

# UC Riverside

## UCR Honors Capstones 2017-2018

### Title

A Test of the M06-2X Functional for Alkane Conformations

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Interim Vice Provost, Undergraduate Education

## **Abstract**

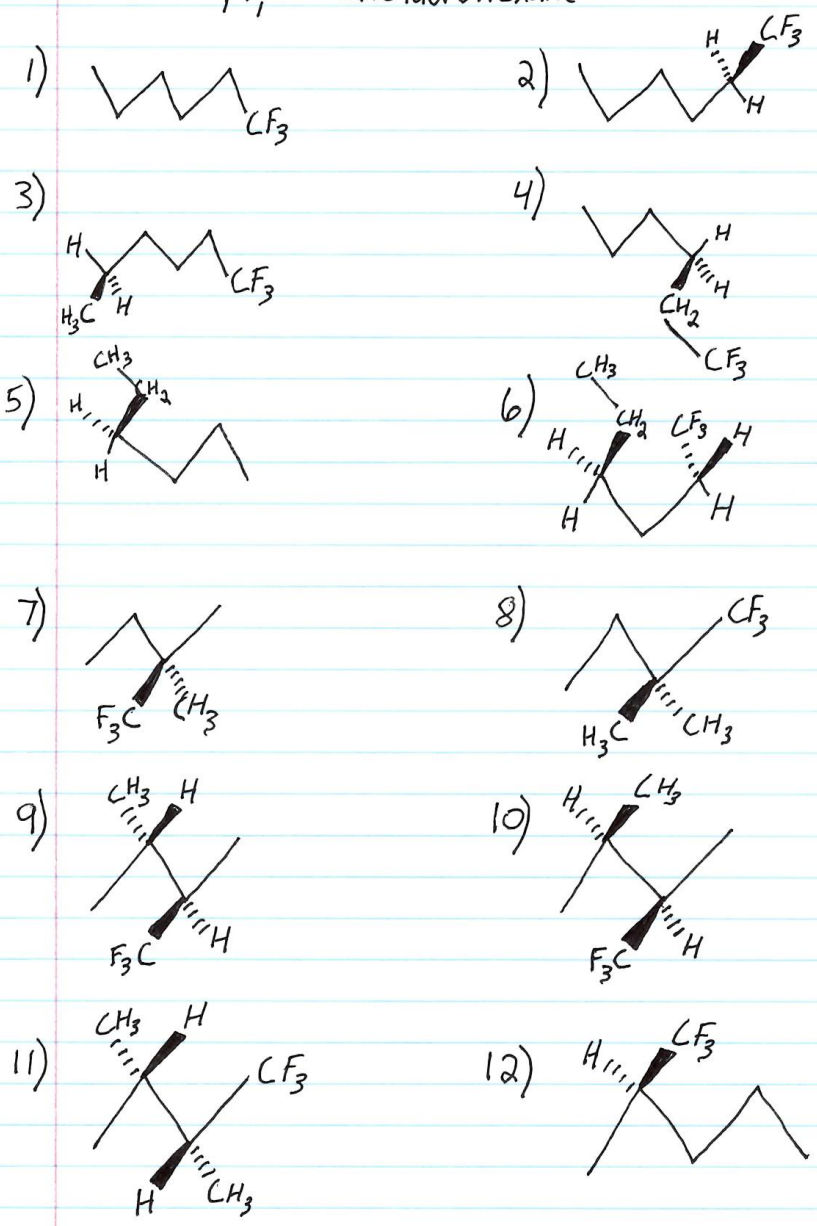
## Acknowledgments

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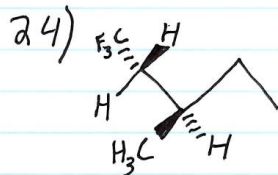
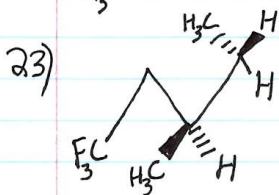
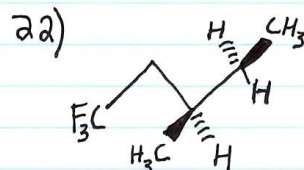
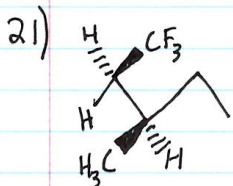
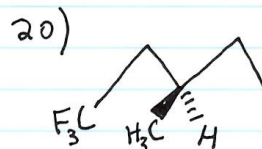
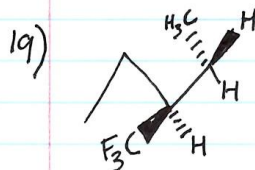
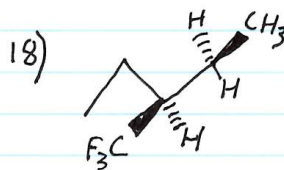
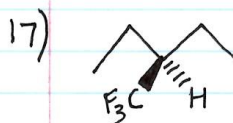
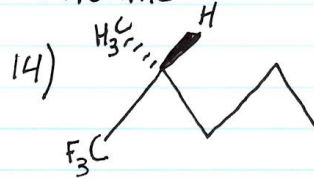
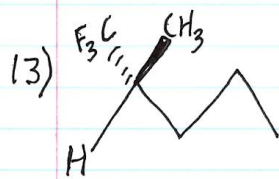
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### Conformations of 1,1,1-trifluorohexane

1,1,1 Trifluorohexane

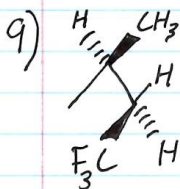
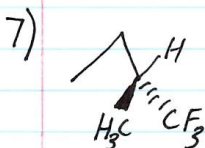
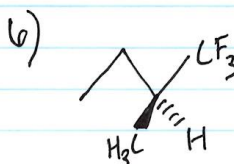
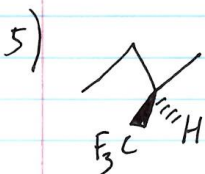
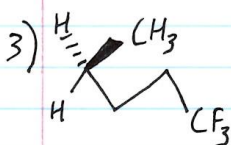
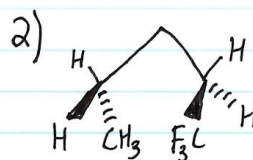
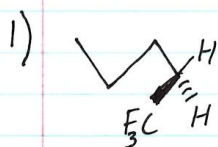


1,1,1 Trifluorohexane



### Conformations of 1,1,1-trifluoropentane

1, 1, 1 Trifluoropentane





## Introduction:

The goal of this research was to test the M06-2X functional for alkane conformations. The M06-2X functional is a high nonlocality functional with double the amount of nonlocal exchange (2X), and it is parametrized only for nonmetals (1). Using this functional, the anomaly of whether H-F intramolecular interactions stabilize the molecule was investigated. It has been known; that when two hydrogen atoms come closer than 2.35 angstroms they have a *gauche* interaction which causes the energy to increase. A *gauche* interaction is an interaction between two atoms that are at least four atoms away from each other and oriented in close proximity of one another. This can then cause a distortion in the bond angles which leads to an increase in energy and an unlikely conformation. Occasionally, however, the distortion can decrease the energy by allowing the conformation to have less angle strain due to the *gauche* interaction. The conformational energy levels are important because it can estimate which conformation a molecule rests in, as molecules prefer the lowest energy geometry. With isomers of 1,1,1-trifluoropentane and 1,1,1-trifluorohexane, it was thought that the fluoro-hydrogen interaction from the CF<sub>3</sub>-CH<sub>3</sub> interactions stabilize the molecule. The assumption was also made that CF<sub>3</sub>-CH<sub>3</sub> *gauche* interactions were the same as CF<sub>3</sub>-CH<sub>2</sub> *gauche* interaction and that CH<sub>3</sub>-CH<sub>3</sub> *gauche* interactions were the same as CH<sub>3</sub>-CH<sub>2</sub> *gauche* interactions. It was hoped that this research could provide insight to better understand this anomaly and why the hydrogen and fluorine interactions stabilize the molecule when increased steric hindrance should be present. This research explores the M06-2X functional for alkane conformations -- the energies were found and compared to get a better understanding of these molecules, as few of them have been synthesized.

## Methods:

In order to test the M062X functional for these alkane conformations, the thirty-three molecules were built in the GaussView program and were then optimized with the Gaussian09 program using the 6-31g\*\* basis set. The output file from this program was then used to check the energies and vibrational states. Specifically, we looked for any negative vibrational states which would indicate that the optimization had not completed. After acquiring the energies in Tables 1 and 2, the molecules were split into respective groups based on where the CF<sub>3</sub> was located. For the 24 conformations of isomers of 1,1,1-trifluorohexane it was divided into six groups; group one contained conformations 1-6 with 1 as a reference, group 2 contained the conformation 7 and 8 with 8 as the reference, group three contained conformations 9-11 with 11 as the reference, group four contained conformations 12-16 with 15 as the reference, group five contained conformations 17-19 with 18 as the reference, and group six contained conformations 20-24 with 23 as the reference. The 9 conformations of isomers of 1,1,1-trifluoropentane were divided into three groups; group one contained conformations 1-4 with 4 as the reference, group two contained conformations 5-7 with 5 as the reference, and group three contained conformations 8 and 9 with 8 as the reference. The reference molecule in each group was decided based on the highest, negative energy value so that the differences were all positive values. These energy values also had to be switched from atomic units, which is what is given from Gaussian09, to kJ/mol by the conversion factor of 1 atomic unit is equivalent to 2624.5 kJ/mol. Each molecule was then investigated for *gauche* interactions between CH<sub>3</sub>-CH<sub>3</sub> and CF<sub>3</sub>-CH<sub>3</sub>, as well as interactions between H-F. To better help visualize the H-F interactions a third program, Atoms in Molecules (AIM) which gives a topographical construct of each conformation, was used. After uploading a wavefunction file of the conformation, it was run through the AIM program in which

critical points and the nuclear positions were selected before observing the 3D representation. Obtaining the interactions, as well as the energy values associated with all thirty-three conformations, allowed a multiple linear regression line to be created. The y-values for the multiple linear regression were the energy differences between the reference molecule in each group and the other conformations. The x-values had three columns which were the three types of interactions, CH<sub>3</sub>-CH<sub>3</sub>, CF<sub>3</sub>-CH<sub>3</sub>, and H-F. The coefficients of the three interactions were all then found as shown in table 3 and 4 which led to the conclusion that the calculations of pentyl and hexyl atoms does not have any regularity.

**Results:**

Conformation (According to List of Figures)	Energy Level (Atomic Units)	Energy Level Difference from Reference (KJ/mol)	CH <sub>3</sub> -CH <sub>3</sub> Interactions	CF <sub>3</sub> -CH <sub>3</sub> Interactions	H-F Interactions
1(Reference for 1-6)	-534.60440	0	0	0	0
2	-534.60400	1.1	1	0	1
3	-534.60370	1.8	0	1	0
4	-534.60372	1.8	0	1	0
5	-534.60372	1.8	0	1	0
6	-534.60437	0.069	1	1	1
7	-534.61004	0.86	1	1	1

8 (Reference for 7-8)	-534.61036	0	0	2	0
9	-534.60642	2.8	1	1	1
10	-534.60660	2.4	2	1	2
11(Reference for 9-11)	-534.60751	0	1	2	1
12	-534.60659	0.93	1	0	1
13	-534.60631	1.7	1	1	1
14	-534.60692	0.042	0	1	0
15(Reference for 12-16)	-534.60694	0	1	1	1
16	-534.60631	1.7	1	1	1
17	-534.60476	2.6	2	0	2
18(Reference for 17-19)	-534.60574	0	2	1	2
19	-534.60543	0.82	1	1	1
20	-534.60502	0.20	1	1	1
21	-534.60389	3.2	2	1	2
22	-534.60454	1.4	1	2	1
23(Reference for 20-24)	-534.60509	0	1	1	1
24	-534.60501	0.21	1	1	1

**Table 1: 1,1,1-trifluorohexane Conformational Energy Levels and Interactions**

Conformation Number	Energy Level (Atomic Units)	Energy Level Difference from Reference (KJ/mol)	CH <sub>3</sub> -CH <sub>3</sub> Interactions	CF <sub>3</sub> -CH <sub>3</sub> Interactions	H-F Interactions
1	-495.30901	1.3	1	0	1
2	-495.30944	0.14	1	1	1
3	-495.30884	1.7	0	1	0
4 (Reference for 1-4)	-495.30949	0	0	0	0
5	-495.31160	1.3	1	0	1
6(Reference for 5-7)	-495.31208	0	0	1	0
7	-495.31128	2.1	1	1	1
8(Reference for 8-9)	-495.31098	0	1	0	1
9	-495.30952	3.8	2	0	2

**Table 2: 1,1,1-trifluoropentane Conformational Energy Levels and Interactions**

Regression Statistics								
Multiple R	0.360257584							
R Square	0.129785527							
Adjusted R Square	-0.049602878							
Standard Error	1.664669151							
Observations	18							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	3	6.612654116	2.204218039	1.193135997	0.348226816			
Residual	16	44.3379741	2.771123381					
Total	19	50.95062821						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
CF3-CH3	0.924990571	0.633728715	1.459600219	0.163754938	-0.41845429	2.268435432	-0.41845429	2.268435432
CH3-CH3	-0.173764341	0.530215484	-0.327724004	0.747369533	-1.297770955	0.950242272	-1.29777095	0.950242272
H-F	0	0	65535	#NUM!	0	0	0	0

**Table 3: Multiple Linear Regression of 1,1,1-trifluorohexane Data**

Regression Statistics								
Multiple R	0.129583513							
R Square	0.016791887							
Adjusted R Square	-0.972013522							
Standard Error	2.876369144							
Observations	6							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	3	0.423901101	0.141300367	0.01707867	0.996052342			
Residual	3	24.82049835	8.27349945					
Total	6	25.24439945						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
CF3-CH3	0.82313	5.213861845	0.157873381	0.884584471	-15.76970536	17.41596536	-15.76970536	17.41596536
CH3-CH3	0.37162	2.174330695	0.170912364	0.875169915	-6.548070687	7.291310687	-6.548070687	7.291310687
H-F	-0.52828	4.210573286	-0.1254651	0.908091068	-13.9282034	12.8716434	-13.9282034	12.8716434

**Table 4: Multiple Linear Regression of 1,1,1-trifluoropentane Data**

The results from this research listed throughout tables 1 and 2 were defined by the energy values, which were obtained from the Gaussian09 program, and the CH<sub>3</sub>-CH<sub>3</sub> and CF<sub>3</sub>-CH<sub>3</sub> gauche interactions which were obtained from investigating each conformation. The AIM program, which gives 3D representations of the conformations, was used to determine if the molecule had a bond critical point. The conformations of particular interest, have the *gauche* interaction between CF<sub>3</sub>-CH<sub>3</sub> because of the H-F bond that was associated. On the AIM program the topography of the conformations indicated that there was a bond critical point between the hydrogen and fluorine atoms, indicating that the number of bonds exceeds those in a model. This

extra bond critical point was thought to stabilize the molecule resulting in a decrease in energy, which would make the conformation more favorable. Tables 3 and 4 were constructed using the difference in energy as the y-axis and the difference in interactions as the x-axis, with a y-intercept set at 0. After obtaining the data from tables 3 and 4, the coefficients of the CH<sub>3</sub>-CH<sub>3</sub> interactions were not expected as they were extremely low and negative compared to what the value of this interaction should be, 3.5kJ/mol. This discrepancy between the calculated coefficient and the real value, led us to believe that the data could not be used to calculate the H-F interaction. In table 3, the coefficient for H-F interaction associated with 1,1,1-trifluorohexane was calculated to be 0, which led to another issue. These two facts from the data led us to the conclusion that by the calculations of pentyl and hexyl atoms, there does not seem to be any regularity between the H-F interactions with the M06-2X functional.

### **Discussion:**

Some anomalies were discovered when performing this research. One specific comparison was the conformations 1 and 6 of 1,1,1-trifluorohexane. Conformation 1 was a linear molecule with all components in the same plane and no *gauche* interactions or H-F interactions to be seen. Conformation 6 had one bond coming out of the plane and one bond going into the plane: one *gauche* interaction between CH<sub>3</sub>-CH<sub>2</sub> as well as a *gauche* interaction between CF<sub>3</sub>-CH<sub>2</sub> (and an interaction between a hydrogen and fluorine). This indicates that conformation 6 should have had a much greater energy than conformation 1 due to steric hindrance. This, however, is not the case and the energy levels are almost the same with an extremely low difference of just 0.069kJ/mol. The other molecules in this reference group, which had either a CH<sub>3</sub>-CH<sub>3</sub> *gauche* interaction or a CF<sub>3</sub>-CH<sub>3</sub> *gauche* interaction all had an energy difference of greater than 1.0kJ/mol. This anomaly appeared again when comparing molecules in group three of the isomers of 1,1,1-

trifluorohexane. Conformation 15 had a CH<sub>3</sub>-CH<sub>2</sub> *gauche* interaction and a CF<sub>3</sub>-CH<sub>2</sub> *gauche* interaction (and an interaction between a hydrogen and fluorine). Conformation 14, however, only had the CH<sub>3</sub>-CH<sub>2</sub> interaction but still had a very similar energy, with the difference being only 0.042kJ/mol. When we looked at two conformations in the same group and with the same number of interactions, however, the energy difference is considerably larger than these two cases. In group six, conformation 20 had one *gauche* interaction between CH<sub>3</sub>-CH<sub>3</sub> and one between CF<sub>3</sub>-CH<sub>3</sub> (and an interaction between a hydrogen and fluorine). Conformation 23 also had these three interactions present. When comparing their energy differences, the value was 0.20kJ/mol which is much larger than the other two examples. We also found energy differences around 0.80kJ/mol to be an irregularity as well. In group two, conformation 7 had one CH<sub>3</sub>-CH<sub>3</sub> *gauche* interaction and one CF<sub>3</sub>-CH<sub>3</sub> *gauche* interaction (and an interaction between a hydrogen and fluorine). Conformation 8, had two CH<sub>3</sub>-CH<sub>3</sub> *gauche* interactions with no CF<sub>3</sub>-CH<sub>3</sub> interactions present but an energy difference of 0.85kJ/mol greater than conformation 7. Conformation 19, in group five, also had an unexpected energy difference of 0.82kJ/mol. This was unusual due to conformation 19 having one less CF<sub>3</sub>-CH<sub>3</sub> *gauche* interaction than the reference conformation, 18. These discrepancies also held true when researching the nine conformations of isomers of 1,1,1-trifluoropentane. Conformation 4 was linear, with no part coming in or out of the plane and no interactions of any type. Conformation 2, however, had one CH<sub>3</sub> group coming into the plane and one CF<sub>3</sub> group going out of the plane and one *gauche* interaction between CH<sub>3</sub>-CH<sub>2</sub> and CF<sub>3</sub>-CH<sub>2</sub> (and an interaction between hydrogen and fluorine). The energy difference between these two molecules was also extremely small being only 0.14kJ/mol while the other two molecules in reference group one had a difference greater than 1.0kJ/mol. This was intriguing because having all three types of interactions should lead to a



much higher energy level than having no interactions. With these energy differences having such low values when they should be much greater, it led us to believe that a greater computational level than the M06-2X functional was needed. Future research could use a greater computational level, which could help determine if there is a regularity in the calculations of the pentyl and hexyl atoms.

**Reference:**

1. Yan Zhao & Donald G. Truhlar (2006). "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals". *Theor Chem Acc.* **120**: 215–241. [doi:10.1007/s00214-007-0310-x](https://doi.org/10.1007/s00214-007-0310-x)