

A DFT Study on Stepwise Fluorinated Methylenecyclopentane \rightleftharpoons 1-Methylcyclopentene System

Ghassab M. Al-Mazaideh^{1*}, Wafa B. Ejli² and Salim M. Khalil¹

¹Department of Chemistry and Chemical Technology, Faculty of Science, Tafila Technical University, P.O.Box 179, Tafila 66110, Jordan.

²Department of Chemistry, School of Basic Science, Libyan Academy for Graduate Studies, P.O.Box 79031, Tripoli, Libya.

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

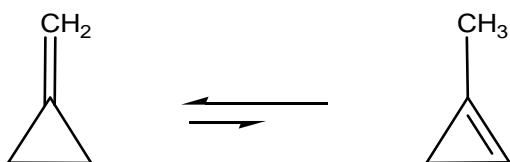
Density functional theory (DFT) calculations have been performed to calculate the optimized geometries of stepwise fluorinated methylenecyclopentanes and 1-methylcyclopentenenes. Increasing the number of fluorine atoms caused a destabilization of methylenecyclopentane. Perfluorinated 1-methylcyclopentene was found to be present in substantial concentration. This is supported by calculations of the Gibbs free energy and isodesmic reactions. These results are compared with fluorinated methylenecyclopropane and the fluorinated cyclopentanones keto-enol systems. Enthalpies, entropies and dipole moments are reported.

Keywords: Fluorinated methylenecyclopentane; tautomerism; DFT.

*Corresponding author: E-mail: gmazideh@ttu.edu.jo;

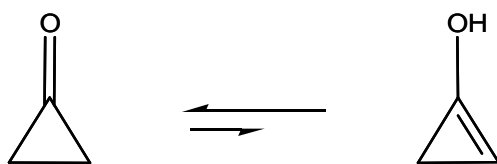
1. INTRODUCTION

Recently [1] we have studied methylenecyclopropane / 1-methylcyclopropene system (Scheme 1) and have shown that methylenecyclopropane is 11.535 kcal/mol more stable than 1-methylcyclopropene.



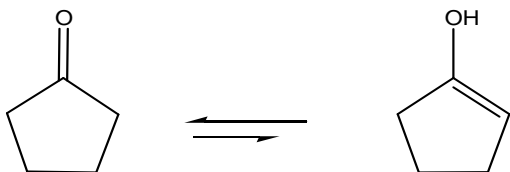
Scheme 1

This was confirmed by a positive Gibbs free energy, ΔG ($\Delta G = 11.615$ kcal/mol), which indicates that this system is non-spontaneous and methylenecyclopropane is more stable than 1-methylcyclopropene. Also, it was found [1] that an increase in the number of substituting fluorine atoms causes a destabilization of methylenecyclopropane. This system [1] was compared with the cyclopropanone and cyclopropenol system [2] (Scheme 2) and found that an increase in the number of fluorine atoms also causes a destabilization of cyclopropanone.



Scheme 2

Also, we have studied cyclopentanone and its enol [3] (Scheme 3), and



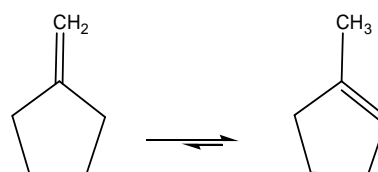
Scheme 3

have shown that perfluorination destabilizes the ketone form at the expense of the enol form.

In this paper we study the effect of the methylene group on the five-membered ring and also of the stepwise fluorination of this methylenecyclopentane

and 1-methylcyclopentene system in order to compare this effect with the recent previous work [1–3]. While much work has been done on the reactions of methylenecyclopentane [4–11], the stepwise fluorination of methylenecyclopentane has not been examined.

This study will employ DFT/B3LYP (G 03, Revision B.03) [12] is applied to examine first the methylenecyclopentane/1-methylcyclopentene system (Scheme 4) and then the stepwise fluorinated methylenecyclopentane /1-methylcyclopentene system. All calculations will be performed in the gas phase at 298.15 K.



methylenecyclopentane (1) 1-methylcyclopentene (2)

Scheme 4

2. RESULTS AND DISCUSSION

Density functional theory (DFT) calculations [12] are used to calculate fully the optimized geometries of fluorinated methylenecyclopentane and 1-methylcyclopentene. The molecular structures of the fluorinated methylenecyclopentane (1) / 1-methylcyclopentene (2) systems and Mulliken atomic charges are given in Fig. 1.

The calculated entropies, enthalpies and dipole moments of 21 compounds are listed in Table 1.

The calculated Gibbs free energies and isodesmic reactions, are given in Tables 2 and 3 respectively.

2.1 Parent Compounds

DFT calculations have shown that the difference in energy between compound 2 and compound 1 is 0.008943 Hartrees (5.612 kcal/mol) as shown in Table 1, suggesting that 2 is more stable than 1 by 5.612 kcal/mol. This is confirmed by thermodynamic calculations (Table 2) which shows a negative Gibbs free energy ($\Delta G = -4.614$ kcal/mol) indicating a spontaneous reaction and that 1-methylcyclopentene is the more stable (Scheme 5).

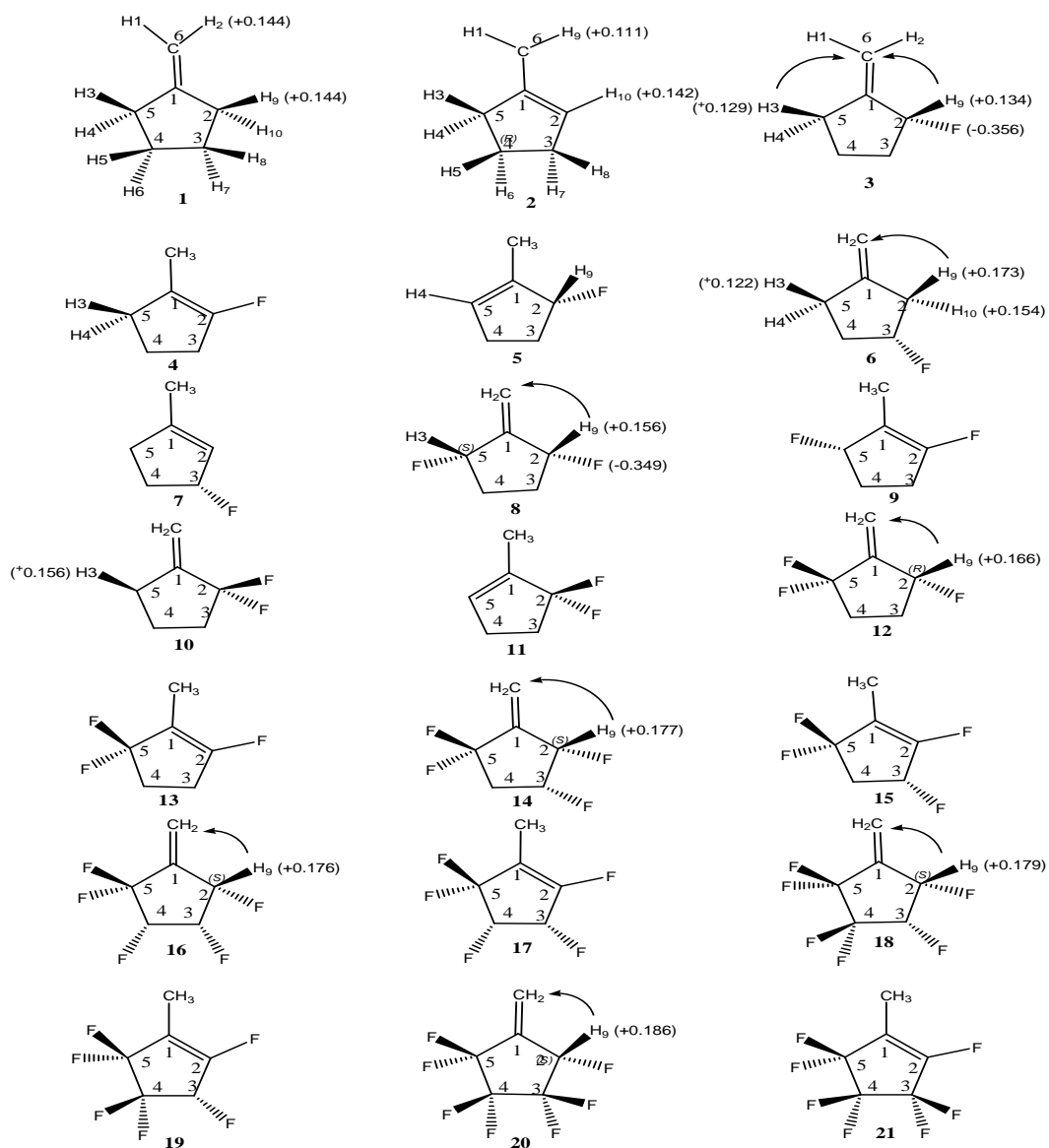


Fig. 1. Molecular structure of fluorinated methylenecyclopentanes and 1-methylcyclopentenes with Mulliken atomic charges in parenthesis

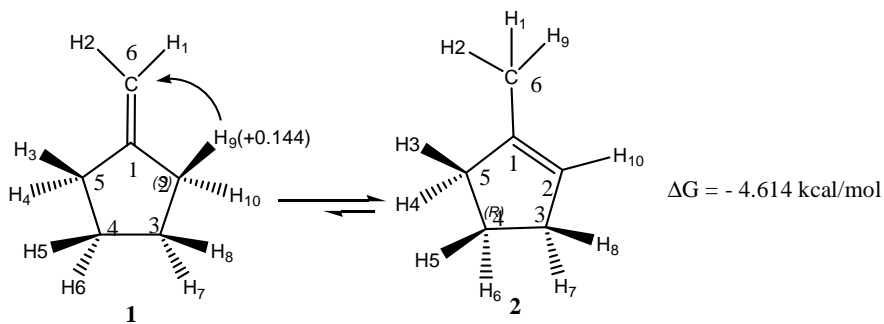


Table 1. Calculated entropy S (cal/mol. K), Enthalpy H (Hartrees), Dipole moment μ (Debye) of fluorinated methylenecyclopentanes and 1-methylcyclopentenes (see Fig. 1 for numbering)

Compound	S	H	μ
1	75.464	-231.661846	0.606
2	72.116	-231.670789	0.247
3	77.438	-329.438723	2.252
4	77.397	-329.462072	1.976
5	76.426	-329.446368	2.208
6	78.578	-329.440658	1.935
7	76.489	-329.446440	2.752
8	78.518	-427.212426	1.856
9	81.869	-427.238649	2.015
10	82.454	-427.235813	3.059
11	80.719	-427.244527	3.029
12	82.126	-525.012274	2.239
13	86.240	-525.036999	2.015
14	86.223	-622.785610	2.391
15	91.484	-622.811321	1.333
16	90.891	-720.557933	4.227
17	96.583	-720.584404	3.377
18	95.441	-818.350420	3.151
19	100.815	-818.377611	3.162
20	99.839	-916.143831	3.796
21	99.366	-916.172101	3.685

1 Hartree = 627.5095 kcal/mol

Comparing this energy with that of the keto-enol system ($\Delta G = 5.311$ kcal/mol) [3], suggests that the carbonyl group stabilizes the five membered ring more than that of methylene group. This agrees with the work on methylenecyclopropane [1]. It was found that in all alkene isomerizations [13], the forward reaction is favored far more than in their ketone-to-enol counterparts, which agrees with present work. This ΔG value ($\Delta G = -4.614$ kcal/mol) will be taken as reference for determining the relative stability of fluorinated methylenecyclopentanes and 1-methylcyclopentenes.

2.2 Relative Stability of the Fluorinated Methylenecyclopentane \rightleftharpoons 1-Methylcyclopentene System

Introduction of fluorine atom causes a change in the atomic Mulliken charges of methylenecyclopentane \rightleftharpoons 1-methylcyclopentene system, mainly where the fluorine atom is attached (Fig. 1).

2.2.1 Effect of one F atom

There are two possibilities, case **a** and case **b**:

- a) 2-fluoromethylenecyclopentane **3** (Fig. 1) is an unsymmetrical compound and has

two possibilities of forming **4** and **5** (Scheme 6). Compound **4** is formed from an H9 shift from C2 (compound **3**), while compound **5** is formed by an H3 shift from C5.

The H9 in compound **3** is more acidic (+ 0.134) than H3 (+ 0.129). So the compound **4** formed from H9 shift may be favorable. This is indicated by No. 2 in Table 2, where $\Delta G = -14.640$ kcal/mol is less than of compound **5** ($\Delta G = -4.496$ kcal/mol, No. 3 in Table 2). This suggests that the transformation from **3** to **4** is more likely to occur than from **3** to **5**, i.e. compound **4** is more stable than **5**. The stabilization effect is also supported by using the isodesmic reactions [14-21]. A negative value for the reaction indicates a less stable, and a positive value a more stable product. It can be seen that $\Delta H_{rxn} = 10.133$ kcal/mol of compound **4** (No.2 in Table 3) is more positive than that of compound **5** ($\Delta H_{rxn} = 0.279$ kcal/mol, No.3 in Table 3), suggesting **4** is a stable relative to **5**.

- b) 3-fluoromethylenecyclopentane **6** (Fig. 1) is unsymmetrical. The compound that might be formed is **7** resulting from an H9 shift on the C2 (Scheme 7). The ΔG value for transformation from **6** to **7** is calculated to be -3.005 kcal/mol (No.4 in Table 2).

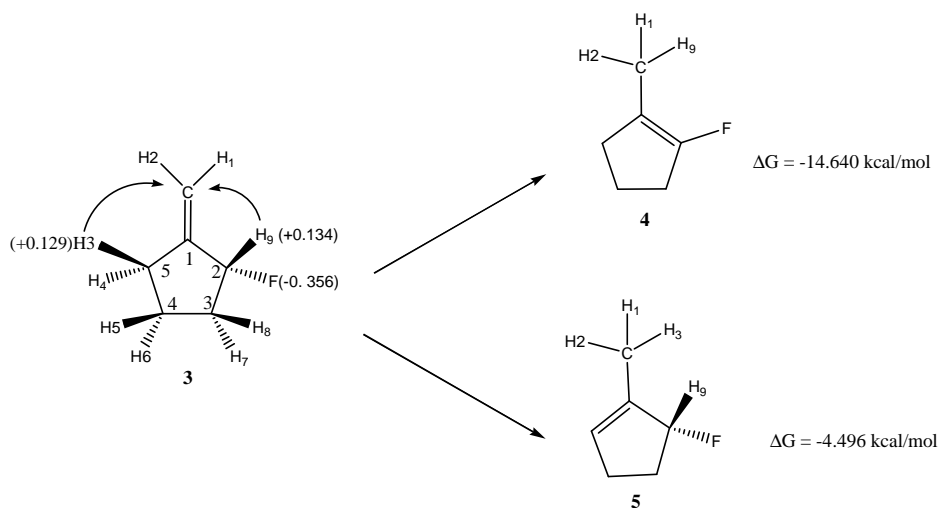
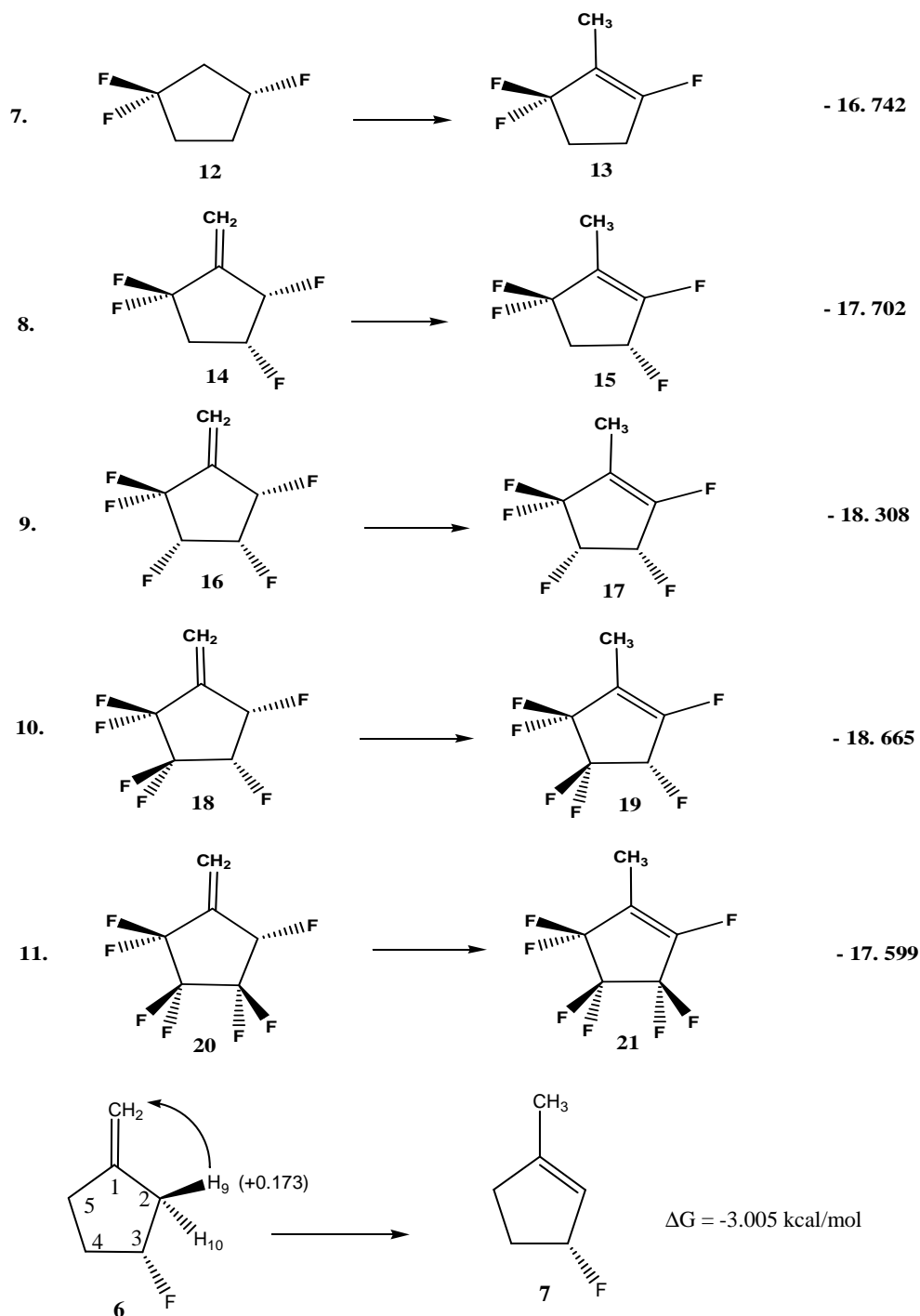


Table 2. Gibbs free energy (ΔG) of fluorinated methylenecyclopentanes and 1-methylcyclopentene

No.		$\Delta G(\text{kcal/mol})$
1.		-4.614
2.		- 14. 640
3.		- 4. 496
4.		- 3. 005
5.		- 17. 454
6.		- 4. 950

Table 2. (continued)



Scheme 7

As expected, the F atom has a greater inductive effect when it is adjacent to methylene group (Scheme 6), than when it is further away from methylene group (Scheme 7).

2.2.2 Effect of two F atoms

There are six possibilities, but only the two most possibilities (a and b) are to be considered, since

a distal F substituent from methylene group has little effect on the five-membered ring (similar to that shown for a single F atom).

- a) 2,5-Difluoromethylenecyclopentane **8** is a symmetrical compound (Fig. 1). The possible compound formed is compound **9** resulting from H9 shift on C2 or H3 shift on C5 (Scheme 8).

The ΔG value is calculated to be -17.454 kcal/mol (No.5 in Table 2), which is less than the parent compound (No.1 in Table 2) indicating the increase in the compound **9** stability. This is also supported by the isodesmic reaction where $\Delta H_{rxn} = 10.589$ kcal/mol of **9** (No.7 in Table 3), is more positive than that of **8** ($\Delta H_{rxn} = -0.255$ kcal/mol, No.6 in Table 3) indicating that **9** is relatively more stable than **8**. (i.e the two fluorine atoms destabilized the methylenecyclopentane).

Table 3. Evaluation of substituent effects on methylenecyclopentanes and 1-methylcyclopentenes via isodesmic reactions

No.		ΔH_{rxn} (kcal/mol)
1.		1.093
2.		10.133
3.		0.272
4.		2.307
5.		0.324
6.		-0.255
7.		10.589

Table 3. (continued)

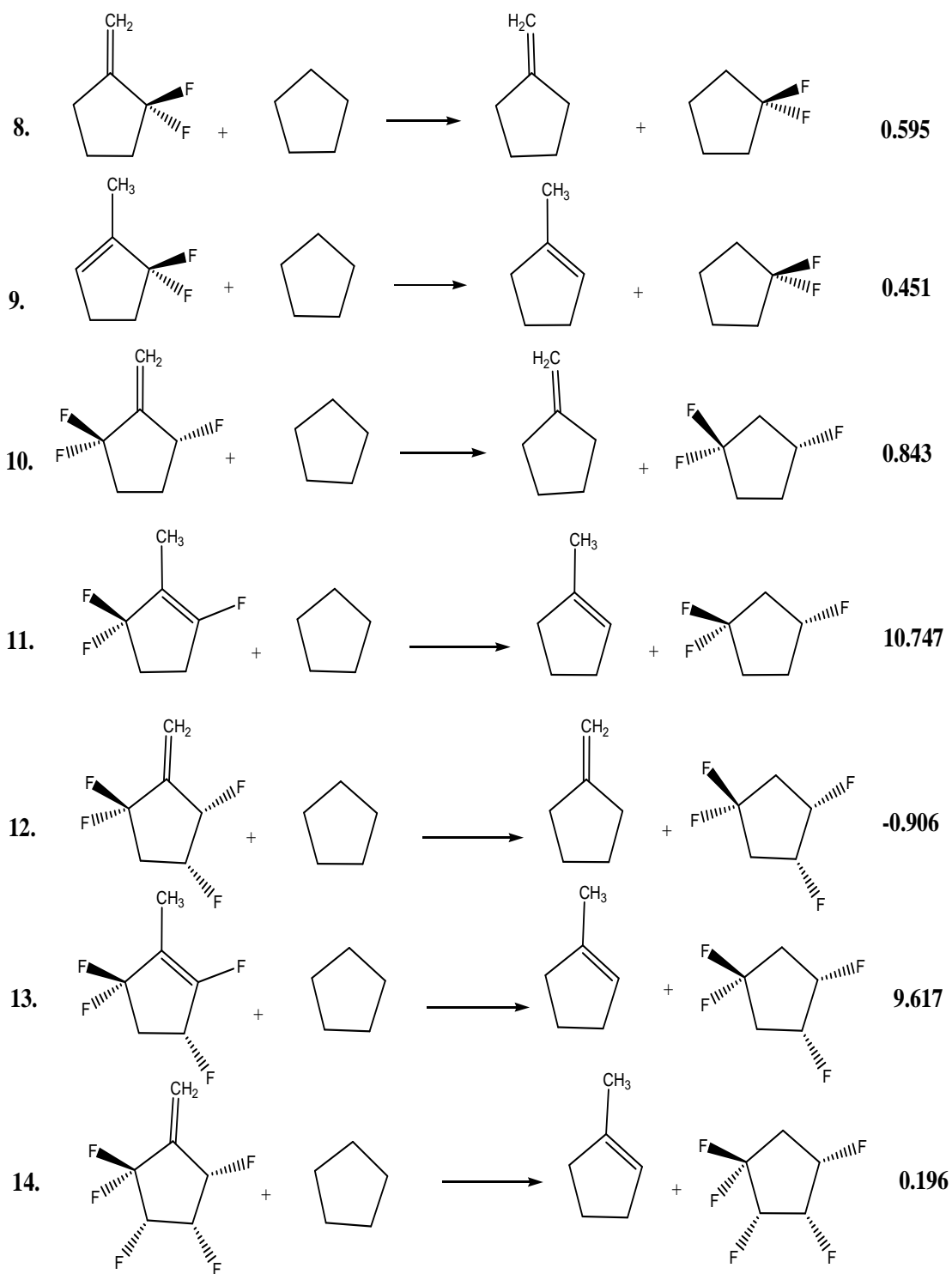
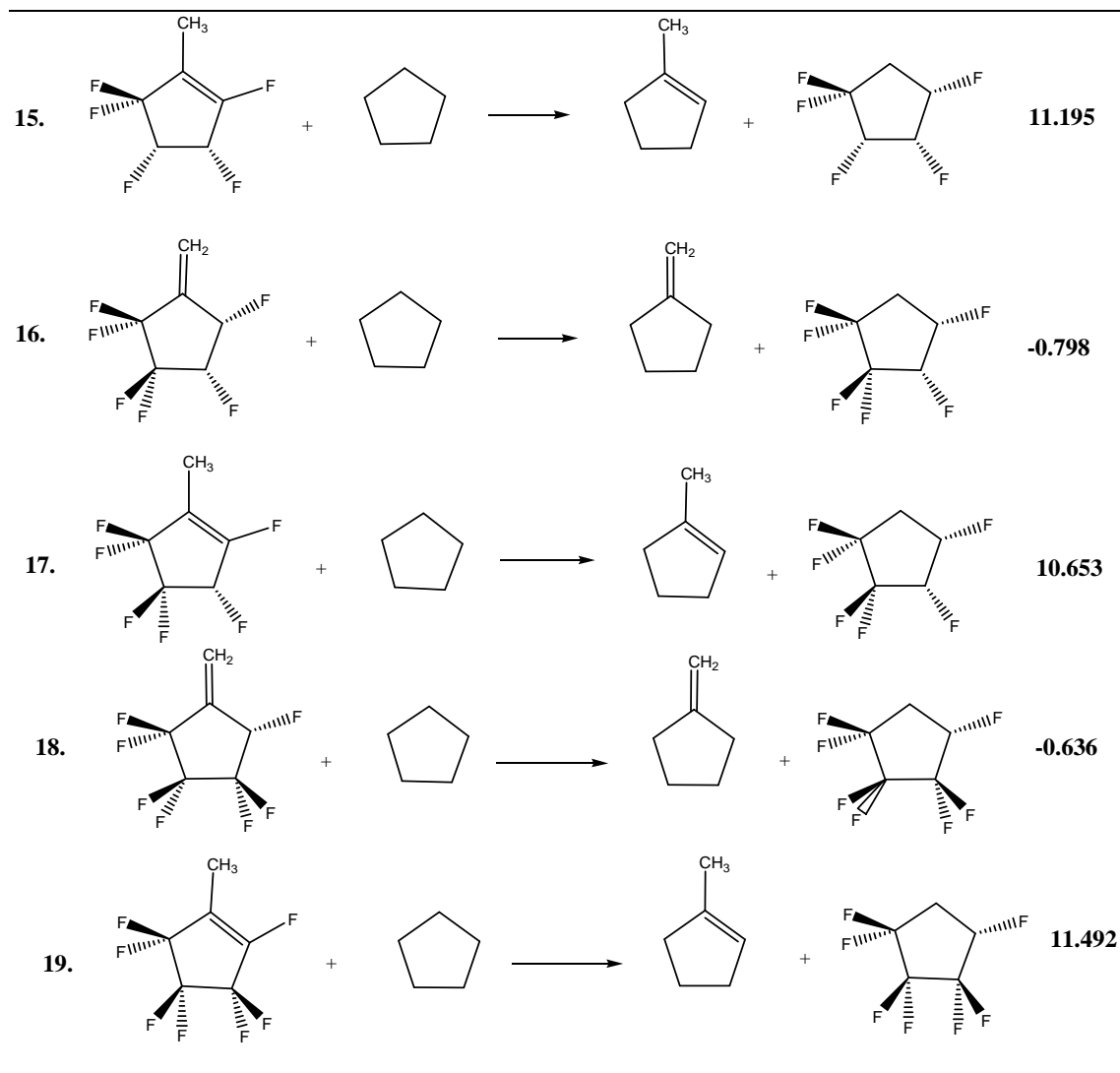


Table 3. (continued)



$$\Delta H = \sum \Delta H_{\text{product}} - \sum \Delta H_{\text{reactant}}$$

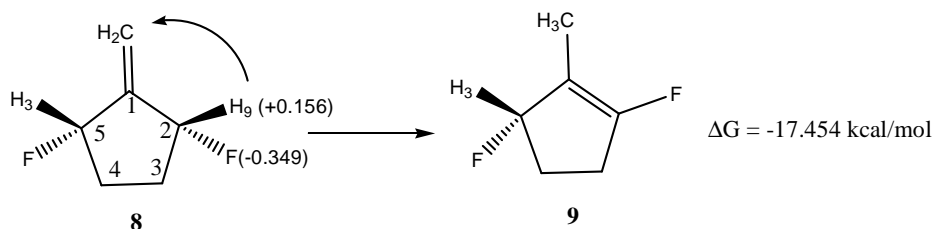
b) 2,2-Difluoromethylenecyclopentane **10** (Fig. 1) is unsymmetrical. The compound that might be formed is **11** resulting from an H3 shift on C₅ (Scheme 9).

The ΔG value of **10** is calculated to be -4.950 kcal/mol (No.6 in Table 2), which is less than that of the parent compound ($\Delta G = -4.614$ kcal/mol). This suggests that the two fluorine atoms slightly destabilize the methylenecyclopentane. It can be seen from Table 2, that ΔG value of compound **8** to **9** (No.5 in Table 2) is less than that of compound **10** to **11** (No.6 in Table 2), suggesting the greater effect of the two fluorine atoms in case a compared to that of case b (two F atoms on the same C atom). This agrees with the

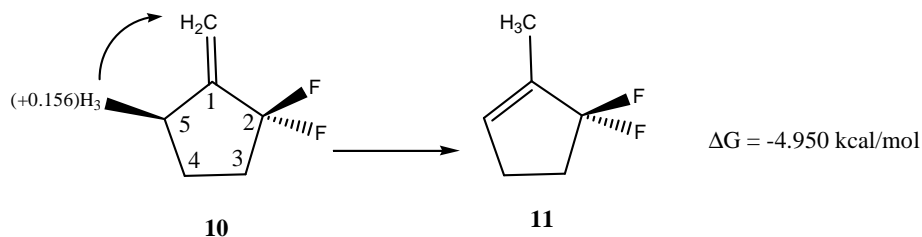
recent work [1], on stepwise fluorinated methylenecyclo-propane.

2.2.3 Effect of three F atoms

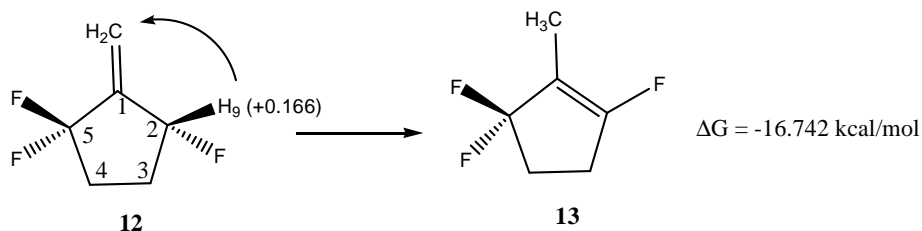
There are five possibilities, and the most stable possibility is considered for the same reason mentioned before. 2,5,5-Trifluoromethylenecyclopentane **12** (Fig. 1) has one possibility of compound formation. The compound formed is a compound **13** resulting from H9 shift on C2. The positive charge of H9 (+ 0.166) in compound **12** (Scheme 10) is more acidic than that of the parent methylenecyclopentane proton (+ 0.144) (Fig. 1).



Scheme 8



Scheme 9



Scheme 10

So the compound formation may have a relatively higher stability than the parent compound. This is indicated by No.7 in Table 2, where $\Delta G = -16.742$ kcal/mol is less than the parent compound ($\Delta G = -4.614$ kcal/mol)

This result is also supported by the isodesmic reactions, where $\Delta H_{rxn} = 10.747$ kcal/mol of **13** (No.11 in Table 3) is more positive than that of **12** ($\Delta H_{rxn} = 0.843$ kcal/mol, No.10 in Table 3). Thus **13** is favored over **12**.

2.2.4 Effect of four F atoms

There are four possibilities, and only the most stable possibility is considered.

2,3,5,5-tetrafluoromethylenecyclopentane **14** (Fig. 1). The compound formed is a compound **15** resulting from H9 shift on C2 (Scheme 11).

The positive charge of H9 (+ 0.177) in compound **14** (Scheme 11) is more acidic than that of the parent methylenecyclopentane proton (+ 0.144)

(Fig. 1). So the compound formation may have a relatively higher stability than the parent compound. This is indicated by No.8 in Table 2, where $\Delta G = -17.702$ kcal/mol is less than the parent compound ($\Delta G = -4.614$ kcal/mol). This result is also supported by the isodesmic reactions, where $\Delta H_{rxn} = 9.617$ kcal/mol of **15** (No.13 in Table 3) is more positive than that of **14** ($\Delta H_{rxn} = -0.906$ kcal/mol, No.12 in Table 3). Thus the compound **15** is favored over compound **14**.

2.2.5 Effect of five F atoms

There are three possibilities, and the most stable possibility is considered 2,3,4,5,5-pentafluoromethylenecyclopentane **16** (Fig. 1). The compound that might be formed is **17** resulting from an H9 shift on the C2 (Scheme 12).

The ΔG value is calculated to be -18.308 kcal/mol (No.9 in Table 2), which is less than the parent compound (No.1 in Table 2) indicating the increase in the compound **17** stability. This is

also supported by the isodesmic reaction where $\Delta H_{rxn} = 11.195$ kcal/mol of **17** (No.15 in Table 3) is more positive than that of **16** ($\Delta H_{rxn} = 0.196$ kcal/mol, No.14 in Table 3) indicating that **17** is relatively more stable than **16**.

2.2.6 Effect of six F atoms

There are two possibilities, and the most stable possibility is considered 2,3,4,4,5,5-hexafluorocyclopentane **18** (Fig. 1). The compound formed is a compound **19** (Scheme 13).

The $\Delta G = -18.665$ kcal/mol is less than the parent compound ($\Delta G = -4.614$ kcal/mol). This result is also supported by isodesmic reaction, where $\Delta H_{rxn} = 10.653$ kcal/mol of **19** (No.17 in Table 3) is more positive than that of **18** ($\Delta H_{rxn} = -0.798$ kcal/mol, No.16 in Table 3), indicating that **19** is relatively more stable than **18**.

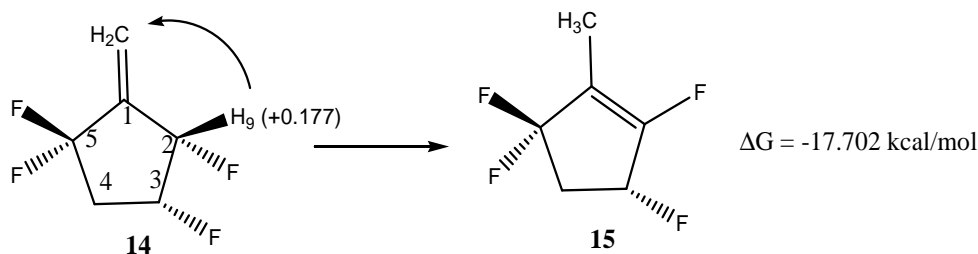
2.2.7 Effect of seven F atoms

2,3,3,4,4,5,5-heptafluoromethylenecyclopentane **20** (2*H*-perfluoromethylenecyclopentane) (Fig. 1) has one possibility of compound formation. The compound formed is a compound **21** resulting from H9 shift on C2. The positive charge of H9 in compound **20** is + 0.186 (Scheme 14), which is more acidic than that of the parent methylenecyclopentane proton (+ 0.144) (Fig. 1).

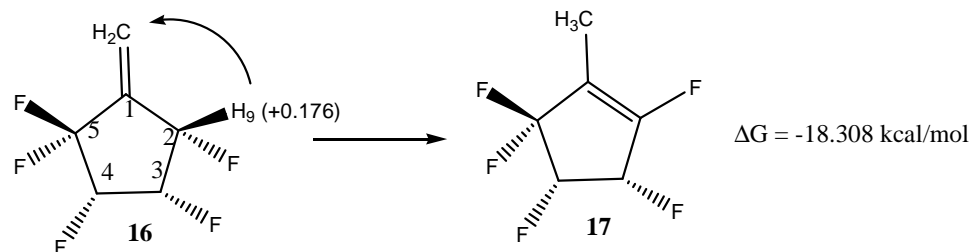
So the product formation may be favored by a relatively higher stability compared to the parent compound. This is indicated by No.11 in Table 2,

where $\Delta G = -17.599$ kcal/mol is less than the parent compound ($\Delta G = -4.614$ kcal/mol). This result is also supported by isodesmic reactions, where $\Delta H_{rxn} = 11.492$ kcal/mol of **21** (No.19 in Table 3) is more positive than that of **20** ($\Delta H_{rxn} = -0.636$ kcal/mol, No.18 in Table 3). This suggests a relative stability of compound **21**. Thus **21** is favored over **20**, which agrees with the previous works on the methylenecyclopropane/1-methylcyclopropene system [1], where 1-methylcyclopropene is favored over methylenecyclopropane, and the keto-enol system [2,22], where the enol form is favored over the ketone form.

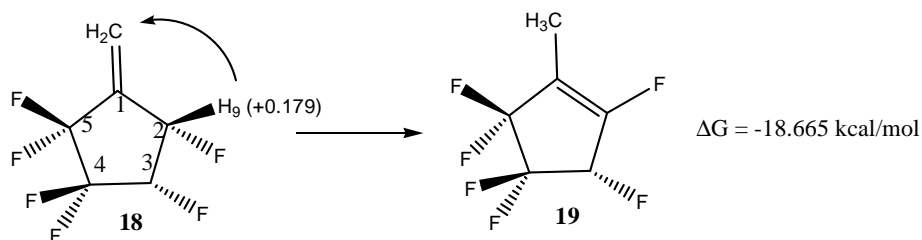
The calculated Mulliken charge distribution in compound **20** may give a plausible explanation for its destabilization. The calculated charges at carbon atoms 2 and 5 are more positive in **20** than in **1** (Scheme 15). The positive charge adjacent to methylene group is destabilizing due to the electrostatic repulsion between the two carbon atoms C2 and C5, and C1. Therefore, this repulsion might be responsible for the destabilization of **20**. The hydrogen atom H9 becomes more acidic (+0.186) in compound **20** than in compound **1** (+0.144). Increasing the acidity of the hydrogen atom H9 is likely to be important for the easy formation of compound **21** (Scheme 14). Thus the compound **21** is favored over compound **20** in a similar explanation to that given in previous works on 2*H*-perfluoromethylenecyclopropane [1], 2*H*-perfluorocyclobutanone [14], and 2*H*-perfluorocyclopentanone [3,23,24].



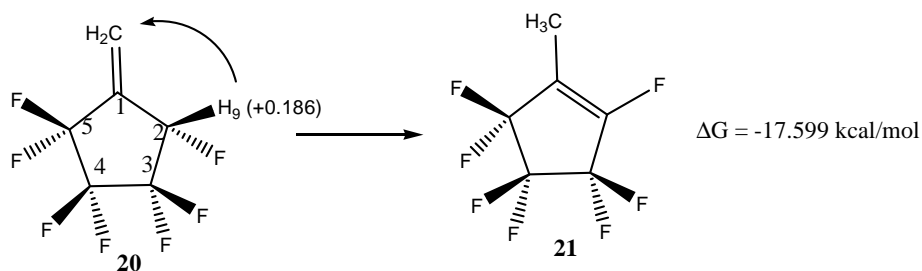
Scheme 11



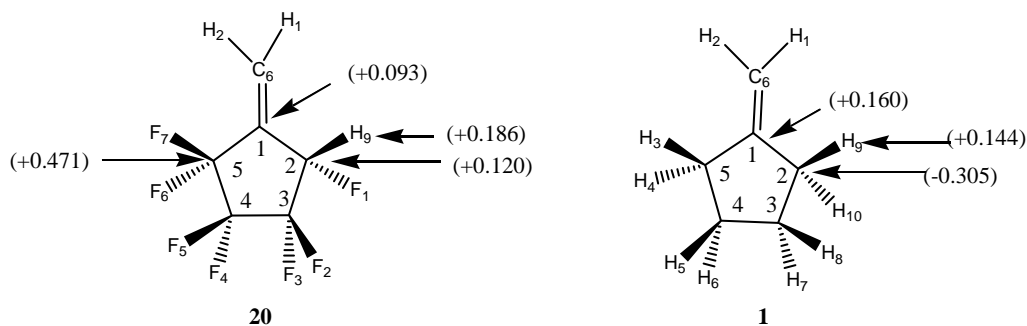
Scheme 12



Scheme 13



Scheme 14



Scheme 15

2.3 Dipole Moment of Fluorinated Methylene-cyclopentane and 1-methylcyclopentene System

Stepwise fluorination affects the dipole moment of all compounds, as shown in Table 1. Introduction of a fluorine atom into methylenecyclopentane increases the dipole moment from 0.606 Debye (**1** without fluorination) to 2.752 Debye (**3** with fluorination). This is due to the presence of the fluorine atom with the constructive resultant with a $-\text{CH}_2$ group, which agrees with the recent work [1] on stepwise fluorination of methylenecyclopropane. It can be seen from Table 1, that introduction of two fluorine atoms increases the dipole moment from 1.856 Debye in compound **8** to 3.059 Debye in compound **10**. Thus, as the number of fluorine atoms increases, the

dipole moments also increase, but not in a uniform fashion. This depends on constructive resultant of F atom with a $-\text{CH}_2$ group. Similarly, the changes in the dipole moments of fluorinated 1-methylcyclopentenes can be explained.

3. CONCLUSION

It can be concluded that the 1-methylcyclopentene is more stable than methylenecyclopentane by 5.612 kcal/mol. The methyl group stabilizes the five membered ring less than the carbonyl group. The stability of methylenecyclopentane was found to decrease on fluorination similar to that in the case of methylene-cyclopropane. Perfluorinated 1-methylcyclopentene was found to be present in substantial concentration, similar to that in the case of cyclopentanone and its

enol. These results were confirmed by Gibbs free energy calculations and isodesmic reactions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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