

Effect of Substituents on Methylene cyclobutane / 1-Methylcyclobutene System

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

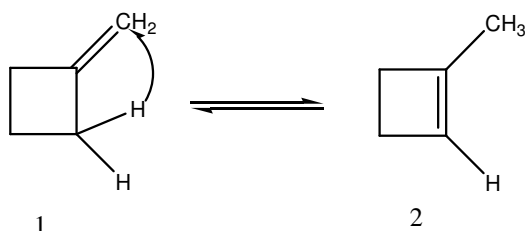
A theoretical study was performed on the methylenecyclobutane and 1-methylcyclobutene in the gas and aqueous phases using PM3 and DFT calculations. Methylenecyclobutane was found to be more stable than 1-methylcyclobutene in the gas and aqueous phases according to PM3 calculations, and only slightly more stable than 1-methylcyclobutene in the case of DFT calculations. Also the effect of substituents (X = F, CH₃, NH₂, CN, NO₂, CHO and CF₃) was studied on the relative stabilities of these two tautomers. It was found that all the substituents increase the stability of 1-methylcyclobutene in the gas and aqueous phases. Heats of formation, and electron densities, were reported. The stability effect of X- substituents on the methylenecyclobutane and 1-methylcyclobutene was explained by Gibbs free energies calculations and confirmed by isodesmic reactions.

Keywords: Cyclic alkene; tautomerism; PM3; DFT; substituents.

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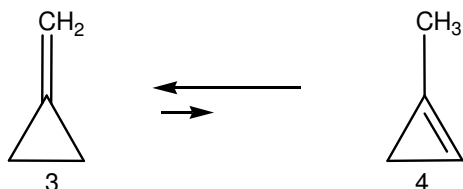
1. INTRODUCTION

Process involving proton transfers between interconversion tautomers are of fundamental importance in synthetic and mechanistic chemistry [1]. Tautomerism is a prototropic rearrangement in which a hydrogen atom migrates to exo- C=C double bond for example in methylenecyclobutane **1** to form 1-methylcyclobutene **2** as shown in scheme 1.



Scheme 1. Methylenecyclobutane / 1-methylcyclobutene tautomerism

The subject of tautomerism has been extensively reviewed, but it is receiving renewed interest because of improved experimental and theoretical methods [2]. Recently [3], methylenecyclopropane / 1-methylcyclopropene system (Scheme 2) has been studied and shown that methylenecyclopropane **3** is more stable than 1-methylcyclopropene **4**.



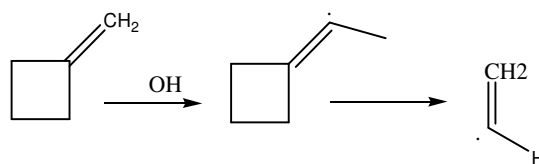
Scheme 2. Methylenecyclopropane / 1-methylcyclopropene system

This was confirmed by a positive Gibbs free energy (11.615 kcal/mol), which indicates that this system is non-spontaneous and compound **3** is more stable than **4**.

In regard to the effect of methylene group on the four-member ring (compound **1**), much work has been done by the reaction of methylenecyclobutane **1** with hydroxyl radicals to decompose to vinyl radical [4] (Scheme 3).

Also, work has been done on degenerate rearrangement of methylenecyclobutane by the synthesis and heating of dideuteromethylenecyclobutane [5], gas

photolysis of methylenecyclobutane [6], reaction of methylenecyclobutane with PdCl₂ [7], and theoretical study of thermal degenerate rearrangement in methylenecyclobutane [8], but no work was done on the tautomerism and effect of substituents as far as the literature is concerned.



Scheme 3. Decomposition of four-member ring

The aim of this paper is to extend our work on the effect of methylene group on the four-member ring and to give more theoretical insight to the problem of the tautomerism of methylenecyclobutane / 1-methylcyclobutene. In addition, the effect of substituents X (X = F, NH₂, CH₃, CN, NO₂, CF₃ and CHO) were studied in the gas phase and aqueous environment using semi-empirical PM3 [9] and DFT/B3LYP methods using G03 at 6-31G (d) main set in the MOPAC program, version 8.3 (2004) Cambridge Soft Corporation [10].

2. RESULTS AND DISCUSSION

Theoretical calculations (PM3 and DFT method) were carried out with complete optimization of geometries on methylenecyclobutane and 1-methylcyclobutene at temperature 298.15 K in the gas ($\epsilon = 1.00$) and aqueous ($\epsilon = 78.4$) phase.

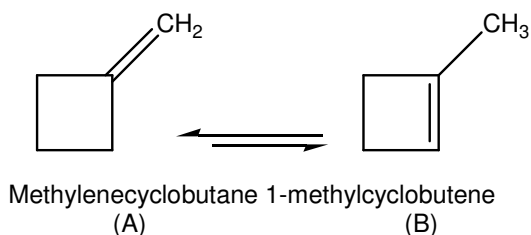
2.1 PM3 Calculations

Calculations are first performed on the methylenecyclobutane and 1-methylcyclobutene without substitution, and then on the substituted parent compound at temperature 298.15 K.

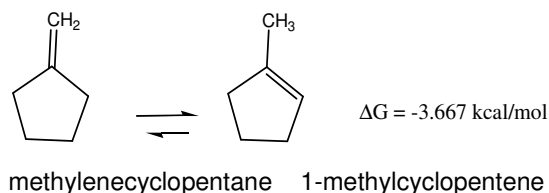
2.1.1 Parent compounds (methylenecyclobutane and 1-methylcyclobutene)

2.1.1.1 Tautomerism

The calculated heat of formation of methylenecyclobutane ($\Delta H_f = 19.599$ kcal/mol) in the gas phase is less than that of 1-methylcyclobutene ($\Delta H_f = 26.848$ kcal/mol), which suggests that methylenecyclobutane is the more stable. This is supported by calculated Gibbs free energies of the tautomerization.



The Gibbs free energies of the tautomerization (ΔG_r) at 298.15 K were predicted by adding the heat of formation (ΔH_f) and entropic ($-T\Delta S$) terms. The calculated value of the Gibbs free energy (G_A) of compound (A) is $G_A = -0.954$ kcal/mol (Table 1) and that of (B) is $G_B = 5.227$ kcal/mol. The Gibbs free energy for the tautomerization ΔG_r ($\Delta G_r = G_B - G_A$) is 6.182 kcal/mol which is less than that of methylenecyclopropane [3]. This is because the ring strain of the 1-methylcyclobutene is less than that of 1-methylcyclopropene which causes a decrease in free energies from three-member ring to four-member ring. Recently [11], it was found that ΔG_r for tautomerization of methylenecyclopentane / 1-methylcyclopentene ($\Delta G_r = -3.667$ kcal/mol) is less than that of the present result (methylenecyclobutane / 1-methylcyclobutene), which suggests a decrease in ring strain in going from 1-methylcyclobutene to 1-methylcyclopentene.



Similar thermodynamic calculations of the Gibbs free energies ΔG_r of cyclopropanone /cyclopropanol [12], cyclobutanone /cyclobutenol [1], and cyclopentanone /cyclopentenol [13] show that the values of ΔG_r are 17.509 kcal/mol, 7.792 kcal/mol and 5.311 kcal/mol, respectively. From these values it can be seen that ΔG_r decrease from three-member ring, to the four and five-member ring, suggesting an increase of the enol tautomer when going from three-member ring to five-member ring. This is due to a decrease in the ring strain of the enol tautomer when going from the three to five-member ring [14].

In the aqueous phase, the calculated heat of formation of methylenecyclobutane (18.062 kcal/mol) is less than that of 1-methylcyclobutene ($\Delta H_f = 24.925$ kcal/mol), which suggests that methylenecyclobutane is the more stable. The calculated value of the Gibbs free energy (G_A) of

compound (A) is $G_A = -2.594$ kcal/mol and that of (B) is $G_B = 4.030$ kcal/mol. The Gibbs free energy for the tautomerization ΔG_r ($\Delta G_r = G_B - G_A$) is 6.625 kcal/mol. This (ΔG_r) is very close to that calculated in the case of the gas phase ($\Delta G_r = 6.182$ kcal/mol). The ΔG_r ($\Delta G_r = 6.182$ kcal/mol) of methylenecyclobutane /1-methylcyclobutene will be taken as reference for determining the relative stability of substituted methylenecyclobutane and 1-methylcyclobutene tautomerism.

2.1.2 Effect of substituents

The semi-empirical PM3 method was used to calculate the optimized geometrical parameters of substituted methylenecyclobutane and 1-methylcyclobutene. The molecular geometrical structures of the optimized molecules are given in Fig. 1.

All substituents (F, NH_2 , CH_3 , CN, NO_2 , CF_3 , CHO) cause changes in the geometrical parameters compared to the parent (without substitution) and mostly where the substituent is attached.

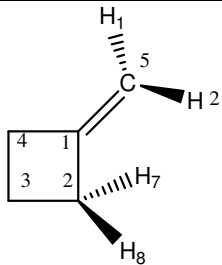
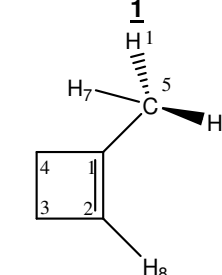
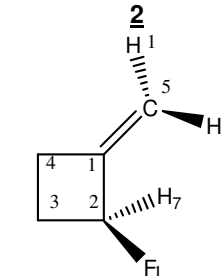
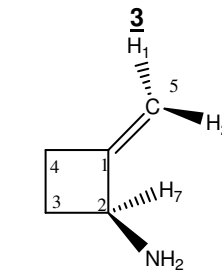
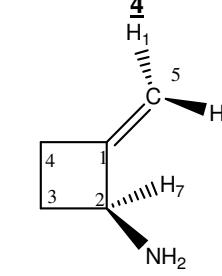
2.1.3 Electron density

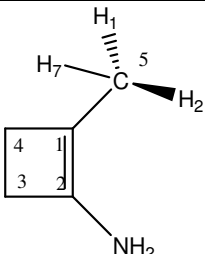
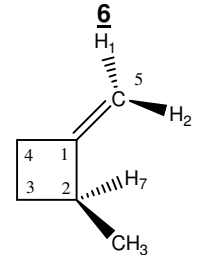
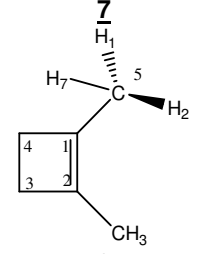
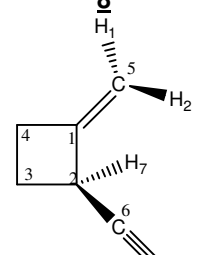
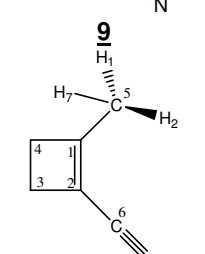
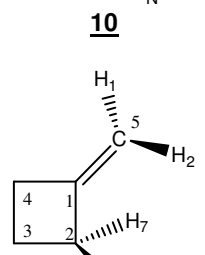
F, NH_2 and CH_3 substituents are found to decrease the electron density at which they are attached (C2) and increases it on the adjacent carbons (C1 and C3) as shown in Table 2. Therefore, these substituents act as electron releasing [13]. The CN, NO_2 , CF_3 and CHO substituents increase the electron density at which they are attached and decrease it on the adjacent carbons. Therefore, these substituents act as electron withdrawing [15].

2.1.4 Thermodynamic calculations

All substituents show less Gibbs free energies than that of the parent compounds as shown in Table 1, which suggests a destabilization of the methylenecyclobutane. The stabilization effect is often confirmed by the isodesmic reactions [3,15-17]. Positive substituent stabilization energy (ΔH_{rxn}) value indicates stability of the reactant and negative value is more stability to the product.

It can be seen that ΔH_{rxn} values of the isodesmic reactions of methylenecyclobutane are less than that of 1-methylcyclobutenes for all the substituents, which suggests that all the substituents destabilize the methylenecyclobutane as compared to 1-methylcyclobutenes (Table 3).

Cpd #	Bond	Bond length (Å)	Bond angle	Angle degree
	C1-C2	1.511	C2-C1=C5	133.757
	C1=C5	1.320	C4-C1-C2	92.536
	C2-H8	1.113	C1-C2-H8	114.688
	C3-C2	1.523	C3-C2-C1	89.035
	C4-C1	1.497	C4-C3-C2	89.391
	C4-C3	1.523	C3-C4-C1	89.038
	C5-H1	1.098	C1=C5-H1	122.473
	C1=C2	1.352	C1-C5-H1	110.678
	C1-C5	1.459	C2=C1-C5	135.862
	C2-H8	1.081	C4-C1=C2	94.085
	C3-C2	1.518	C3-C2=C1	94.045
	C4-C1	1.522	C4-C3-C2	86.125
	C4-C3	1.567	C3-C4-C1	85.745
	C5-H1	1.098		
	C1-C2	1.525	C1-C2-F1	115.631
	C1=C5	1.318	C2-C1-C5	133.358
	C2-F1	1.356	C4-C1=C5	134.256
	C2-H7	1.106	C4-C1-C2	92.383
	C3-C2	1.565	C3-C2-C1	88.436
	C4-C1	1.506	C4-C3-C2	89.337
	C4-C3	1.547	C3-C4-C1	89.782
	C5-H1	1.086		
	C1=C2	1.356	C2=C1-C5	133.631
	C1-C5	1.458	C4-C1-C2	92.717
	C2-CF1	1.322	C1-C2-N1	114.866
	C3-C2	1.520	C3-C2-C1	88.343
	C4-C1	1.525	C4-C3-C2	89.438
	C4-C3	1.569	C3-C4-C1	89.482
	C5-H1	1.098		
	C1-C2	1.519	C2-C1=C5	133.631
	C1=C5	1.319	C4-C1-C2	92.717
	C2-N1	1.468	C1-C2-N1	114.866
	C2-H7	1.112	C3-C2-C1	88.343
	C3-C2	1.565	C4-C3-C2	89.438
	C4-C1	1.507	C3-C4-C1	89.482
	C4-C3	1.547		
	C5-H1	1.086		

Cpd #	Bond	Bond length (Å)	Bond angle	Angle degree
	C1=C2	1.361	C2-C1=C5	136.111
	C1-C5	1.458	C4-C1-C5	130.335
	C2-N1	1.404	C4-C1=C2	93.553
	C3-C2	1.523	C1=C2-N1	135.218
	C4-C1	1.520	C3-C2=C1	94.227
	C4-C3	1.567	C4-C3-C2	85.719
	C5-H1	1.098	C3-C4-C1	86.501
	C1-C2	1.516	C2-C1=C5	133.552
	C1=C5	1.319	C4-C1=C5	133.771
	C2-C6	1.506	C4-C1-C2	92.677
	C3-C2	1.557	C1-C2-C6	115.320
	C4-C1	1.507	C3-C2-C1	88.556
	C4-C3	1.523	C4-C3-C2	89.545
	C5-H1	1.085	C3-C4-C1	89.212
	C1=C2	1.355	C2=C1-C5	135.710
	C1-C5	1.459	C4-C1-C5	130.299
	C2-C6	1.459	C4-C1=C2	93.991
	C3-C2	1.521	C1=C2-C6	135.783
	C4-C1	1.521	C3-C2=C1	93.986
	C4-C3	1.567	C4-C3-C2	86.019
	C5-H1	1.098	C3-C4-C1	86.004
	C1-C2	1.549	C2-C1=C5	109.500
	C1=C5	1.319	C4-C1=C5	109.500
	C2-C6	1.445	C4-C1-C2	109.510
	C2-H7	1.112	C1-C2-C6	112.400
	C3-C2	1.560	C3-C2-C1	109.390
	C4-C1	1.508	C4-C3-C2	110.510
	C4-C3	1.549	C3-C4-C1	109.390
C5-H1	1.086			
	C1=C2	1.357	C2-C1=C5	132.739
	C1-C5	1.458	C4-C1=C5	134.707
	C2-C6	1.402	C4-C1-C2	92.541
	C3-C2	1.521	C3-C2-C1	88.695
	C4-C1	1.523	C4-C3-C2	89.458
	C4-C3	1.568	C3-C4-C1	89.301
	C5-H1	1.099		
	C1-C2	1.516	C2-C1=C5	132.739
	C1=C5	1.319	C4-C1=C5	134.707
	C2-N1	1.528	C4-C1-C2	92.541
	C2-H7	1.115	C1-C2-N1	115.354
	C3-C2	1.558	C3-C2-C1	88.695
	C4-C1	1.509	C4-C3-C2	89.458
	C4-C3	1.548	C3-C4-C1	89.301

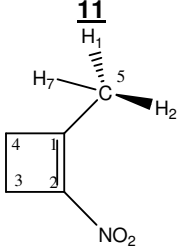
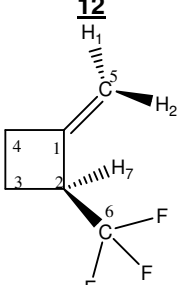
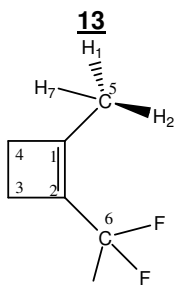
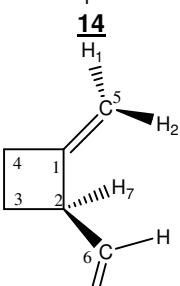
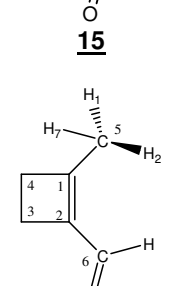
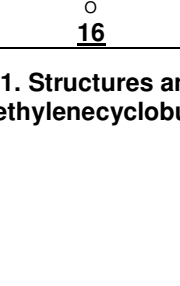
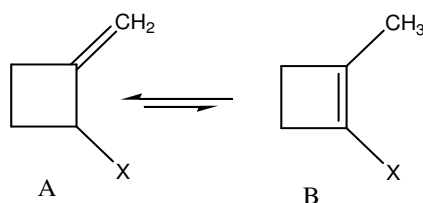
Cpd #	Bond	Bond length (Å)	Bond angle	Angle degree
	C1=C2	1.362	C2=C1-C5	136.313
	C1-C5	1.457	C4-C1-C5	130.172
	C2-N1	1.458	C4-C1=C2	93.516
	C3-C2	1.524	C1=C2-N1	135.504
	C4-C1	1.521	C3-C2=C1	94.160
	C4-C3	1.566	C4-C3-C2	85.772
	C5-H1	1.099	C3-C4-C1	86.552
		C1-C2	1.512	C2-C1=C5
C1=C5		1.319	C4-C1=C5	134.216
C2-C6		1.551	C4-C1-C2	92.520
C2-H7		1.110	C1-C2-C6	115.319
C3-C2		1.553	C3-C2-C1	88.897
C4-C1		1.508	C4-C3-C2	89.389
C4-C3		1.549	C3-C4-C1	89.187
C5-H1		1.086		
	C1=C2	1.354	C2=C1-C5	136.233
	C1-C5	1.458	C4-C1-C5	130.307
	C2-C6	1.496	C4-C1=C2	93.460
	C3-C2	1.518	C1=C2-C6	135.545
	C4-C1	1.523	C3-C2=C1	94.607
	C4-C3	1.568	C4-C3-C2	85.686
	C5-H1	1.098	C3-C4-C1	86.246
		C1-C2	1.515	C2-C1=C5
C1=C5		1.319	C4-C1=C5	133.871
C2-C6		1.509	C4-C1-C2	92.655
C2-H7		1.111	C1-C2-C6	113.529
C3-C2		1.556	C3-C2-C1	88.632
C4-C1		1.508	C4-C3-C2	89.541
C4-C3		1.549	C3-C4-C1	89.169
		C1=C2	1.358	C2=C1-C5
	C1-C5	1.458	C4-C1-C5	130.076
	C2-C6	1.455	C4-C1=C2	93.833
	C3-C2	1.521	C1=C2-C6	136.599
	C4-C1	1.522	C3-C2=C1	93.992
	C4-C3	1.566	C4-C3-C2	86.051
			C3-C4-C1	86.124
				

Fig. 1. Structures and optimized geometrical parameters calculated by PM3 for the substituted methylenecyclobutane and 1-methylcyclobutene in the gas phase ($\epsilon = 1.00$) at temperature 298.15K and liquid ($\epsilon = 78.4$) phase

Table 1. Calculated gibbs free energies ΔG (kcal/mol) of the substituted methylenecyclobutane and 1-methylcyclobutene in the gas phase, obtained from PM3 program

X	G_A	G_B	ΔG_r
H	-2.594	4.030	6.625
F	-49.278	-43.909	5.368
NH ₂	-5.621	-7.124	-1.503
CH ₃	11.390	10.061	-1.329
CN	23.873	27.800	3.926
NO ₂	-36.493	-38.944	-2.450
CF ₃	-169.995	-165.818	4.176
CHO	-45.502	-44.328	1.173

$$\Delta G_r = G_B - G_A$$

Table 2. Calculated electron densities of substitute methylenecyclobutane and 1- methylcyclobutene (see Fig.1 for numbering), obtained from PM3 in the gas phase ($\epsilon = 1.00$)

Cpd #	C1	C2	C3	C4	C5	C6	H7	N1	O1	F1
1	4.134	4.067	4.109	4.067	4.152		0.938			
2	4.147	4.170	4.078	4.072	4.036		0.956			
3	4.179	3.900	4.135	4.056	4.106		0.929			7.138
4	4.174	4.021	4.069	4.055	4.030		0.951			
5	4.148	4.054	4.144	4.063	4.125		0.916	5.018		
6	4.217	4.183	4.057	4.050	4.016		0.964	4.880		
7	4.134	4.048	4.111	4.066	4.149	4.098	0.925			
8	4.152	4.152	4.067	4.067	4.032	4.032	0.957			
9	4.148	3.909	4.102	4.062	4.115	4.139	0.935	5.066		
10	4.069	4.068	4.046	4.080	4.052	4.059	0.931	5.071		
11	4.147	4.296	4.082	4.060	4.100		0.908	3.759	6.581	
12	3.934	4.520	4.006	3.105	4.084		0.925	3.646	6.607	
13	4.413	4.100	4.094	4.054	4.111	3.648	0.928			7.141
14	4.014	4.292	4.029	4.086	4.064	3.559	0.926			7.143
15	4.129	4.138	4.088	4.067	4.143	3.706	0.939		6.311	
16	4.074	4.289	4.162	4.147	3.991	3.574	0.921		6.306	

Table 3. Evaluation of the substituent effects on the substituted methylenecyclobutane and 1-methylcyclobutene tautomerism via isodesmic reactions (ΔH_{rxn} kcal/mol), obtained from PM3 in the gas phase ($\epsilon = 1$)

Isodesmic reactions	X						
	F	NH ₂	CH ₃	CN	NO ₂	CF ₃	CHO
	1.648	1.030	0.095	1.550	2.016	1.949	1.007
	2.765	8.310	4.543	4.844	9.898	3.713	5.097

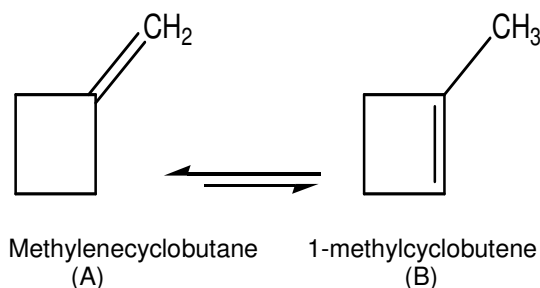
$$\Delta H_r = \sum \Delta H_{product} - \sum \Delta H_{reactant}$$

2.2 DFT Calculations

Density Functional Theory (DFT) type (B3LYP) has been performed in the gas phase with complete optimization of geometrical parameters first on the parent compounds (methylenecyclobutane and 1-methylcyclobutene) and then on substituted methylenecyclobutane and 1-methylcyclobutene.

2.2.1 Tautomerism

The calculated enthalpy (H_A) of methylenecyclobutane ($H_A = -192.814$ Hartrees) is smaller than that of 1-methylcyclobutene ($H_B = -192.810$ Hartrees), which suggests that compound (A) is the more stable. This is supported by the calculated Gibbs free energy (G_A) of compound (A) ($G_A = -192.846$ Hartrees) and that of (B) ($G_B = -192.844$ Hartrees) (Table 4), where $\Delta G_B > \Delta G_A$. The Gibbs free energy (ΔG_r) for the tautomerization ($\Delta G_B - \Delta G_A$) is $\Delta G_r = 0.00217$ Hartrees (1.362 kcal/mol), which suggests that compound (A) is slightly predominant in the gas phase. But the present PM3 calculations show that the compound (A) is predominant in the gas and aqueous phases.



2.2.2 Effect of substituents

2.2.2.1 Thermodynamic calculations

All substituents show less Gibbs free energies than that of the parent compounds as shown in Table 4, which suggests a destabilization of the methylenecyclobutane. The stabilization effect is confirmed by the isodesmic reactions. It can be seen that ΔH_{rxn} values of the isodesmic reactions of methylenecyclobutane are less than that of 1-methylcyclobutenes for all the substituents, which suggests that all the substituents destabilize the methylenecyclobutane as compared to 1-methylcyclobutenes (Table 5).

Table 4. Calculated Gibbs free energies ΔG (kcal/mol) of the substituted methylenecyclobutane and 1-methylcyclobutene system obtained from DFT calculations

X	G_A	G_B	ΔG_r
H	-192.846	-192.844	0.002
F	-290.626	-290.642	-0.016
NH ₂	-247.430	-247.446	-0.016
CH ₃	-231.668	-231.671	-0.003
CN	-283.882	-283.893	-0.011
NO ₂	-247.558	-247.557	0.001
CF ₃	-525.043	-525.044	-0.001
CHO	-304.620	-304.631	-0.011

$\Delta G_r = G_B - G_A$

Table 5. Evaluation of substituent effects on the substituted methylenecyclobutane 1-methylcyclobutene tautomerism via isodesmic reactions (ΔH_{rxn} kcal/mol), obtained from DFT in the gas phase ($\epsilon = 1$)

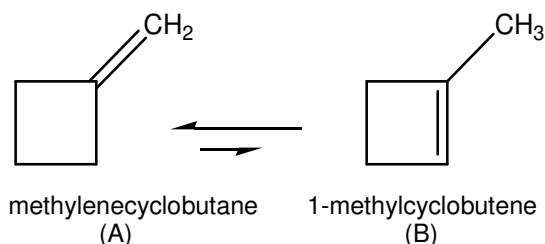
Isodesmic reactions	X						
	F	NH ₂	CH ₃	CN	NO ₂	CF ₃	CHO
	0.700	0.188	-0.629	0.167	0.002	0.155	0.181
	2.740	10.650	8.330	8.330	0.003	2.797	5.742

$\Delta H_{rxn} = \sum \Delta H_{product} - \sum \Delta H_{reactant}$

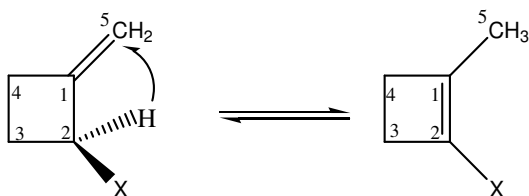
3. CONCLUSIONS

The present theoretical study indicates the following:

- 1- PM3 method has shown that the methylenecyclobutane is predominant in the gas and aqueous phases.



- 2- DFT method has shown that the methylenecyclobutane is slightly predominant in the gas phase.
- 3- All substituents (X = F, NH₂, CH₃, CN, NO₂, CF₃ and CHO) were found to affect the geometrical parameters (bond lengths and angles) especially at which the substituents are attached in position 2.



- 4- All substituents were found to stabilize the 1-methylcyclobutene in the gas phase.
- 5- The relative stabilities of substituted methylenecyclobutane and 1-methylcyclobutene were explained by thermodynamic calculations and supported by the isodesmic reactions.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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