

Theoretical Gas Phase Study of the Gauche and Trans Conformers of 1-Fluoro-2-Haloethanes $\text{CH}_2\text{F}-\text{CH}_2\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) by Ab Initio and Density Functional Methods: Absence of Gauche Effect

Ponnadurai Ramasami

Faculty of Science, Department of Chemistry,
University of Mauritius, Réduit, Mauritius
p.ramasami@uom.ac.mu
www.pages.intnet.mu/ramasami/

Abstract. This is a systematic theoretical gas phase study of the gauche and trans conformers of 1-fluoro-2-haloethanes ($\text{FCH}_2\text{CH}_2\text{X}$, $\text{X}=\text{Cl}, \text{Br}$ and I). The methods used are second order Møller-Plesset theory (MP2) and density functional theory (DFT). The basis set used is 6-311++(d,p) for all atoms except that 3-21G and CRENBL ECP are used for iodine atom. The functional used for DFT method is B3LYP. G2/MP2 calculation has also been carried out using MP2 optimised structure. The results indicate that unlike 1,2-difluoroethane, there is the absence of gauche effect and thus there is more preference for the trans conformer. The preference for the more stable trans conformer increases with increasing atomic size of the substituted halogen atom. The same trend is observed for energy difference between the gauche and trans conformers. The 1-fluoro-2-haloethanes have also been subjected to vibrational analysis.

1 Introduction

1,2-Disubstituted ethanes are amongst the simplest molecules showing conformational isomerism due to restricted rotation about carbon-carbon single bond [1]. Elemental analysis suggests that the 1,2-disubstituted ethanes can exist as a gauche and a trans conformer. It is generally found that the trans conformer is more stable than the gauche form and this is due to steric hindrance in the gauche conformation [2]. However fluorine has strong stereoelectronic and polar effects on the conformers of fluorine substituted molecules [3-8]. The net effect is that the gauche conformer is unusually more stable for the fluoro substituted conformers and this has been associated with the “gauche effect” [2,9]. To put this into context of this work, gauche-1,2-difluoroethane predominates in the gas phase and this has been found both experimentally [10-12] and from theoretical calculations [1,13-15]. It is generally agreed that the gauche conformer of 1,2-difluoroethane is more stable than the trans conformer by about 4.18 kJ/mol.

Although 1-fluoro-2-chloroethane has been the target [15] for conformational studies, 1-fluoro-2-bromoethane and 1-fluoro-2-iodoethane have not been explored. The scope of theoretical conformational studies has increased in recent years with the

availability of fast computers and quantum mechanical software. In order to provide more understanding to the gauche and trans conformers of 1,2-disubstituted-haloethanes and in continuation with the previous work [16], this theoretical study aims to explore the gauche and trans conformers, figure 1, of 1-fluoro-2-haloethane ($\text{FCH}_2\text{CH}_2\text{X}$, $\text{X}=\text{Cl}$, Br and I) in the gas phase. These conformers have been studied with a view to obtain (i) the optimised structural parameters, (ii) the energy difference between the gauche and trans conformers or the torsional barrier and (iii) related thermodynamics properties for torsional rotation. Apart from energy calculations, the conformers of 1-fluoro-2-haloethanes have also been subjected to vibrational analysis. The results of this study are reported herein.

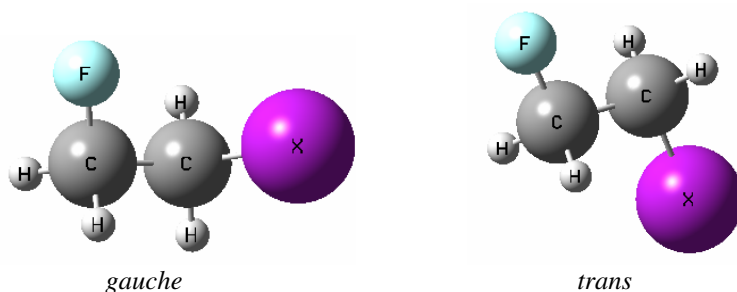


Fig. 1. Gauche and trans conformers of 1-fluoro-2-haloethane

2 Calculations

In this study all the calculations have been carried out using Gaussian 03W [17] program. GaussView 3.0 [18] has been used for visualising the molecules.

The calculations have been carried out using second order Møller-Plesset perturbation theory (MP2) and density functional theory (DFT). The basis set used is 6-311++G(d,p) for all atoms except that 3-21G and CRENBL ECP [19] are used for iodine only. The basis set 6-311++G(d,p) is appropriate for conformational studies for small molecules [15,16]. The functional used for DFT method is B3LYP. A conformer has first been optimised and the optimised structure has then been used for frequency calculations using the same method and basis set involved for optimisation. G2/MP2 calculation has also been carried out but could not be done for 1-fluoro-2-iodoethane due to unavailability of basis sets used by the method for iodine atom. Optimised structure at MP2/6-311++G(d,p) level has been used for G2/MP2 calculation.

3 Results and Discussion

The optimised structural parameters for the trans and gauche conformers of the 1-fluoro-2-haloethanes which are of interest and obtained using the MP2 and B3LYP methods and the basis set described in the calculations section are summarised in Table 1. The available literature values for the gauche conformer of 1-fluoro-2-chloroethane are also

included and it can be found that there is a good comparison. It is interesting to note that there is little difference between the MP2 and B3LYP calculated parameters. However bond lengths prediction from B3LYP are generally larger than MP2 values. The angles predicted by the two methods show more of random variations for a general statement.

Table 1. Optimised structural parameters for the 1-fluoro-2-haloethanes

Parameter	MP2		B3LYP	
	Trans	Gauche	Trans	Gauche
1-fluoro-2-chloroethane				
r (C-F)	1.392 Å	1.388 Å (1.365 Å)*	1.402 Å	1.395 Å
r (C-C)	1.515 Å	1.509 Å (1.530 Å)*	1.517 Å	1.509 Å
r (C-Cl)	1.779 Å	1.778 Å (1.787 Å)*	1.811 Å	1.810 Å
∠ (CCF)	108.3°	111.5° (109.7°)*	107.9°	110.8°
∠ (CCCl)	108.7°	110.2° (111.1°)*	109.2°	112.6°
τ (FCCCl)	180.0°	67.2° (68.3°)*	180.0°	69.8°
1-fluoro-2-bromoethane				
r (C-F)	1.394 Å	1.387 Å	1.404 Å	1.394 Å
r (C-C)	1.515 Å	1.510 Å	1.515 Å	1.508 Å
r (C-Br)	1.940 Å	1.940 Å	1.972 Å	1.974 Å
∠ (CCF)	108.1°	110.4°	107.9°	111.0°
∠ (CCBr)	109.1°	112.0°	109.2°	112.8°
τ (FCCBr)	180.0°	66.5°	180.0°	68.6°
1-fluoro-2-iodoethane				
r (C-F)	1.392 Å	1.386 Å	1.402 Å	1.393 Å
r (C-C)	1.506 Å	1.504 Å	1.513 Å	1.508 Å
r (C-I)	2.148 Å	2.150 Å	2.190 Å	2.193 Å
∠ (CCF)	108.4°	110.6°	108.0°	111.0°
∠ (CCI)	110.5°	113.5°	110.0°	113.6°
τ (FCCI)	180.0°	64.5°	180.0°	67.1°

* Reference 9

The energies of the trans and gauche conformers of the 1-fluoro-2-haloethanes calculated at MP2 and B3LYP and basis sets described in the calculations section are given in Table 2. These energies have been obtained after full geometry optimisation which has been verified by frequency calculation. G2/MP2 energies are also given in Table 2. The torsional barrier and related thermodynamic parameters are summarized in Table 2. A glance at Table 2 clearly shows that the trans conformer is more stable than the gauche form unlike the behaviour of 1,2-difluoroethane. The energies of all the conformers are more negative using the DFT calculation and thus this means that conformers should be more stable than on the basis of DFT rather than MP2 calculations. The rotational barrier becomes larger with increasing atomic size of the substituted halogen atom. The rotational barriers predicted using MP2 calculations are greater than DFT calculations but they are all within acceptable deviations. The results for 1-fluoro-2-haloethanes are in agreement with literature values [9,20]. The free energy barrier has been used to estimate the relative percentages of the trans and gauche conformers. It is found that at 298 K, the percentages of the trans conformer calculated using MP2 values are 70, 80 and 86 respectively for X=Cl, Br and I (FCH₂CH₂X). These percentages are of the same order based on DFT calculations.

Table 2. Calculated energies and thermodynamic parameters of the 1-fluoro-2-haloethanes

Compound	Trans (Hartrees)	Gauche (Hartrees)	Torsional barrier (kJ/mol)	ΔG (298 K) (kJ/mol)
MP2/6-311++G(d,p) for all atoms except 3-21G for iodine atom				
1-fluoro-2-chloroethane	637.7023655	637.7014765	2.33	2.10
1-fluoro 2-bromoethane	2750.5506970	2750.5492520	3.79	1.81
1-fluoro 2-iodoethane	7065.3805704	7065.3785745	5.24	4.41
MP2/6-311++G(d,p) for all atoms except CRENBL ECP for iodine atom				
1-fluoro 2-iodoethane	287.7294325	287.7274743	5.14	4.65
B3LYP/6-311++G(d,p) for all atoms except 3-21G for iodine atom				
1-fluoro-2-chloroethane	638.7430021	638.7422184	2.06	3.46
1-fluoro 2-bromoethane	2752.6650578	2752.6637633	3.40	2.96
1-fluoro 2-iodoethane	7068.5253779	7068.5235271	4.86	4.01
B3LYP/6311++G(d,p) for all atoms except CRENBL ECP for iodine atom				
1-fluoro 2-iodoethane	289.9790627	289.9771779	4.95	4.40
G2/MP2				
1-fluoro-2-chloroethane	637.9201750	637.9193236	2.24	2.24
1-fluoro 2-bromoethane	2750.7580730	2750.7566020	3.86	3.83

The trans and gauche conformers of the 1-fluoro-2-haloethanes have also been subjected to vibrational analysis. All the 18 fundamentals of the trans and gauche

conformers have been assigned. The calculated frequencies are reported in Tables 3 and 4. These uncorrected frequencies have been assigned after visualization using GaussView. The values indicate that predictions with MP2 level of theory are systematically larger than B3LYP level of theory. The calculated frequencies for 1-fluoro-2-chloroethane are in agreement with literature values obtained theoretically [9] using B3LYP/6-311+G(d,p) and experimentally [21].

Table 3. Calculated frequencies (cm^{-1}) of the 1-fluoro-2-haloethanes and their assignments obtained at MP2/6-311+G(d,p) for all atoms except 3-21G for iodine atom

1-fluoro -2-chloroethane		1-fluoro -2-bromoethane		1-fluoro -2-iodoethane		Assignment
Trans	Gauche	Trans	Gauche	Trans	Gauche	
138.7 (10.3)	140.3 (2.3)	133.9 (8.9)	122.6 (1.9)	135.6 (6.9)	108.8 (2.2)	FCCX torsion
247.8 (12.3)	294.8 (0.9)	220.7 (7.5)	269.4 (1.6)	190.2 (4.4)	243.2 (1.2)	XCC bend
395.4 (3.0)	476.1 (13.0)	343.0 (5.3)	457.4 (12.9)	320.1 (7.1)	441.9 (10.0)	FCC bend
817.1 (0.2)	731.5 (24.7)	722.8 (25.8)	615.6 (10.6)	681.2 (14.6)	555.5 (0.9)	C-X str
827.5 (38.4)	872.9 (13.0)	800.4 (0.8)	849.7 (6.3)	786.5 (0.7)	818.8 (3.5)	CH ₂ rock
1066.8 (106.9)	1005.9 (7.6)	1043.0 (3.5)	982.2 (8.7)	1028.3 (2.8)	995.4 (24.1)	CH ₂ wag
1101.4 (2.4)	1087.9 (45.1)	1056.4 (114.2)	1054.7 (33.6)	1047.4 (122.3)	1046.7 (26.0)	C-F str
1113.0 (23.7)	1132.3 (44.3)	1106.4 (33.5)	1126.9 (58.2)	1126.4 (38.2)	1133.4 (53.3)	C-C str
1240.1 (0.9)	1248.9 (1.4)	1236.1 (1.0)	1226.7 (2.5)	1255.1 (0.9)	1245.9 (2.1)	CH ₂ twist
1326.2 (0)	1301.2 (0.6)	1282.3 (16.4)	1283.1 (2.9)	1309.8 (21.7)	1283.3 (1.8)	CH ₂ twist
1333.4 (14.5)	1381.2 (30.2)	1322.8 (0)	1344.0 (41.1)	1338.0 (0)	1364.5 (51.3)	CH ₂ wag
1447.8 (3.6)	1452.3 (12.2)	1436.7 (5.4)	1446.2 (12.6)	1433.8 (5.5)	1430.1 (1.8)	CH ₂ wag
1510.0 (5.4)	1477.6 (10.6)	1506.3 (6.2)	1474.1 (11.7)	1488.7 (12.7)	1470.3 (25.2)	CH ₂ scissor
1532.8 (0.8)	1517.1 (2.4)	1532.5 (1.0)	1519.0 (2.5)	1537.7 (1.8)	1519.1 (1.3)	CH ₂ scissor
3119.3 (14.8)	3099.0 (24.2)	3118.6 (13.7)	3093.7 (25.9)	3119.8 (18.9)	3098.8 (34.0)	CH ₂ sym str
3140.8 (17.8)	3124.6 (16.9)	3143.2 (11.0)	3128.5 (10.6)	3175.4 (9.4)	3156.4 (5.8)	CH ₂ sym str
3184.4 (9.8)	3170.5 (16.3)	3185.0 (11.1)	3166.8 (15.5)	3187.0 (17.7)	3170.6 (24.4)	CH ₂ antisym str
3215.8 (9.4)	3196.7 (6.4)	3220.3 (4.4)	3202.5 (2.6)	3257.3 (2.3)	3237.9 (2.2)	CH ₂ antisym str

Values in bracket are infrared intensities in (km/mol), (X=Cl, or Br or I).

Table 4. Calculated frequencies (cm^{-1}) of the 1-fluoro-2-haloethanes and their assignments obtained at B3LYP/6-311++G(d,p) for all atoms except 3-21G for iodine atom

1-fluoro -2-chloroethane		1-fluoro -2-bromoethane		1-fluoro -2-iodoethane		Assignment
Trans	Gauche	Trans	Gauche	Trans	Gauche	
125.1 (11.1)	129.6 (2.5)	123.8 (9.4)	111.9 (1.9)	127.3 (8.0)	99.1 (2.0)	FCCX torsion
241.9 (13.3)	285.4 (1.2)	212.1 (8.0)	258.8 (2.1)	188.9 (5.6)	241.5 (1.8)	XCC bend
376.9 (2.7)	461.5 (14.7)	327.3 (5.1)	444.3 (15.6)	295.7 (5.2)	427.7 (14.6)	FCC bend
753.6 (50.9)	662.0 (34.0)	672.8 (36.8)	565.9 (15.8)	620.1 (29.2)	496.7 (4.3)	C-X str
797.9 (0.8)	848.0 (15.3)	785.1 (1.6)	828.1 (7.8)	758.4 (1.1)	794.3 (4.0)	CH ₂ rock
1017.9 (131.1)	968.9 (9.4)	1006.2 (142.1)	952.4 (12.3)	979.8 (1.5)	951.4 (21.7)	CH ₂ wag
1061.5 (1.9)	1046.6 (58.5)	1010.8 (2.8)	1019.5 (42.2)	1001.2 (149.3)	1002.4 (28.1)	C-F str
1069.8 (11.4)	1089.6 (40.7)	1068.1 (18.8)	1085.1 (57.8)	1076.9 (27.1)	1090.3 (62.5)	C-C str
1211.4 (0.9)	1215.2 (2.5)	1206.4 (1.0)	1199.2 (3.3)	1219.7 (0.9)	1205.0 (3.8)	CH ₂ twist
1290.1 (12.3)	1270.8 (0.28)	1246.4 (16.7)	1250.1 (6.4)	1230.9 (25.2)	1235.7 (16.0)	CH ₂ twist
1297.6 (0)	1335.6 (33.6)	1295.9 (0)	1308.0 (44.1)	1305.0 (0)	1302.8 (54.4)	CH ₂ wag
1409.5 (2.6)	1416.4 (10.9)	1402.5 (3.8)	1413.8 (12.3)	1405.3 (7.6)	1420.4 (11.4)	CH ₂ wag
1492.4 (4.0)	1462.2 (9.7)	1488.4 (5.0)	1458.3 (10.6)	1477.7 (6.3)	1444.0 (13.4)	CH ₂ scissor
1510.5 (2.5)	1489.3 (4.1)	1509.3 (2.4)	1490.2 (4.2)	1510.3 (1.7)	1494.9 (3.1)	CH ₂ scissor
3063.5 (16.4)	3034.7 (25.3)	3065.4 (14.9)	3028.5 (26.3)	3065.5 (17.5)	3025.2 (30.6)	CH ₂ sym str
3095.8 (16.2)	3081.5 (11.6)	3105.1 (9.8)	3090.0 (6.0)	3118.7 (17.8)	3091.4 (14.2)	CH ₂ sym str
3116.2 (12.4)	3098.7 (20.2)	3119.1 (13.3)	3099.3 (19.0)	3127.0 (9.1)	3112.9 (13.7)	CH ₂ antisym str
3160.8 (8.1)	3143.7 (5.4)	3173.9 (3.3)	3158.0 (2.1)	3200.4 (2.7)	3181.4 (2.3)	CH ₂ antisym str

Values in bracket are infrared intensities in (km/mol), (X=Cl, or Br or I).

4 Conclusions

The objectives of this work using theoretical methods, have been achieved with the determination of the optimised structural parameters, torsional barrier and related thermodynamics parameters for the 1-fluoro-2-haloethanes. The results indicate a preference for the trans conformer and hence the absence of gauche effect. The latter is common for fluorine substituted conformers such as 1,2-difluoroethane. It can also be deduced that there is increasing preference for the trans conformer with increasing

size of the substituted halogen atom. The results of this study are also in agreement with literature findings for 1,2-disubstituted ethanes and thus they are promising for the modelling of conformers of these molecules by theoretical method.

Acknowledgements

The author acknowledges facilities from the University of Mauritius and anonymous reviewers for their comments to improve the manuscript.

References

1. Dixon D.A., Matsuzawa N., Walker S.C.: Conformational Analysis of 1,2-Dihaloethanes: A Comparison of Theoretical Methods. *J. Phys. Chem.* 96 (1992) 10740-10746
2. Wolfe S.: The Gauche Effect. Some Stereochemical Consequences of Adjacent Electron Pairs and Polar Bonds. *Acc. Chem. Res.* 5 (1972) 102-111
3. O'Hagan D., Rzepa H.S.: Some Influences of Fluorine in Bioorganic Chemistry. *Chem. Commun.* (1997) 643-652
4. Rablen P.R., Hoffman R.W., Hrovat D.A.: Is Hyperconjugation Responsible for the "Gauche Effect" in 1-fluoropropane and 1-fluoroethanes?. *J. Chem. Soc. Perkin Trans. 2.* 8 (1999) 1719-1726
5. O'Hagan D., Bilton C., Howard J.A.K., Knight L., Tozer D. J.: The Preferred Conformation of N- β -fluoroethylamides. Observation Fluorine Amide Gauche Effect. *J. Chem. Soc. Perkin. Trans. 2.* 8 (2000) 600-607
6. Tavasli M., O'Hagan D., Pearson C. Petty M.C.: The Fluorine Gauche Effect. Langmuir Isotherms Reprot the Relative Conformational Stability of (+/-)-Erythro- and (+/-)-Threo-9,10-Difluorostearic acids. *Chem. Commun.* 7 (2002) 1226-1227
7. Briggs C.R., Allen M.J., O'Hagan D., Tozer D.J., Slawin A.M., Geota A.E., Howard J.A.: The Observation of a Large Gauche Preference when 2-Fluoroethylamine and 2-Fluoroethanol Become Protonated. *Org. Biomol. Chem.* 2 (2004) 732-740
8. Banks J.W., Batsanov A.S., Howard J.A.K., O'Hagan D., Rzepa H.S., Martin-Santamaria S.: The Preferred Conformation of α -Fluoroamides. *J. Chem. Soc., Perkin Trans. 2.* 8 (1999) 2409-2411
9. Wiberg K.B., Murcko M. A., Laidig E.K., MacDougall P. J.: Origin of the "Gauche Effect" in Substituted Ethanes and Ethenes. The Gauche Effect. *J. Phys. Chem.* 96 (1992) 6956-6959 and references therein
10. Harris W.C., Holtzclaw J.R., Kalasinsky V.F.: Vibrational Spectra and Structure of 1,2-Difluoroethane: Gauche-Trans Conformers. *J. Chem. Phys.* 67 (1977) 3330-3338
11. Friesen D., Hedberg K.: Conformational Analysis. 7. 1,2-Difluoroethane. An Electron-Diffraction Investigation of the Molecular Structure, Composition, Trans-Gauche Energy and Entropy Differences, and Potential Hindering Internal Rotation. *J. Am. Chem. Soc.* 102 (1980) 3987-3994
12. Takeo H., Matsumura C., Morino Y.: Microwave Spectrum and Molecular Structure of Gauche-1,2-Difluoroethane. *J. Chem. Phys.* 84 (1986) 4205-4210
13. Martell J.M., Boyd R.J.: An Ab initio Study of the Series $C_2H_nF_{6-n}$ (n=0-6): Geometries, Total Energies, and C-C Bond Dissociation Energies. *J. Phys. Chem.* 96 (1992) 6287-6290

14. Durig J.R., Liu J., Little T.S., Kalasinsky V.F.: Conformational Analysis, Barriers to Internal Rotation, Vibrational Assignment, and Ab Initio Calculations of 1,2-Difluoroethane. *J. Phys. Chem.* 96 (1992) 8224-8233
15. Wiberg K.B., Keith T.A., Frisch M.J., Murcko M.: Solvent Effects on 1,2-Dihaloethane Gauche/Trans Ratios. *J. Phys. Chem.* 99 (1995) 9072-9079
16. Ramasami P.: Gauche and Trans Conformers of 1,2-Dihaloethanes: A Study by Ab Initio and Density Functional Theory Methods. *Lecture Series on Computer and Computational Sciences, Vol. 1, Brill Academic Publishers, The Netherlands* (2005) 732-734
17. Gaussian 03, Revision C.02, Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi, R. Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A.: *Gaussian, Inc., Wallingford CT, 2004.*
18. http://www.gaussian.com/gv_plat.htm
19. Hurley M.M., Pacios L.F., Christiansen P.A., Ross R.B., Ermler W.C.: Ab Initio Relativistic Effective Potentials with Spin-Orbit Operators. II. K through Kr. *J. Chem. Phys.* 84 (1986) 6840-6853
20. Durig J.R., Pan C., Witkowski W., Guirgis G.A.: Conformational Stability, Infrared and Raman spectra, and Vibrational assignment of Ethyl Bromogermane. *Can. J. Chem.* 82 (2004) 964-977
21. Tanabe K.: Calculation of Infrared Band Intensities and Determination of Energy Differences of Rotational Isomers of 1,2-Dichloro-, 1,2-Dibromo- and 1-Chloro-2-Bromoethane. *Spectrochim. Acta* 28 (1972) 407-424