

Theoretical Gas Phase Study of the Gauche and Trans Conformers of 1-Bromo-2-Chloroethane and Solvent Effects

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Abstract. This is a systematic gas phase study of the gauche and trans conformers of 1-bromo-2-chloroethane. The methods used are second order Møller-Plesset theory (MP2) and density functional theory (DFT). The basis set used is 6-311++G(d,p) for all atoms. The functional used for DFT method is B3LYP. G2/MP2 and CCSD(T) calculations have also been carried out using MP2 optimised structure. The results indicate that there is more preference for the trans conformer. The energy difference between the trans and gauche conformers (ΔE_{tg}) and related rotational thermodynamics are reported. The MP2/6-311++G(d,p) energy difference (ΔE_{tg}) for 1-bromo-2-chloroethane is 7.08 kJ/mol. The conformers of 1-bromo-2-chloroethane have also been subjected to vibrational analysis. This study has also been extended to investigate solvent effects using the Self-Consistent Reaction Field methods. The structures of the conformers are not much affected by the solvents but the energy difference (ΔE_{tg}) decreases with increasing polarity of the solvent. The results from the different theoretical methods are in good agreement.

1 Introduction

100 years ago, Bischoff found that C-C single bond in ethane is not completely free [1]. Due to the hindered internal rotation, 1,2-disubstituted ethanes are the simplest molecules showing conformational isomerism thus leading to the gauche and trans conformers. 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]. Theoretical calculations of the energy difference between the trans and gauche conformers (ΔE_{tg}) have been actively pursued for over 40 years, as they are important parameters to the conformational analysis of molecules [3].

In previous communications, energy differences (ΔE_{tg}) have been calculated for 1,2-dihaloethanes (XCH_2CH_2X , X=F, Cl, Br and I) [4] and for 1-fluoro-2-haloethanes (FCH_2CH_2X , X=Cl, Br and I) [5] in the gas phase. These studies indicate that except for 1,2-difluoroethane, the trans conformer is more stable than the gauche conformer. The energy difference (ΔE_{tg}) increases with the size of the halogen. The atypical

behaviour of 1,2-difluoroethane has been associated with the gauche effect [6-10] but the latter is not observed for the 1-fluoro-2-haloethanes. Solvent effects have also been explored for 1,2-dichloroethane and 1,2-dibromoethane [11]. The study indicates that an increase in the solvent polarity decreases the energy difference (ΔE_{tg}). It is worth to point out at this stage that literature involving theoretical studies is limited with respect to solvent effects [11,12] although polarity of the solvent is known to affect conformational equilibrium [13].

As part of a continuing series of studies on internal rotation [4-5,11], 1-bromo-2-chloroethane has been the target of this work. 1-Bromo-2-chloroethane, being a 1,2-disubstituted ethane, can exist as the gauche (C_1 symmetry) and trans (C_s symmetry) conformers as illustrated in Figure 1.



Fig. 1. Gauche and Trans conformers of 1-bromo-2-chloroethane

These gauche and trans conformers of 1-bromo-2-chloroethane have been studied with a view to obtain (i) the optimised structural parameters, (ii) the energy difference (ΔE_{tg}) and (iii) related thermodynamics properties for torsional rotation. Apart from energy calculations, the conformers of 1-bromo-2-chloroethane have also been subjected to vibrational analysis. Solvent effects, using Self-Consistent Reaction Field (SCRF) methods [14], have also been explored with the dielectric constant of the solvent varying from 5 to 40. The results of the present investigation are reported herein and to the best of our knowledge there has not been such a type of investigation.

2 Calculations

All the calculations have been carried out using Gaussian 03W [15] program suite and GaussView 3.0 [16] 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. The functional used for DFT method is B3LYP. A conformer has first been optimised and the optimised structure has then been used for frequency calculation using the same method and basis set involved for optimisation. G2/MP2 and

CCSD(T) calculations have also been carried out using MP2/6-311++G(d,p) optimised structure. For all the converged structures, frequencies calculations have also been carried out in order to ensure that this conformation corresponds to a minimum. The SCRF methods used are Isodensity Model (SCRF=IPCM) [14] and Self-Consistent Isodensity Model (SCRF=SCIPCM) [14]. MP2/6-311++G(d,p) gas phase optimised structures have been used for the single point calculations for the Isodensity Model and B3LYP/6-311++G(d,p) full geometry optimisation calculations have been carried for the Self-Consistent Isodensity Model.

3 Results and Discussion

The optimised structural parameters, which are of interest for the two conformers of 1-bromo-2-chloroethane, are summarised in Table 1. Analysis of Table 1 allows some conclusions to be made. Firstly, for both conformers the predicted C-Cl and C-Br bond lengths are longer from B3LYP calculation although the C-C and C-H bond lengths are nearly same. Secondly the bond angles CCl and CCB are larger for the gauche conformer than the trans conformer. This can be explained in terms of greater amount of steric repulsion between the halogen atoms in the gauche conformation. Further these bond angles are larger from B3LYP calculation. However, these bond angles are nearly same for the trans conformer for both methods. Thirdly, the torsional angle ClCCBr for the gauche conformer is larger from B3LYP calculation. Lastly the moments of inertia are generally greater from MP2 calculation with $I_A > I_B \approx I_C$.

Table 1. Optimised structural parameters for the gauche and trans conformers of 1-bromo-2-chloroethane using 6-311++G(d,p) as the basis set

Parameter	B3LYP		MP2	
	Gauche	Trans	Gauche	Trans
$r(\text{C-Cl})/\text{\AA}$	1.809	1.821	1.776	1.783
$r(\text{C-C})/\text{\AA}$	1.511	1.512	1.512	1.512
$r(\text{C-Br})/\text{\AA}$	1.973	1.980	1.937	1.941
$r(\text{C-H})/\text{\AA}$	1.090	1.087	1.090	1.089
$\angle(\text{CCCl})/\text{\AA}$	113.2	109.0	112.3	109.0
$\angle(\text{CCBr})/\text{\AA}$	113.3	109.2	112.6	109.5
$\tau(\text{ClCCBr})/\text{\AA}$	70.4	180.0	68.0	180.0
Dipole moment/ D	2.826	0.013	3.067	0.015
I_A/GHz	8.870	28.689	8.862	28.909
I_B/GHz	1.427	0.961	1.509	0.991
I_C/GHz	1.283	0.941	1.347	0.970

The energies of the gauche and trans conformers of the 1-bromo-2-chloroethane are given in Table 2. These energies have been obtained after full geometry optimisation which has been verified by frequency calculation. G2/MP2 and CCSD(T) energies are also given in Table 2. As part of G2/MP2 and CCSD(T) calculations, MP2/6-311+G(3df,2p) and MP3/6-311++G(d,p) energies are included in Table 2. The energy difference (ΔE_{tg}) and related rotational thermodynamic parameters are also summarised in Table 2. A glance at Table 2 clearly shows that the trans conformer is more stable. The energy difference (ΔE_{tg}) predicted using B3LYP method is greater than MP2 method for the same basis set. The free energy difference (ΔG_{tg}) can be used to estimate the relative percentage of the trans and gauche conformers. It is found that at 298 K, the percentage of the trans conformer is generally greater than 90%. At this stage, it is interesting to compare the energy difference (ΔE_{tg}) of the unsymmetrical 1-bromo-2-chloroethane with the symmetrical 1,2-dichloroethane and 1,2-dibromoethane. The MP2/6-311++G(d,p) values for these compounds are 6.08 and 8.79 kJ/mol respectively [4].

Table 2. Calculated energies and rotational thermodynamic parameters for the conformers of 1-bromo-2-chloroethane

Method	Gauche (Hartrees)	Trans (Hartrees)	ΔE_{tg} (kJ/mol)	ΔH_{tg} (0 K) (kJ/mol)	ΔH_{tg} (298 K) (kJ/mol)	ΔG_{tg} (298 K) (kJ/mol)
B3LYP/6-311++G(d,p)	-3113.0202578	-3113.0234642	8.42		7.65	8.01
MP2/6-311++G(d,p)	-3111.0127999	-3111.0154953	7.08		6.45	6.86
MP2/6-311+G(3df,2p)	-3110.6755106	-3110.6778141	6.05			
G2/MP2	-3110.7491862	-3110.7515898		6.31	5.88	6.26
MP3/6-311++G(d,p)	-3110.5697388	-3110.5725913	7.49			
CCSD(T)/6-311++G(d,p)	-3110.5944679	-3110.5972661	7.35			

The gauche and trans conformers of 1-bromo-2-chloroethane have also been subjected to vibrational analysis. The calculated frequencies are reported in Table 3 and the simulated spectra are illustrated in Figure 2. The 18 modes of vibrations account for the irreducible representations $\Gamma_v = 18A$ of the C_1 point group of the gauche conformer and $\Gamma_v = 11A' + 7A''$ of the C_s point group of the trans conformer. All the 18 fundamentals of the gauche and trans conformers have been assigned appropriately. The values indicate that predictions with MP2 level of theory are systematically larger than B3LYP level of theory. Since steric interaction between the atoms is more in the gauche than trans conformer, the CCCI and CCB_r bending modes have higher frequencies in the gauche conformation than the trans conformation. The bending vibrational modes of the CH₂ group are in the order scissoring > wagging > twisting > rocking. The bending mode of the CH₂ group attached to bromine atom is at a lower frequency compared to CH₂ group attached to chlorine atom. This can be explained on the basis of reduced mass for CH₂ group when attached to bromine atom. However the stretching vibrational modes of the CH₂ group bonded to the halogen atoms are reversed in terms of frequency. The calculated frequencies for 1-bromo-2-chloroethane are in agreement with literature values obtained experimentally [17].

Table 3. Calculated frequencies (cm^{-1}) of the conformers of 1-bromo-2-chloroethane and their assignments

		Gauche		Trans			
B3LYP	MP2	Literature [17]	Assignments	B3LYP	MP2	Literature [17]	Assignments
3158.9 (1.4)	3206.7 (1.7)	3010	CH ₂ a str	3185.5 (0.9)	3229.5 (1.1)	3010	CH ₂ a str
3138.2 (1.2)	3190.4 (1.4)	3010	CH ₂ a str	3159.9 (0.4)	3207.5 (0.4)	3010	CH ₂ a str
3090.1 (12.3)	3131.8 (13.9)	2960	CH ₂ s str	1292.6 (0.02)	1314.6 (0.02)	1259	CH ₂ twist
3071.8 (8.9)	3120.2 (9.6)	2960	CH ₂ s str	11219.3 (2.6)	1158.3 (3.1)	1111	CH ₂ twist
1469.1 (3.0)	1481.0 (1.0)	1428	CH ₂ scis	975.6 (0.3)	1011.3 (0.5)	961	CH ₂ rock
1461.7 (10.8)	1471.7 (10.6)	1428	CH ₂ scis	771.1 (3.3)	785.0 (2.2)	763	CH ₂ rock
1338.6 (25.4)	1382.1 (24.3)	1299	CH ₂ wag	109.2 (6.0)	119.0 (5.1)	123	Torsion
1296.5 (57.3)	1337.9 (45.2)	1260	CH ₂ wag	3113.3 (7.7)	3151.1 (10.4)	2960	CH ₂ s str
1211.4 (3.2)	1244.7 (3.0)	1190	CH ₂ twist	3102.3 (1.9)	3142.4 (1.5)	2960	CH ₂ s str
1146.6 (1.5)	1179.2 (2.0)	1127	CH ₂ twist	1490.9 (1.5)	1499.7 (0.04)	1446	CH ₂ scis
1038.2 (1.8)	1077.7 (1.3)	1025	CC str	1486.8 (5.6)	1493.9 (5.1)	1444	CH ₂ scis
928.7 (9.1)	968.6 (6.9)	923	CH ₂ rock	1320.9 (2.7)	1372.4 (2.9)	1284	CH ₂ wag
868.5 (23.1)	898.7 (18.5)	856	CH ₂ rock	1237.0 (49.6)	1272.9 (49.1)	1203	CH ₂ wag
658.4 (26.0)	724.2 (13.8)	664	CCl str	1060.7 (1.0)	1100.8 (1.2)	1052	CC str
555.0 (13.9)	610.6 (8.7)	571	CBr str	716.3 (30.4)	803.3 (24.5)	726	CCl str
382.0 (8.7)	397.1 (5.5)	385	CCCl deform	616.2 (70.1)	688.6 (40.6)	630	CBr str
241.6 (1.4)	251.0 (0.9)	251	CCBr deform	242.2 (0.9)	259.1 (0.7)	251	CCCl deform
94.1 (0.6)	106.6 (0.5)	107	Torsion	191.1 (7.8)	201.0 (6.4)	202	CCBr deform

-Values in bracket are infrared intensities in (km/mol)

-For the trans conformer, first 11 frequencies are of A' symmetry and last 8 frequencies are of A'' symmetry

-For the gauche conformer, all 18 frequencies are of A symmetry

This study has also been extended to study solvent effects. The structures of the conformers are not much affected by the polarity of the solvents. The effects of solvent on the energy of the gauche and trans conformers and energy difference (ΔE_{ig}) are summarised in Table 4 and illustrated in Figure 3. It can be found that solvent effects are small but they can be calculated and an increase in the polarity of

the solvent decreases the energy difference (ΔE_{tg}). However in the polar solvents, the decrease in the energy of the more polar gauche conformer is larger than the trans conformer.

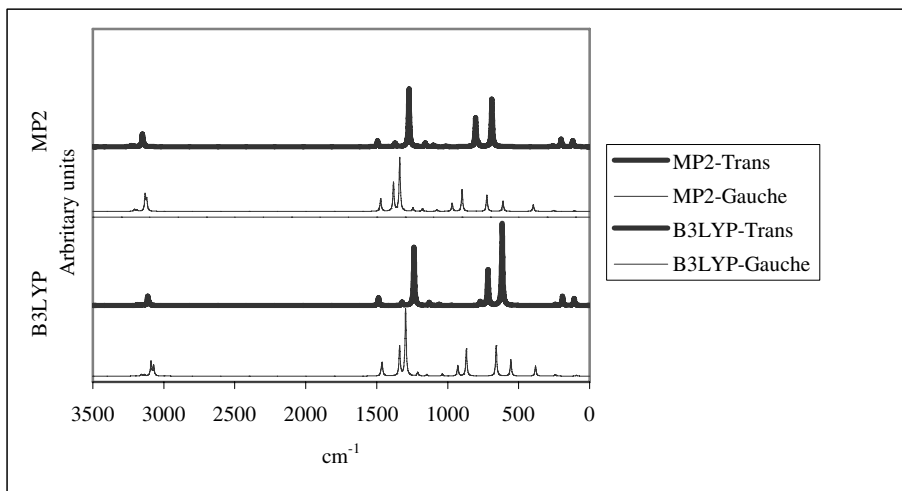


Fig. 2. Simulated spectra of the gauche and trans conformers of 1-bromo-2-chloroethane

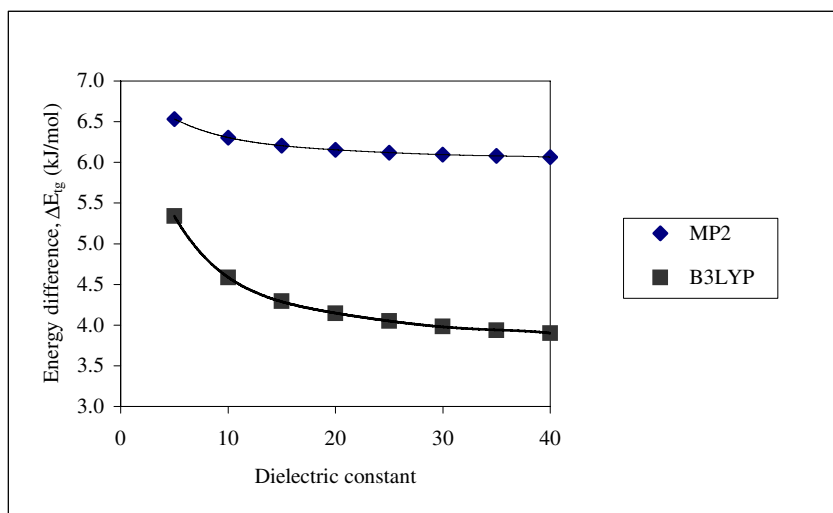


Fig. 3. Energy difference (ΔE_{tg}) for 1-bromo-2-chloroethane in solvents with different dielectric constants

Table 4. Energy and energy difference (ΔE_{tg}) for the conformers of 1-bromo-2-chloroethane in solvents with different dielectric constants

ϵ	MP2			B3LYP		
	Gauche (Hartrees)	Trans (Hartrees)	ΔE_{tg} (kJ/mol)	Gauche (Hartrees)	Trans (Hartrees)	ΔE_{tg} (kJ/mol)
5	-3110.5351096	-3110.5326210	6.53	-3113.0262618	-3113.0242279	5.34
10	-3110.5356523	-3110.5332507	6.31	-3113.0268009	-3113.0250547	4.58
15	-3110.5358531	-3110.5334889	6.21	-3113.0269959	-3113.0253597	4.30
20	-3110.5359575	-3110.5336138	6.15	-3113.0270967	-3113.0255187	4.14
25	-3110.5360216	-3110.5336906	6.12	-3113.0271582	-3113.0256163	4.05
30	-3110.5360649	-3110.5337428	6.10	-3113.0271996	-3113.0256822	3.98
35	-3110.5360961	-3110.5337807	6.08	-3113.0272295	-3113.0257298	3.94
40	-3110.5361197	-3110.5338094	6.07	-3113.0272520	-3113.0257657	3.90

ϵ : Dielectric constant.

4 Conclusions

This theoretical study has led to the determination of the optimised structural parameters, the energy difference (ΔE_{tg}) and related thermodynamics parameters for 1-bromo-2-chloroethane. The results indicate that there is a preference for the trans conformer both in the gaseous and solution phases. The calculated frequencies of the conformers are in agreement with literature values. The energy difference (ΔE_{tg}) decreases as the solvent becomes more polar. The results of this study may be used as a set of reference for the conformers of 1-bromo-2-chloroethane.

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