_{gap}	=Energy gap	[kcal/mol]
$E^{(2)}$	=Second order perturbation energy	[kcal/mol]
εi , εj	=Diagonal elements (orbital energies)	[kcal/mol]
ED/e	=Orbital occupancy	[-]
ESP	=The Electrostatic Potential	[-]
η	=Hardness	[eV]
$F(i,j)$	=The off-diagonal NBO Fock matrix element	[kcal/mol]
FMO	=The frontier molecular orbital	[-]
G	=Gibbs energy	[kcal/mol]
G_{cor}	=The thermal correction of the Gibbs free energy	[kcal/mol]
ΔG^{o}	=Gibbs free energy	[kcal/mol]
$\Delta G^{\#}$	=Gibbs free energy of activation	[kcal/mol]
ΔG_{com}	=Comparative isomerization Gibbs free energy	[kcal/mol]
H	=Enthalpy	[kcal/mol]
H_{cor}	=The thermal correction of the enthalpy	[kcal/mol]
h	=Planck constant	[J.s]
ΔH_{com}	=Comparative isomerization enthalpy	[kcal/mol]
ΔH_f^{o}	=Heat of formation	[kcal/mol]
HOMO	=Highest Occupied Molecular Orbital	[-]
ICT	=Intermolecular charge transfer	[-]
IR	=Infrared	[-]
k_B	=Boltzmann constant	[J/K]
k_f	=Rate constant for the forward reaction	[s^{-1}]
K_{eq}	=Equilibrium constant	[-]
k_r	=Rate constant for the backward reaction	[s^{-1}]
LUMO	=Lowest Unoccupied Molecular Orbital	[-]
m	=Medium	[-]
1-MCP	=1-methylcyclopropene	[-]
M06	=Minnesota 06 functional	[-]
NBO	=Natural Bond Orbital	[-]
QST2	=Quadratic Synchronous Transit	[-]
qi	=The donor orbital occupancy	
R	=Universal gas constant	[J/(K.mol)]
S	=The softness	[eV]
s	=Strong	[-]
ΔSE	=Strain energy difference	[kcal/mol]
T	=Temperature	[K]
TS	=Transition state	[-]
μ	=The chemical potential	[eV]
vs	=Very strong	[-]
w	=Weak	[-]
ω	=Global electrophilicity index	[eV]

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