

# A Study effect of Substituents X on Methylene cyclopentane and 1-Methylcyclopentene System

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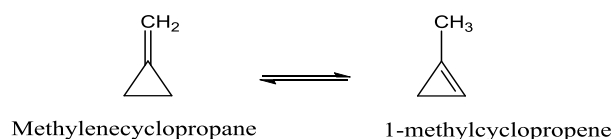
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In this study, the geometry optimizations, orbital energies (HOMO-LUMO) and relative stabilities of methylene cyclopentane and 1-methylcyclopentene were investigated by DFT calculations. 1-methylcyclopentene was found to be more stable than methylene cyclopentane isomer with enthalpy value  $H=18.518$  kJ/mol. Also, the effect of substituents X (F, OH, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) also studied on the relative stabilities of these two tautomers. The results showed that the stability of both isomers is increased by all substituents. Gibbs free energy calculations have been used to find the effect of substituents X on the system.

Keywords: methylene cyclopentane, 1-methylcyclopentene, substituent, tautomer, DFT

## Introduction

Tautomerism is a constitutional isomer, where one or a group of atoms can be moved to provide a new form that differs from initial instability (Moradi *et al.*, 2012). Currently, the system with a transfer proton between the two-tautomer is important in mechanistic chemistry and industrial synthesis (Sway *et al.*, 2004). Methylene cyclopropane/1-methylcyclopropene system (**Scheme 1**) has been studied by DFT/B3LYP; and it was found that methylene cyclopropane is more stable than 1-methylcyclopropene by 11.535 kcal/mol (Khalil, 2008). This agreed with a calculated Gibbs free energy,  $\Delta G$  for the system ( $\Delta G = 11.615$  kcal/mol), which indicates that this system is non-spontaneous; and methylene cyclopropane is more stable than 1-methylcyclopropene. Also, it was found that an increase in the number of substituting fluorine atoms causes a destabilization of methylene cyclopropane.



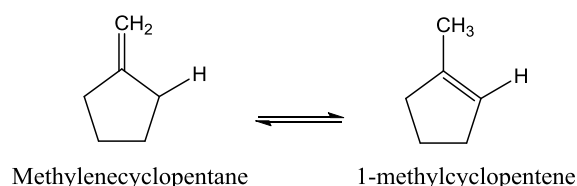
**Scheme 1**

This system was compared to fluorinated Cyclopropanone Keto-Enol and Fluorinated Methylene cyclopentane/1-Methylcyclopentene system. It was found that an increase in the number of fluorine atoms causes a destabilization of cyclopropanone and methylene cyclopentane (El-Alali *et al.*, 2003). Both experimental data and quantum mechanical calculations indicate that fluorination strongly destabilize the acyclic alkenes and the forward reaction less favorable. Theoretical calculations show that multiple fluorination strongly destabilizes a double bond, but a single fluorine atom stabilizes a double bond by an amount near to methyl group (2-3 kcal/mol) (Lindner *et al.*, 1997; Smart, 1986).

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Parameterized Model number 3 PM3 and DFT (Density Functional Theory) calculations were performed on the methylene cyclobutane, 1-methylcyclobutene with different substituents X (F, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) in the gas and aqueous phases. The results show that methylene cyclobutane is more stable than 1-methylcyclobutene in the gas and aqueous phases. Also, it is found that the stability of 1-methylcyclobutene increases by all substituents (Al-Mazaideh *et al.*, 2016). DFT is the most accurate method in chemical calculations, where DFT at the B3LYP/6-311G basis set level and semiempirical methods (PM3, AM1, and MINDO/3) are applied using G03 on six new substituted Schiff bases derivatives of INHC (N-(3-(phenylidene-allylidene) isonicotino-hydrazide). In addition, it is found that DFT calculations of vibration frequencies and IR absorption intensities for these new INHC Schiff bases derivative molecules give very good assignment values in comparison to the experimental values (Kubba and Abood, 2015). Optimized geometries of stepwise fluorinated methylenecyclopentane and 1-methylcyclopentene are determined by DFT; and it is found that 1-methylcyclopentene is more stable than methylenecyclopentane by 5.612 kcal/mol (**Scheme 2**). Perfluorination of 1-methylcyclopentene is found to be present in substantial concentration (Al-Mazaideh *et al.*, 2016). Recently (Wedian and Al-Qudaha, 2016; Al-Msiedeem *et al.*, 2016; Al-Mazaideh *et al.*, 2017; Al-Mazaideh *et al.*, 2016; Al-Mazaideh *et al.*, 2016; Khalil *et al.*, 2016; Al-Mazaideh, 2017; Al-Mazaideh, Al-Quran, 2018), DFT has been applied on the corrosion inhibitors of metals; and very satisfactory results reached.



**Scheme 2**

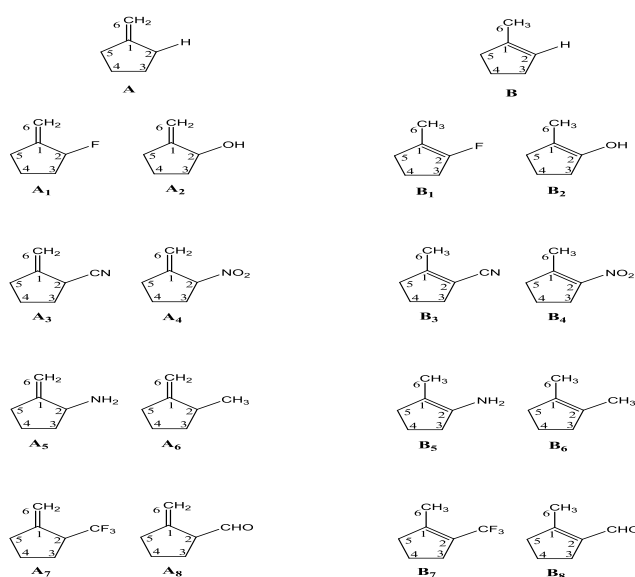
The aim of this work is to give more theoretical insights to the problem of tautomerism of methylenecyclopentane and 1-methylcyclopentene by calculating the effects of substituents X (F, OH, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) on the relative stabilities of these two tautomers. Gibbs free energy ( $\Delta G$ ) has been used to calculate and give indications about the spontaneity of the system. Dipole moments and the optimized geometries will be reported for the first time using DFT calculations.

### 1. Materials and Methods

DFT calculations of methylenecyclopentane and 1-methylcyclopentene tautomerism and the effects of substituents X (F, OH, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) on the relative stabilities of these two tautomers have been investigated by using the Gaussian 03 package program (Frisch *et al.*, 2003). The geometry and molecular energy of target compounds are completely minimized by DFT at the hybrid level of the three-parameter function of Becke (B3LYP) with 6-31G\* (d, p) basis set in G03 program. In this work, the structures of the parent compounds have been designed by using Chem Office 2008 software. The final optimization of the methylenecyclopentane and its counterpart together with different substituents have been calculated and investigated by DFT method which is operated in theory of the levels B3LYP/6-31G\*.

### 2. Results and Discussion

All DFT calculations of the structural geometry of Methylenecyclopentane and 1-methylcyclopentene and their derivatives (**Figure 1**) are carried out using the B3LYP/6-31G\* basis set. Bond lengths and angles of all optimized compounds calculated in a gaseous state. These data are given in **Tables 1** and **2**.



**Fig. 1** Molecular structure of substituted methylene cyclopentane (A) and 1-methylcyclopentene (B)

The effect of substituents X on both parent structures shows that some C-C bonds have not been influenced. Methylene cyclopentane has been the most distinction bond length of C1-C2 on molecule A3 where the maximum difference value is at  $0.017\text{Å}$ . 1-methylcyclopentene has the most distinction bond length of C1-C2 on molecule B8 where the maximum difference value is at  $0.015\text{Å}$ . Thus C-C bond length dissimilarity is not significant for all derivatives of parent compounds. It is clear from Table 1 that there is no variation between bond length in methylene cyclopentane and its substituted derivatives and their counterparts in the 1-methylcyclopentene compounds, except for the bonds C1-C6 and C1-C2 in compound A and B, where the variation in these bond lengths in all derivatives result from the existence of conjugation.

## 2.1 Orbital Energies (HOMO and LUMO) of parent compounds and their derivatives

**Table 1** Calculated bond lengths for methylene cyclopentane / 1-methylcyclopentene and their derivatives

Molecule	Bond distance (Å)								
	C1-C6	C1-C2	C2-C3	C3-C4	C4-C5	C5-C1	C2-X		
<b>A</b>	1.333	C1=C6	1.526	C1-C2	1.543	1.540	1.543	1.526	<b>3.336</b> C2-H
<b>A1</b>	1.333	C1=C6	1.517	C1-C2	1.527	1.542	1.547	1.525	1.411 C2-F
<b>A2</b>	1.335	C1=C6	1.523	C1-C2	1.531	1.542	1.547	1.524	1.438 C2-OH
<b>A3</b>	1.331	C1=C6	1.543	C1-C2	1.555	1.537	1.541	1.522	1.471 C2-CN
<b>A4</b>	1.332	C1=C6	1.532	C1-C2	1.535	1.540	1.541	1.521	1.528 C2-NO <sub>2</sub>
<b>A5</b>	1.333	C1=C6	1.532	C1-C2	1.549	1.540	1.541	1.515	1.474 C2-NH <sub>2</sub>
<b>A6</b>	1.334	C1=C6	1.532	C1-C2	1.549	1.540	1.542	1.524	1.541 C2-CH <sub>3</sub>
<b>A7</b>	1.333	C1=C6	1.534	C1-C2	1.551	1.540	1.539	1.521	1.522 C2-CF <sub>3</sub>
<b>A8</b>	1.334	C1=C6	1.539	C1-C2	1.554	1.543	1.539	1.517	1.517 C2-CHO
<b>B</b>	1.499	C1-C6	1.339	C1=C2	1.511	1.552	1.549	1.518	<b>3.199</b> C2-H
<b>B1</b>	1.496	C1-C6	1.334	C1=C2	1.500	1.551	1.557	1.515	1.351 C2-F
<b>B2</b>	1.497	C1-C6	1.341	C1=C2	1.509	1.548	1.553	1.514	1.372 C2-OH
<b>B3</b>	1.495	C1-C6	1.350	C1=C2	1.521	1.549	1.548	1.513	1.425 C2-CN
<b>B4</b>	1.495	C1-C6	1.348	C1=C2	1.507	1.548	1.549	1.516	1.445 C2-NO <sub>2</sub>
<b>B5</b>	1.499	C1-C6	1.348	C1=C2	1.513	1.545	1.549	1.515	1.400 C2-NH <sub>2</sub>
<b>B6</b>	1.500	C1-C6	1.345	C1=C2	1.518	1.547	1.547	1.518	1.500 C2-CH <sub>3</sub>
<b>B7</b>	1.499	C1-C6	1.344	C1=C2	1.518	1.547	1.545	1.519	1.492 C2-CF <sub>3</sub>
<b>B8</b>	1.498	C1-C6	1.354	C1=C2	1.515	1.548	1.548	1.515	1.463 C2-CHO

In Table 2, the effect of substituent X on bond angle has no significance. On the other hand, in all derivatives of both parent compounds, a fluctuation exists among many bond angles that go from 0.01 degrees to 1.79 degrees for methylenecyclopentane compounds; and from 0.03 degrees to 3.57 degrees for 1-methylcyclopentene. For the methylenecyclopentane compounds, the bond angle C6–C1–C5 on molecule **A4** has the maximum value of 127.55 degrees. For 1-methylcyclopentene compounds the bond angle C6–C1–C2 on molecule **B7** has the maximum value of 130.84 degrees. In addition, C3–C4–C5 and C2–C3–C4 bond angles on molecules **A5** and **B1** are found to have the minimum value at 102.92 and 101.29 degrees compared to other compounds.

**Table 2** Calculated bond angle for methylenecyclopentane / 1-methylcyclopentene and their derivatives

Molecule	Bond angle in degree (°)						
	C6–C1–C2	C6–C1–C5	C2–C1–C5	C1–C2–C3	C2–C3–C4	C3–C4–C5	C4–C5–C1
<b>A</b>	<b>125.78</b>	<b>125.78</b>	<b>108.44</b>	<b>104.70</b>	<b>103.48</b>	<b>103.48</b>	<b>104.70</b>
<b>A1</b>	124.18	127.30	108.51	104.27	103.11	103.69	104.73
<b>A2</b>	124.15	127.19	108.65	103.73	103.37	103.87	104.90
<b>A3</b>	124.43	127.08	108.49	103.94	103.69	103.40	104.76
<b>A4</b>	124.14	127.55	108.30	105.38	104.89	103.47	104.56
<b>A5</b>	124.73	126.40	108.79	104.48	105.24	102.92	103.28
<b>A6</b>	125.27	125.60	109.13	103.67	104.31	103.23	104.66
<b>A7</b>	125.24	126.02	108.74	104.59	104.70	103.47	104.67
<b>A8</b>	124.39	126.82	108.73	104.61	105.27	103.52	103.83
<b>B</b>	<b>127.27</b>	<b>121.85</b>	<b>110.83</b>	<b>112.84</b>	<b>102.87</b>	<b>105.28</b>	<b>103.70</b>
<b>B1</b>	127.04	124.06	108.85	115.93	101.29	105.92	104.22
<b>B2</b>	126.72	123.29	109.90	113.80	102.28	105.34	103.95
<b>B3</b>	127.37	122.33	110.27	112.72	102.51	105.31	104.14
<b>B4</b>	130.58	120.81	108.57	114.62	101.79	105.20	104.77
<b>B5</b>	127.56	121.76	110.55	112.28	103.02	104.95	103.63
<b>B6</b>	128.43	120.15	111.38	111.38	103.82	104.80	103.82
<b>B7</b>	130.84	119.20	109.92	112.78	102.84	104.80	104.34
<b>B8</b>	129.10	120.34	110.52	112.10	103.16	104.94	104.02

The introduction of substituents into methylene cyclopentane and 1-methylcyclopentene slightly affects their orbital energies (HOMO and LUMO) compared to parent compounds. In the case of methylene cyclopentane derivatives (**Table 3**), substitution causes a decrease in the energy gaps ( $E_g$ ), suggesting consequently a decrease in the stability of these compounds. An exception is for the substituent  $CF_3$ , which causes a little increase in  $E_g$ .

Similarly, different substituents of 1-methylcyclopentene cause a decrease in  $E_g$  except for the case of structure **B1**. The introduced F atom results in a slight increase in  $E_g$ . In general, the change in  $E_g$  for all investigated structures is not significant in energy gaps for all substituents.  $E_g$  value can be calculated by  $E_{HOMO} - E_{LUMO}$  for the investigated compounds. The  $E_g$  value for methylene cyclopentane was found to be 6.947 eV compared to 7.086eV for 1-methylcyclopentene. This indicates that methylene cyclopentane is more stable than 1-methylcyclopentene by 0.139 eV.

$E_g$  values can be used to investigate and show the effect of substituents on the stability of parent compounds.  $E_g$  values are given in **Table 3** for all compounds. According to these calculations, the substituents X increase the stability of 1-methylcyclopentene, where the differences in  $E_g$  are greater than in the derivatives of methylenecyclopentane except in the case of adding of fluorine (F). B1 has greater  $E_g$  (7.097 eV) than A1 (6.900 eV) by 0.197 eV. As a result, the effect of substituent X on the stability of methylenecyclopentane according to  $E_g$  values is arranged as follows:



Their effect on the stability of 1-methylcyclopentene is arranged as follows:



**Table 3** Calculated orbital energies (HOMO and LUMO, in eV) of methylenecyclopentane / 1-methylcyclopentene and their derivatives

Compound	HOMO	LUMO	$E_g$	$\mu$ (D)
A	-6.3475	0.5999	6.9474	0.59
A1	-6.9251	-0.0243	6.9008	1.74
A2	-6.7656	0.1809	6.9465	1.29
A3	-7.1002	-0.2078	6.8924	4.13
A4	-7.1719	-1.7287	5.4432	3.73
A5	-6.1721	0.4716	6.6437	1.18
A6	-6.3775	0.5680	6.9455	0.51
A7	-6.8704	0.1026	6.9730	2.20
A8	-6.5462	-0.5762	5.9700	3.14
B	-6.0755	1.0108	7.0863	0.23
B1	-6.0041	1.0934	7.0975	1.38
B2	-5.3363	1.4465	6.7828	1.65
B3	-6.7566	-0.8872	5.8694	4.60
B4	-7.1802	-2.1280	5.0522	4.76
B5	-4.9526	1.5278	6.4804	1.33
B6	-5.8312	1.0793	6.9105	0.14
B7	-6.7961	-0.0037	6.7924	2.68
B8	-6.5829	-1.3549	5.2280	3.87

**Table 4** Calculated entropy S, enthalpy H and Gibbs free energy of methylenecyclopentane / 1-methylcyclopentene and their derivatives

Compound	H° (kJ/mol)	S° (J/mol.K)	G° (kJ/mol)
A	<b>-615650.88</b>	<b>304.00</b>	<b>-615741.52</b>
A1	-876200.13	326.66	-876297.53
A2	-813097.42	331.85	-813196.37
A3	-857820.32	341.18	-857922.04
A4	-1152555.24	353.43	-1152660.60
A5	-760899.01	333.41	-760998.41
A6	-718791.87	336.13	-718892.09
A7	-1500527.70	370.00	-1500638.01
A8	-913131.51	345.97	-913234.66
B	<b>-615669.40</b>	<b>317.03</b>	<b>-615763.92</b>
B1	-876226.56	335.41	-876327.35
B2	-813133.32	341.78	-813235.22
B3	-857869.89	349.73	-857974.16
B4	-1152581.90	362.10	-1152689.93
B5	-760952.99	340.95	-761054.65
B6	-718825.69	344.67	-718928.45
B7	-1500546.30	380.10	-1500659.66
B8	-913178.76	354.07	-913284.33

## 2.2 Dipole Moment of parent compounds and their derivatives


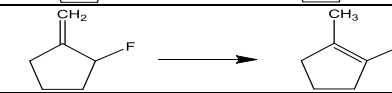
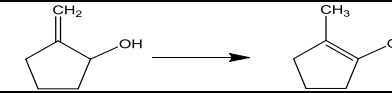
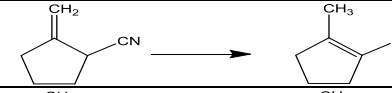
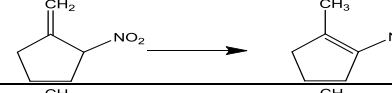
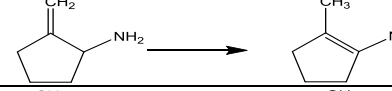
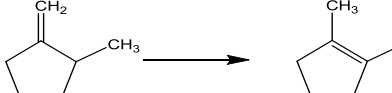
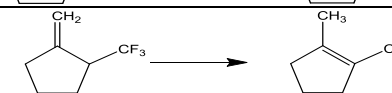
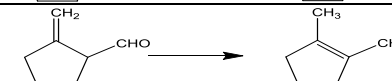
The introduction of substituent X (F, OH, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) into methylene cyclopentane and 1-methylcyclopentene counterpart has also affected their dipole moment as compared to the parent compounds. This change in dipole moment is attributed to the change in the structural parameters and electronic structure of these derivatives. Table 3 shows a change in dipole moments for these compounds, where the dipole moment slightly decreases in the case of CH<sub>3</sub> from 0.59 Debye for parent compound to 0.51 Debye for CH<sub>3</sub> compound. Increases also occur for the rest of substituents. All substituents for 1-methylcyclopentene shows increasing in the dipole moment values except in the case of CH<sub>3</sub> (0.14 Debye) compared to its parent compound (0.23 Debye).

## 2.3 Thermodynamic calculation of parent compounds and their derivatives:

### 2.3.1 Parent compound:

Based on **Table 4**, the enthalpy of 1-methylcyclopentene B is lower than methylenecyclopentane A (Scheme 2), suggesting that B is more stable than A by 0.007053 *Hartrees* (18.518 kJ/mol). Moreover, substituents X increased the stability of compound B as compared to A. This is confirmed by thermodynamic calculations (Table 5), that showed a negative Gibbs free energy ( $\Delta G_r^\circ = -22.401$  kJ/mol). They further indicate that 1-methylcyclopentene (B) is more stable than methylenecyclopentane A. This value of  $\Delta G_r^\circ$  (-22.401 kJ/mol) is less than that of methylenecyclopropane ( $\Delta G_r^\circ = 48.597$  kJ/mol) and methylenecyclopentane ( $\Delta G_r^\circ = 27.719$  kJ/mol) (Al-Mazaideh *et al.*, 2016) tautomerism. This result has been found due to lowering in the ring strain of the 1-methylcyclopentene (five-member ring) with respect to three and four-member rings. Stabilization of 1-methylcyclopentene agrees with the reported study on methylenecyclopentane / 1-methylcyclopentene system (Al-Mazaideh *et al.*, 2016).

**Table 5** Gibbs free energy ( $\Delta G$ ) of substituted methylenecyclopentane and 1-methylcyclopentene and their derivatives

No.	Tautomerism	$\Delta G_r^\circ$ (kJ/mol)
Parent		-22.401
1		-29.820
2		-38.857
3		-52.121
4		-29.311
5		-56.238
6		-36.366
7		-21.597
8		-49.672

### 2.3.2 Effect of substituents

Introduction of the substituents on the methylenecyclopentane and 1-methylcyclopentene system shows that a negative value of  $\Delta G_r^\circ$  can be obtained for all reactions (Table 5). The calculated values are less than those of methylenecyclopentane and 1-methylcyclopentene system. They indicate a spontaneous reaction as substitution increases the stability of 1-methylcyclopentene as compared to methylenecyclopentane. This conclusion is supported with smaller enthalpy values of all 1-methylcyclopentene substituents compared to methylenecyclopentane substituents (Table 4).

### Conclusions

The present study has investigated the effects of substituents X (F, OH, CH<sub>3</sub>, NH<sub>2</sub>, CN, NO<sub>2</sub>, CHO and CF<sub>3</sub>) on methylenecyclopentane and 1-methylcyclopentene system. The results of DFT method used in this study show that the 1-methylcyclopentene is more stable than methylenecyclopentane by 18.518 kJ/mol. The variation between bonds length of methylenecyclopentane compounds and their counterparts in the 1-methylcyclopentene compounds is due to conjugation for both C1-C6 and C1-C2. Yet, the other bond lengths have no variation. In all derivatives of both parent compounds, a fluctuation exists among many bond angles. All substituents have been found to influence on methylenecyclopentane and 1-methylcyclopentene by directing the reaction forward to products and stabilizing the 1-methylcyclopentene as explained by thermodynamic calculations.

## Nomenclature

$E_{\text{HOMO}}$	=Energy of highest occupied molecule orbital	[eV]
$E_{\text{LUMO}}$	=Energy of lowest un-occupied molecular orbital	[eV]
$\Delta H$	=Enthalpy	[kJ/mol]
<b>DFT</b>	=Density Functional Theory	[-]
<b>B3LYP</b>	=Becke, 3-parameter, Lee-Yang-Parr	[-]
$\Delta G$	=Gibbs free energy	[kJ/mol]
<b>PM3</b>	=Parameterized Model number 3	[-]
<b>AM1</b>	=Austin Model 1	[-]
<b>MINDO</b>	=Modified Intermediate Neglect of Differential Overlap	[-]
<b>G03</b>	= Gaussian 2003	[-]
$E_g$	=Energy gap	[eV]
$\mu$	=Dipole moment	[Debye, D]
<b>S</b>	=Entropy	[J/mol.K]

## References

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