A DFT Study on the Stepwise Fluorinated Methylenecyclopropane ⇌ 1-Methylcyclopropene System

Salim M. Khalil

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

Reprint requests to S. M. K.; E-mail: salimkhalil2002@yahoo.com

Z. Naturforsch. **63a,** 42 – 48 (2008); received July 5, 2007

Density functional theory (DFT) calculations have been performed to calculate the optimized geometries of stepwise fluorinated methylenecyclopropanes and 1-methylcyclopropenes. Increasing the number of fluorine atoms caused a destabilization of methylenecycopropane. Perfluorinated 1-methylcyclopropene was found to be present in substantial concentration. This is supported by calculations of the Gibbs free energy, isodesmic reactions and orbital energies (HOMO-LUMO). These results are compared with the fluorinated cyclopropanes keto-enol system. Enthalpies, entropies and dipole moments are reported.

Key words: Cyclic Alkene; Tautomerism; Fluorinated Cyclic Alkene; DFT.

1. Introduction

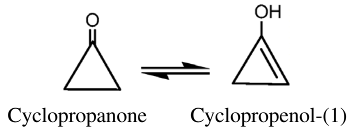
Recently [1] we have studied cyclopropanone and cyclopropenol-(1) (Scheme 1) and have shown that cyclopropanone is by 17.684 kcal/mol more stable than cyclopropenol-(1). This was confirmed by a positive Gibbs free energy, ΔG ($\Delta G = 17.509$ kcal/mol), which indicates that the keto-enol tautomerism is nonspontaneous, and cyclopropanone is more stable than cyclopropenol-(1).

Also, it was found [1] that an increase in the number of substituting fluorine atoms causes a destabilization of cyclopropanone.

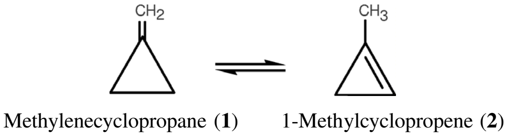
In this paper we study the effect of the methylene group on the three-membered ring and also of the stepwise fluorination of this methylenecyclopropanes/1-methylcyclopropene system in order to compare this effect with the previous work on the keto-enol system [1].

Much work has been done on the rearrangement of methylenecyclopropane [2 – 4], ring opening isomerization [5], decomposition [6], reactive intermediates [7] and single electron oxidation of methylenecyclopropene [8]. But no work was found on the stepwise fluorination of methylenecyclopropane.

DFT/B3LYP (G 03, Revision B.03) [9] is applied to examine first the methylenecyclopropane/1-methylcyclopropene system (Scheme 2) and then the stepwise fluorinated methylenecyclopropane/1-methylcyclopropene system. All calculations are done in the gas phase at 298.15 K.



Scheme 1.



Scheme 2.

2. Results and Discussion

Density functional theory (DFT) calculations [9] are used to calculate fully the optimized geometries of fluorinated methylenecyclopropanes and 1-methylcyclopropenes. The molecular structure of the fluorinated methylenecyclopropane (**1**)/1-methylcyclopropene (**2**) system and Mulliken atomic charges are given in Figure 1. The calculated entropies, enthalpies and dipole moments of 11 compounds are listed in Table 1. The calculated Gibbs free energies, isodesmic reactions and orbital energies are given in Tables 2, 3 and 4.

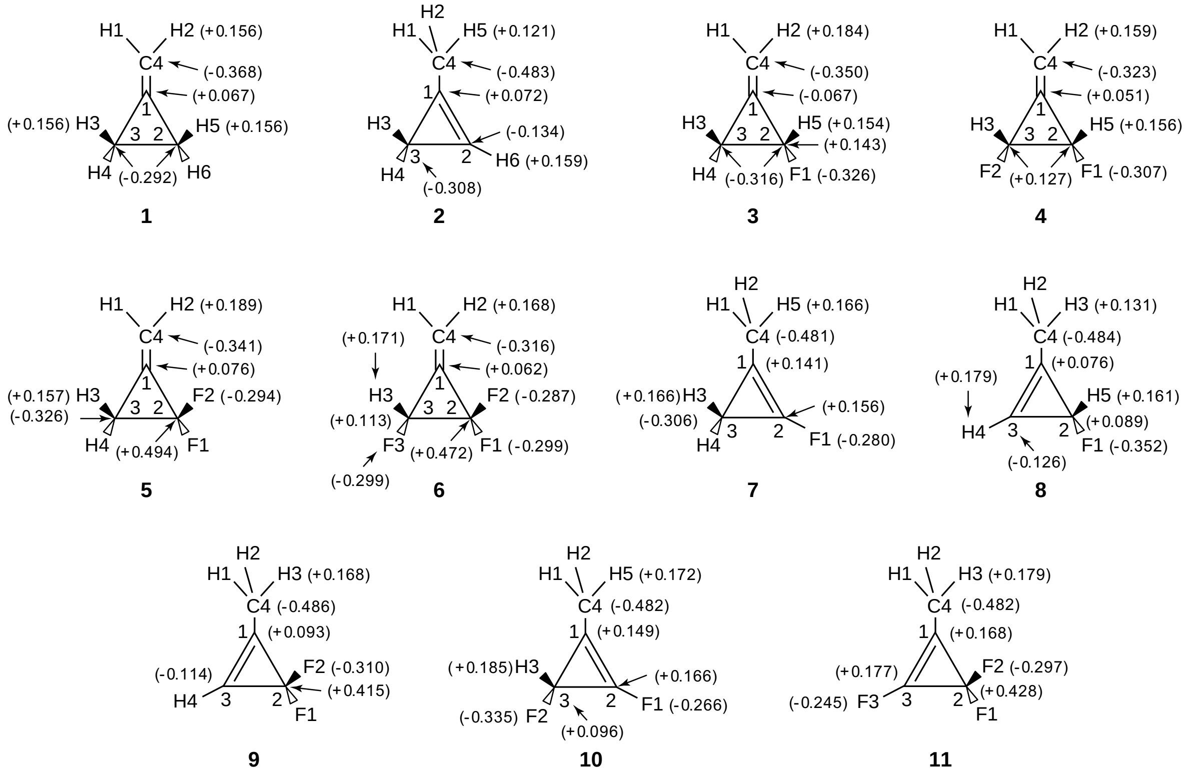


Fig. 1. Molecular structure of fluorinated methylenecyclopropanes and 1-methylcyclopropenes with Mulliken atomic charges in parenthesis.

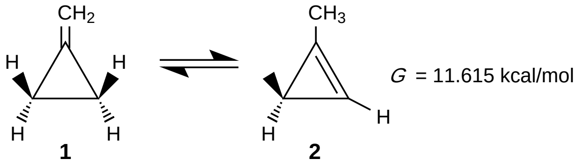
Table 1. Calculated entropy S, enthalpy H and dipole moment μ of fluorinated methylenecyclopropanes and 1-methylcyclopropenes (see Fig. 1 for numbering).

Compound	S (cal mol^{-1}K^{-1})	H (Hartrees)	μ (D)
1	66.077	−153.960025	0.382
2	65.809	−153.941643	0.916
3	71.595	−251.736708	2.078
4	77.298	−349.511797	3.429
5	76.400	−349.529591	2.910
6	82.745	−447.304853	3.316
7	71.136	−251.732551	2.136
8	70.942	−251.726023	2.926
9	75.496	−349.523916	3.928
10	76.130	−349.519106	3.101
11	80.829	−447.318392	3.632

1 Hartree = 627.5095 kcal/mol.

2.1. Parent Compounds

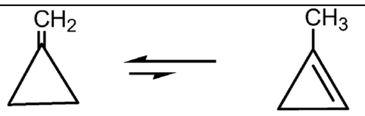
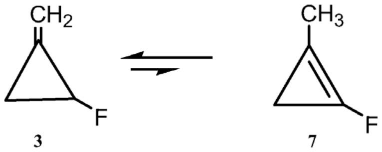
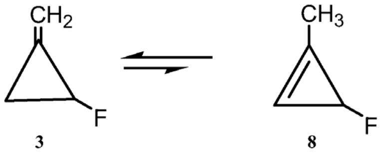
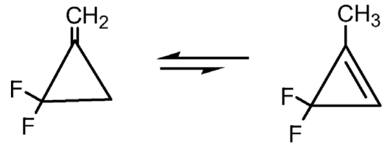
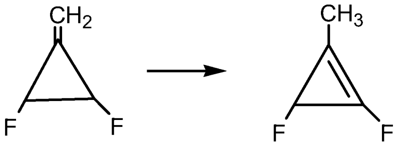
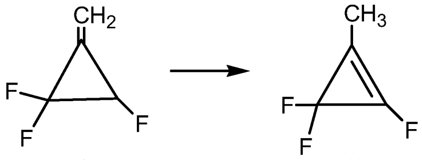
DFT calculations have shown that the difference in energy between compound **2** and compound **1** is 0.018382 Hartrees (11.535 kcal/mol), Table 1, suggesting that **1** is more stable than **2** by 11.535 kcal /mol.



Scheme 3.

This is confirmed by thermodynamic calculations (Table 2) which show a positive Gibbs free energy ($\Delta G = 11.615$ kcal/mol) indicating a nonspontaneous reaction and that methylenecyclopropane (**1**) is more stable (Scheme 3). Comparing this energy with that of the keto-enol system ($\Delta G = 17.509$ kcal/mol) [1] suggests that the carbonyl group stabilizes the three-membered ring more than the methylene group. It was found that in all alkene isomerizations [10], the forward reaction is favoured far more than in their ketone-to-enol counterparts, which agrees with the present work. This ΔG value (11.615 kcal/mol) will be taken as reference for determining the relative stability of fluorinated methylenecyclopropanes and 1-methylcyclopropenes.

Table 2. Gibbs free energy (ΔG) of fluorinated methylenecyclopropanes and 1-methylcyclopropenes.

No.		ΔG (kcal/mol)
1	 **1** **2**	11.615
2	 **3** **7**	2.746
3	 **3** **8**	6.899
4	 **5** **9**	3.831
5	 **4** **10**	−4.243
6	 **6** **11**	−7.924

$\Delta G = \Delta H - T\Delta S$.

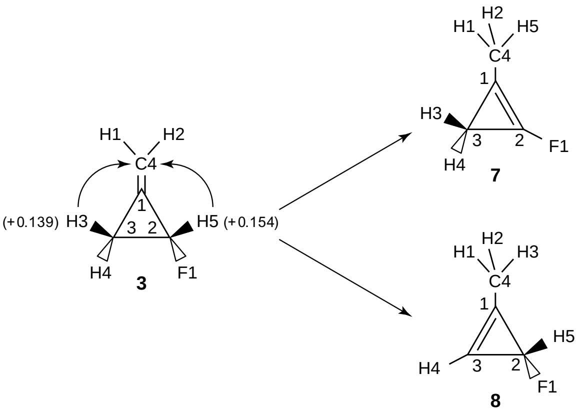
2.2. *Relative Stability of the Fluorinated Methylenecyclopropane $\rightleftharpoons$ 1-Methylcyclopropene System*

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

Effect of One F Atom

Fluoromethylenecyclopropane (**3**) (Fig. 1) is an unsymmetrical compound and has two possibilities of forming **7** and **8** (Scheme 4).

Compound **7** is formed from a H5 shift from C2 (compound **3**), while compound **8** is formed by a H3 shift from C3.



Scheme 4.

The H5 in compound **3** is more acidic (+0.154) than H3 (+0.139). So compound **7** formed from the H5 shift may be favourable. This is indicated by No. 2 in Table 2, where $\Delta G = 2.746$ kcal/mol is smaller than that of compound **8** ($\Delta G = 6.899$ kcal/mol, No. 3 in Table 2). This suggests that the transformation from **3** to **7** is more likely to occur than from **3** to **8**, i. e. compound **7** is more stable than **8**. The stabilization effect is also supported by using the isodesmic reactions [11 – 18]. A negative value for the reaction indicates a less stable, and a positive value a more stable product. It can be seen that $\Delta H_{\mathrm{rxn}} = 2.435$ kcal/mol of compound **7** (No. 2 in Table 3) is more positive than that of compound **8** ($\Delta H_{\mathrm{rxn}} = -0.368$ kcal/mol, No. 3 in Table 3), suggesting that **7** is stable relative to **8**.

Effect of Two F Atoms

There are two possibilities, case a and case b:

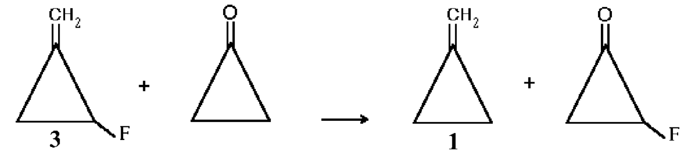
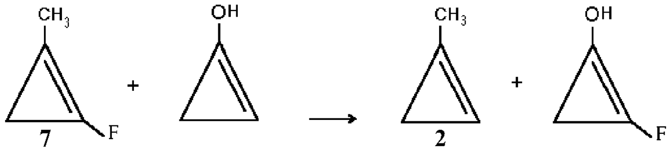
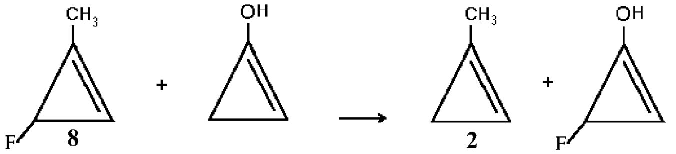
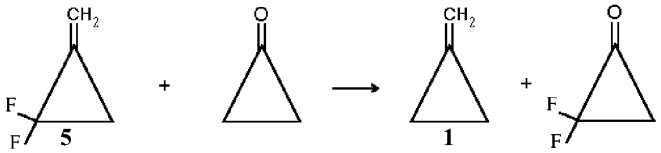
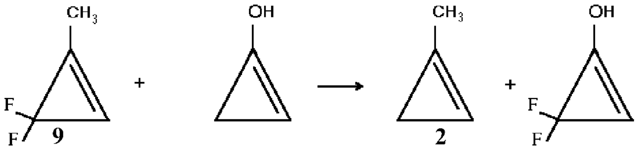
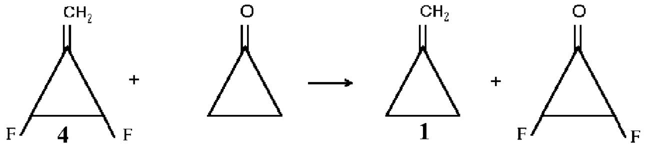
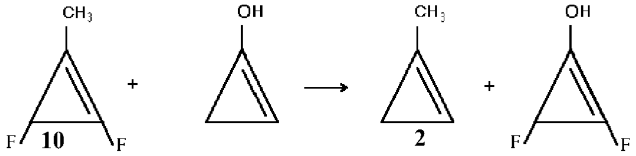
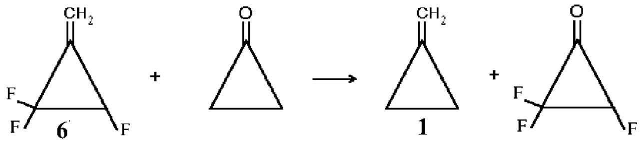
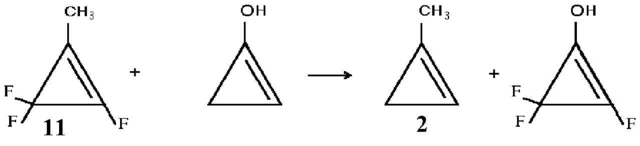
a. 2,3-Difluoromethylenecyclopropane (**4**) is a symmetrical compound (Fig. 1). The possible compound formed is compound **10**, resulting from a H5 shift on C2 or from a H3 shift on C3 (Scheme 5).

The ΔG value is calculated to be −4.243 kcal/mol (No. 5 in Table 2), which is less than the one for the parent compound (No. 1 in Table 2) indicating an increase in the stability of compound **10**.

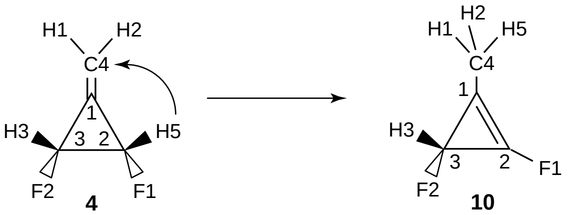
This is also supported by the isodesmic reaction, where $\Delta H_{\mathrm{rxn}} = 2.433$ kcal/mol of **10** (No. 7 in Table 3) is more positive than that of **4** ($\Delta H_{\mathrm{rxn}} = 0.794$ kcal/mol, No. 6 in Table 3), indicating that **10** is relatively more stable than **4**, i. e. the two fluorine atoms destabilize the methylenecyclopropane.

b. 2,2-Difluoromethylenecyclopropane (**5**) (Fig. 1) is unsymmetrical. The compound that might be formed is **9** resulting from a H3 shift on C3 (Scheme 6).

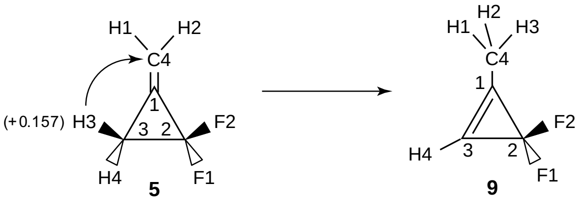
Table 3. Evaluation of substituent effects on methylenecyclopropanes and 1-methylcyclopropenes via isodesmic reactions.

No.		ΔH_{rxm} (kcal/mol)
1		0.474
2		2.435
3		−0.368
4		0.096
5		−0.885
6		0.794
7		2.433
8		0.543
9		2.136

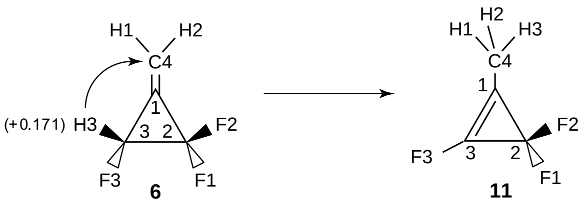
$\Delta H_{\mathrm{rxn}} = \Sigma \Delta H_{\mathrm{product}} - \Sigma \Delta H_{\mathrm{reactant}}$.



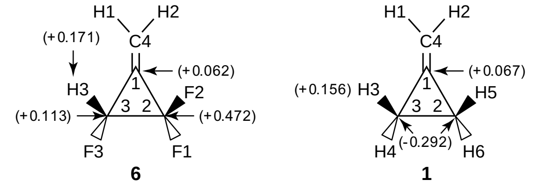
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

The ΔG value of **5** is calculated to be 3.831 kcal/mol (No. 4 in Table 2), which is less than that of the parent compound ($\Delta G = 11.615$ kcal/mol). This suggests that the two fluorine atoms destabilize the methylenecyclopropane (**1**), i. e. increase the stability of 1-methylcyclopropene (**2**), but still **5** is more stable than **9** because of its positive ΔG value 3.831 kcal/mol.

This is also supported by the isodesmic reaction, where $\Delta H_{\mathrm{rxn}} = 0.096$ kcal/mol of compound **5** (No. 4 in Table 3) is more positive than that of **9** ($\Delta H_{\mathrm{rxn}} = -0.885$ kcal/mol, No. 5 in Table 3) indicating that **5** is relatively more stable than **9**.

It can be seen from Table 2, that the ΔG value of compound **4** to compound **10** (No. 5 in Table 2) is smaller than that of compound **5** to compound **9** (No. 4 in Table 2), suggesting the greater effect of the two fluorine atoms in the case of a (two F atoms not on the same C atom) compared to that of case b (two F atoms on the same C atom).

Effect of Three F Atoms

2,2,3-Trifluoromethylenecyclopropane (**6**) (Fig. 1) has one possibility of compound formation. The compound formed is compound **11** resulting from a H3 shift on C3. The positive charge of H3 in compound **6** is +0.171 (Scheme 7), which is more acidic than the parent methylenecyclopropane proton (+0.156, **1**, Fig. 1).

So the product formation may be favoured by a relatively higher stability compared to the parent compound. This is indicated by No. 6 in Table 2, where $\Delta G = -7.924$ kcal/mol is less than the one of the parent compound ($\Delta G = 11.615$ kcal/mol). This result is also supported by isodesmic reactions, where $\Delta H_{\mathrm{rxn}} = 2.136$ kcal/mol of **11** (No. 9 in Table 3) is more positive than that of **6** ($\Delta H_{\mathrm{rxn}} = 0.543$ kcal/mol, No. 8 in Table 3). This suggests a relative stability of compound **11**. Thus **11** is favoured over **6**, which agrees with the previous work on the keto-enol system [1, 19] where the enol form is favoured over the ketone form.

The calculated Mulliken charge distribution in compound **6** (Fig. 1) may give a plausible explanation for its destabilization. The calculated charges at carbon atoms 2 and 3 are more positive in **6** than in **1** (Scheme 8). The positive charge adjacent to methylene group is destabilizing due to the electrostatic repulsion between the two carbon atoms C2 and C3, and C1. Therefore this repulsion might be responsible for the destabilization of **6**. The hydrogen atom H3 becomes more acidic (+0.171) in compound **6** than in compound **1** (+0.156). Increasing the acidity of hydrogen atom H3 is likely to be important for the easy formation of compound **11** (Scheme 7). Thus compound **11** is favoured over compound **6** in a similar explanation to that given in previous works on 2*H*-perfluorocyclobutanone [20] and 2*H*-perfluorocyclopentanone [11, 21, 22].

2.3. Dipole Moment of Fluorinated Methylenecyclopropane and 1-Methylcyclopropene

Stepwise fluorination affects the dipole moment of all compounds, as shown in Table 1.

Introduction of a fluorine atom into methylenecyclopropane increases the dipole moment from 0.382

Table 4. Calculated orbital energies (HOMO and LUMO, in eV) of fluorinated methylenecyclopropanes and 1-methylcyclopropenes (see Fig. 1 for numbering).

Compound	HOMO	LUMO	E_g = LUMO – HOMO
1	−6.913	0.459	7.372
2	−6.418	0.714	7.132
3	−7.482	−0.424	7.058
4	−7.852	−1.346	6.506
5	−8.015	−0.971	7.044
6	−8.403	−1.887	6.516
7	−6.629	0.771	7.400
8	−7.564	0.060	7.624
9	−8.095	−0.517	7.578
10	−7.694	−0.097	7.597
11	−8.385	−0.462	7.923

Debye (**1** without fluorination) to 2.078 Debye (**3** with fluorination). This is due to the presence of the fluorine atom with a constructive resultant with a –CH_2 group. It is shown from compound **4** that the two fluorine atoms increase the dipole moment to 3.429 Debye. This is because the resultant of the two fluorine atoms and the –CH_2 group are in the same direction. In the case of the keto-enol system [1], introducing two fluorine atoms at the two carbon atoms decreases the dipole moment due to the presence of the two fluorine atoms in opposite direction with the carbonyl group. But when the two fluorine atoms are at the same carbon atom (compound **5**, Fig. 1), the dipole moment is less than that of **4**, because the resultant of the two fluorine atoms and the –CH_2 group are not in the same direction. Compound **6** shows that the dipole moment is greater than that in compound **5**, since the resultant of the fluorine atoms has a constructive direction with the –CH_2 group. Similarly, the changes in the dipole moments of fluorinated 1-methylcyclopropenes can be explained (compounds **7** – **11**).

2.4. *Orbital Energies (HOMO and LUMO) of Fluorinated Methylenecyclopropanes and 1-Methylcyclopropenes*

The introduction of fluorine atoms into methylenecyclopropane and 1-methylcyclopropene affects their orbital energies (HOMO and LUMO) compared with their parent compounds.

In the case of fluorinated methylenecyclopropanes (compounds **3** – **6**, Table 4), an increase in the number of fluorine atoms causes a decrease in the energy gaps (E_g), but not steadily. It depends on the geometry of the compound. This suggests a decrease in the stability of compounds **3** – **6**. In the case of fluorinated 1-methylcyclopropene compounds **7** – **11**, Table 4, shows an increase in E_g suggesting a stabilization of these compounds. This agrees with the present isodesmic reactions and thermodynamic calculations, where fluorination destabilizes compound **1** and stabilizes compound **2**.

In the case of perfluorination of methylenecyclopropane (**1**) (Table 4), the energy gap decreases from 7.372 eV (compound **1**, without perfluorination) to 6.516 eV (compound **6**, with perfluorination), suggesting a destabilization of **1**.

In the case of perfluorination of 1-methylcyclopropene (**2**), E_g increases from 7.132 eV (compound **2**, without perfluorination) to 7.923 eV (compound **11**, with perfluorination), suggesting a stabilization of compound **11**. This agrees with the present thermodynamic and isodesmic calculations. Thus perfluorinated 1-methylcyclopropene **11** is present in substantial concentration.

3. Conclusion

It can be concluded that methylenecyclopropane is more stable than 1-methylcyclopropene by 11.535 kcal/mol. The methylene group less stabilizes the three-membered ring relative to the carbonyl group. The stability of methylenecyclopropane was found to decrease on fluorination, similar to that in the case of cyclopropanone. Perfluorinated 1-methylcyclopropene was found to be present in substantial concentration. These results were confirmed by Gibbs free energy calculations, isodesmic reactions and orbital energies.

[1] A. El-Alali, A. A. Marashdeh, and S. M. Khalil, Z. Naturforsch. **58a**, 749 (2003).
[2] W. R. Dolbier, Jr., C. R. Burkholder, A. L. Chaves, and A. Green, J. Fluorine Chem. **77**, 31 (1996).
[3] A. Shancke, J. Fluorine Chem. **45**, 129 (1989).
[4] A. Shancke, L. S. Schaad, and B. A. Hess, Jr., J. Mol. Struct. (Theochem.) **227**, 311 (1991).
[5] M. Itazaki, Y. Nishaihara, H. Takimoto, C. Yoda, and K. Osakada, J. Mol. Catalysis A **241**, 65 (2005).
[6] P. Davison, H. M. Frey, and R. Walsh, Chem. Phys. Lett. **120**, 227 (1985).
[7] W. E. Billups, A. J. Blakeney, N. A. Rao, and J. D. Buynak, Tetrahedron **37**, 3215 (1989).

[8] H. Ikeda, H. Namai, N. Kato, and T. Ikeda, Tetrahedron Lett. **47**, 2857 (2006).

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA 2003.

[10] P. E. Lindner and D. M. Lemal, J. Am. Chem. Soc. **119**, 3267 (1997).

[11] M. S. Al-Noeemat, R. A. Al-Ma'ani, and S. M. Khalil, Z. Naturforsch. **58a**, 738 (2003).

[12] W. H. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, J. Am.. Chem. Soc. **92**, 4796 (1970).

[13] M. H. Lien and A. C. Hopkinson, J. Phys. Chem. **88**, 1513 (1984).

[14] S. M. Khalil and H. M. Jarjis, Z. Naturforsch. **46a**, 247 (1990).

[15] H. M. Jarjis and S. M. Khalil, J. Chem. Soc. Perkin Trans. 2, 1701 (1986).

[16] W. F. Reynolds, P. Dais, R. W. Taft, and R. D. Topsom, Tetrahedron Lett. **22**, 1795 (1981).

[17] W. F. Al-Halasah and S. M. Khalil, Z. Naturforsch. **59a**, 980 (2004).

[18] B. M. Salim and S. M. Khalil, Z. Naturforsch. **60a**, 47 (2005).

[19] P. E. Lindner and D. M. Lemal, J. Am. Chem. Soc. **119**, 3259 (1997).

[20] M. I. Sway, I. D. Al-Shawabkeh, and S. M. Khalil, Z. Naturforsch. **59a**, 838 (2004).

[21] P. E. Lindner and D. M. Lemal, J. Org. Chem. **61**, 5109 (1996).

[22] Y. Kwon, J. Mol. Struct. (Theochem.) **488**, 93 (1999).