THEORETICAL STUDY OF 1,2-DICHLOROETHANE AND 1,2-DIBROMOETHANE IN GASEOUS PHASE, LIQUID PHASE AND ALCOHOL AS SOLVENT

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ABSTRACT

The gauche-trans energy difference of 1,2-dichloroethane and 1,2-dibromoethane in the gas phase has been obtained using molecular mechanics, *ab-initio* and density functional methods. The effect of solvent chain-length on the energy difference for a series of primary straight-chain alcohol ($C_nH_{2n+1}OH$; n=1 to 5) has been investigated. Molecular mechanics studies were carried out using facilities from ChemOffice. *Ab-initio* and density functional studies were carried out using Gaussian 03W. The results obtained are in agreement with each other and the results, which are methods dependent, compare satisfactorily with literature findings. It is found that the gauche-trans energy difference decreases as the size of the halogen increases. It also increases as the chain length of the alcohol increases and the dielectric constant of the solvent decreases.

INTRODUCTION

Conformational analysis is the term used when a molecule is analysed according to its different existing conformers due to free rotation about single bonds. The molecule subjected to analysis must be stable with respect to all the different possible conformers. Experimental analysis of the different conformations of a molecule is possible only if the conformers have different chemical as well as physical properties. Theoretical methods can also be used to obtain reasonable information about the different conformations adopted by the molecules. The ultimate goal of conformational analysis is (1) to predict the relative stabilities of conformers and the differences of

interconversion, and (2) to relate the conformational preferences or relative stability of stereoisomers to reactivity and product distribution [Zefirov (1977)].

In an attempt to understand or correlate new strategies of molecules, prototypes are preferred for studies. 1,2-substituted ethanes, as illustrated in Figure 1, have been such prototypes for various studies [Brown and Beagley (1977); Wiberg and Murcko (1988); Dixon *et al.* (1992); Phillips (1992); Lam *et al.* (1993); Phillips and Jebber (1995); Murcko *et al.* (1996); Erickson and Morris (1998); Hansen *et al.* (1999); Tanuma *et al.* (2000); McClain and Ben-Amotz (2002); Nolan and Linck (2002) and Wladkowski and Broadwater (2002)] and there is a distinction between the energies of the gauche ($\theta = 60°$) and the trans ($\theta = 180°$) rotamers. The difference in energy associated with the gauche to trans rotation is termed as ΔE_{t-g}.
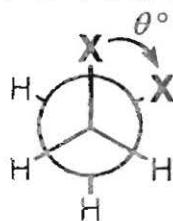

Fig. (1): 1,2-substituted ethane molecule where $\theta°$ is the dihedral angle

The energy profiles of substituted ethanes differ from that of ethane mainly because of the bulky group X. The group X induces steric interaction and due to that, the internal rotation about the single C–C bond is disturbed. As the C–C bond can rotate on its own axis, angle θ will vary and thus there will be an infinite number of rotational isomers. A higher relative energy of the gauche rotamer accounts for the steric interaction between the adjacent bulky groups. In the trans conformation, there is minimum steric repulsion between the big groups and thus the ground energy for that conformer is at minimum of the potential energy curve. It is generally understood that the trans rotamer is relatively more stable than the gauche one. Thus the fractional population of trans species is ultimately greater compared to that of the gauche one. This statement is only true when the molecule is non-polar and has an insignificant dipole moment, which is the case of *n*-butane. However, simple substituted ethanes such as the 1,2-dihaloethanes, which are characterised as polar material and have a specific molecular dipole, have varying population of trans and gauche conformations especially in polar

solvents. As an example, 1,2-difluoroethane (DFE) unexpectedly has its gauche rotamer more stable than the trans rotamer [Dixon *et al.* (1992)]. Moreover, ΔE_{t-g} for DBE in solvent of low dielectric constant (*e.g.* chloroform) is greater than in case of solvents of high dielectric constant (*e.g.* dimethylsulfoxide) [Erickson *et al.* (1998)].

To provide in depth knowledge about conformers of 1,2-dihaloethanes, the present article reports theoretical study of 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE) in the gas and liquid phase. The results obtained are in trend with some studies in the literature [Erickson *et al.* (1998) and Dixon *et al.* (1992)]. Since the ΔE_{t-g} is affected by the nature of the solvent, the effect of solvent chain length on the energy difference for a series of primary straight-chain alcohol ($C_nH_{2n+1}OH$; n=1 to 5) is also reported. To the best of the author's knowledge, this solvent effect has not been undertaken in literature.

METHODS

All the calculations in this work were performed on an Intel Pentium IV computer running Windows 98 using the Chemoffice 2000 (http://www.cambridgesoft.com/) and Gaussian 03W [Frisch *et al.* (1992)] quantum-mechanical program.

Molecular mechanics:

Molecular mechanics (MM2) calculations were performed using Chemoffice 2000, to obtain the strain energies of the conformations of varying dihedral angles for DCE and DBE in the gas phase. The energy profile diagram thus obtained was used to calculate ΔE_{t-g}.

Ab-initio methods:

Ab-initio calculations were performed using the Gaussian 03W software. *Ab-initio* methods such as Hartree-Fock (HF), MØller-Plesset second-order perturbation theory (MP2), Onsager Models were used to obtain appropriate relative energies of the gauche and the trans rotamers of each of the 1,2-dihaloethanes either in the gas phase or in the liquid phase after suitable optimization. The basis sets selected for the investigation include 6-31G(d), a most commonly used basis set for medium size molecule. Further the basis sets 6-31+G(d) and 6-311++G(d,p) were used to study the effect of solvents. The Self Consistent Reaction Field (SCRF) method was used in the Onsager

Model for the determination of the solvent effects of the 1,2-dihaloethanes in the different solvents. The spherical cavity of the solute 1,2-dihaloethane occupied a fixed cavity of radius a_0 is 3.65 Å within the solvent.

Density functional methods:

The methods B3LYP/6-31+G(d) and MPW1PW91/6-31G(d) were used from Gaussian 03W. In these methods the Isodensity PCM model which defines the cavity as an Isodensity surface of the molecule, was used to investigate the effect of solvents on the gauche to trans rotation of the 1,2-dihaloethanes after optimizing the structures

RESULTS AND DISCUSSION

Molecular mechanics:

The total energy (Equation (1)), E_T, is made of several terms, one of which is attributed to stretching (E_s), one to angle bending (E_b), one to van der Waals interactions, (E_{vdW}), one to torsional interactions (E_t) and one to electrostatic interactions (E_e) [Jensen (1999)].

$$E_T = E_s + E_b + E_t + E_{vdW} + E_e \tag{1}$$

The different energy terms for varying dihedral angle obtained for 1,2-dichloroethane are given in Table 1. The energy profile obtained is illustrated in Figure 2.

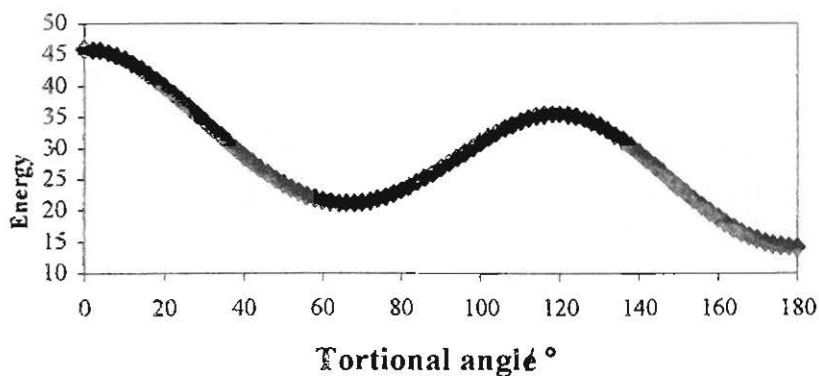**Fig. (2):**Energy profile fo1,2-dichloroethan

Table (1): Energy terms of Equation (1) for 1,2-dichloroethane.

Dihedral angle °	Stretching energy kJ/mol	Bending energy kJ/mol	Stretching-bending energy kJ/mol	Torsional Energy kJ/mol	1,4 Van der Waal's interactions energy kJ/mol	Dipole-dipole interactions energy kJ/mol
0	0.68	8.97	0.67	12.02	14.08	9.45
10	0.66	9.02	0.64	10.72	9.08	14.04
20	0.59	8.61	0.58	7.96	8.15	13.91
30	0.51	7.46	0.51	4.99	7.05	13.69
40	0.45	5.68	0.44	2.69	5.99	13.38
50	0.41	3.97	0.39	1.40	5.03	12.95
60	0.37	2.92	0.34	1.20	4.30	12.42
70	0.35	2.60	0.31	2.20	3.97	11.82
80	0.36	2.85	0.30	4.28	4.19	11.21
90	0.39	3.30	0.31	7.26	4.86	10.63
100	0.45	3.69	0.34	10.55	5.77	10.12
110	0.50	3.52	0.39	13.44	6.74	9.72
120	0.52	3.06	0.42	14.70	7.37	9.40
130	0.50	3.02	0.41	13.28	7.23	9.17
140	0.45	3.09	0.36	9.88	6.45	9.01
150	0.38	2.69	0.30	6.15	5.40	8.90
160	0.33	2.13	0.26	2.87	4.41	8.83
170	0.29	1.61	0.24	0.76	3.69	8.79
180	0.28	1.39	0.23	0.02	3.46	8.78

In molecular mechanics calculations, intermolecular interactions are not considered and the energy differences are for isolated molecules in the gas phase. The minimum gauche conformation for DCE occurs at dihedral angle of 62° whereas that for DBE occurs at dihedral angle of 65° although the ideal is expected to be 60°. The gauche-trans energy difference for DCE and DBE is reported in Table 2.

Table (2): Energy of gauche and trans conformers of 1,2-dihaloethanes and the gauche-trans energy difference.

	1,2-dichloroethane	1,2-dibromoethane
Energy of gauche conformer, kJ/mol	21.08	19.13
Energy of trans conformer, kJ/mol	14.16	13.27
Activation energy difference, kJ/mol	-6.92	-5.86 (-5.89)*

*Literature value is 5.89 kJ/mol [**Erickson** *et al.* **(1998)**].

The equilibrium constant for the ratio of trans to gauche conformers can be estimated from the energy difference. It is assumed that there are no significant changes in vibrations between these conformers. The energy is then associated with ΔU_{t-g} but is ΔH_{t-g} for this system as there is no change in the number of gaseous molecules. Since there are two equivalent gauche conformers and only one trans conformer, $S = R\ln\left(\dfrac{1}{2}\right)$ J/mol K. ΔH_{t-g} and ΔS_{t-g} are then used to estimate change in free energy, ΔG_{t-g} and the equilibrium constant K_{t-g} at 25 °C. These thermodynamics parameters are reported in Table 3. This means that for DCE there are 8 molecules in the trans form for every molecule in the gauche form at 25 °C. Similarly for DBE there are 5 molecules in the trans form for every molecule in the gauche form.

Table (3): Thermodynamics parameters for the gauche and trans interconversion for the 1,2-dihaloethanes.

	1,2-dichloroethane	1,2-dibromoethane
ΔH_{t-g}, kJ/mol	-6.92	-5.86
ΔS_{t-g}, J/mol	-5.76	-5.76
ΔG_{t-g}, kJ/mol	-5.20	-4.14
K_{t-g} at 25 °C	8.2	5.3

Ab-initio and DFT results for the 1,2-dihaloethanes in gas phase

The self-consistent field (SCF) energy for the trans and gauche forms of the 1,2-dihaloethanes were obtained. The results of the *ab-initio* and the DFT computations for different levels of theory and ΔE_{t-g} for DCE and DBE in the gas phase are reported in Tables 4 and 5 respectively. ΔE_{t-g} for DCE compares satisfactorily with literature values

-6.07 kJ/mol using MP2/6-311++G (d, p) and -6.11 kJ/mol using B3LYP/6-311+G (d, p) **[Wiberg *et al.* (1995)]**.

Table (4): Energy difference associated with gauche to trans rotation of DCE in the gas phase.

Level of theory	SCF Energy of trans rotamer Hartree	SCF Energy of gauche rotamer Hartree	ΔE_{t-g} kJ/mol
HF/6-31+G (d)	-997.0328613	-997.0297378	-8.20
HF/6-311++G (d, p)	-997.1056567	-997.1026244	-7.96
MP2/6-311++G (d, p)	-997.1056567	-997.1026244	-7.96
B3LYP/6-31G(d)	-988.0412409	-988.0387835	-6.45
B3LYP/6-31+G (d)	-999.0232365	-999.0204295	-7.37
MPW1PW91/6-31G(d)	-999.0124215	-999.0099129	-6.59

Table (5): Energy difference associated with gauche to trans rotation of DBE in the gas phase.

Level of theory	SCF Energy of trans rotamer Hartree	SCF Energy of gauche rotamer Hartree	ΔE_{t-g} kJ/mol
HF/6-31+G (d)	-5217.8733557	-5217.8714523	-5.00
HF/6-311++G (d, p)	-5222.8234644	-5222.8210004	-6.47
MP2/6-311++G (d, p)	-5222.8234644	-5222.8210004	-6.47
B3LYP/6-31G(d)	-5169.6618910	-5169.6631594	3.33
B3LYP/6-31+G (d)	-5222.0652861	-5222.0654718	0.49
MPW1PW91/6-31G(d)	-5222.3281081	-5222.3270694	-2.73

From Tables 4 and 5, it is found that both HF/6-311++G (d,p) and MP2/6-311++G (d,p) levels of theory predict the same energy in the gas phase. The differences obtained by *ab-initio* methods are in agreement

with molecular mechanics except for DBE using DFT methods. Discrepancies between these results and molecular mechanics can be due to electron interactions to be neglected in the latter.

Ab-initio and DFT results for the 1,2-dihaloethanes in solution phase

The self-consistent field (SCF) energy for the trans and gauche forms of the 1,2-dihaloethanes in solution phase were obtained. The energy difference of the *ab-initio* and the DFT computations for different levels of theory and ΔE_{t-g} for DCE and DBE in the solution phase are reported in Tables 6 and 7.

In liquid state both the Onsager models (HF and MP2) and the IPCM models predict reasonable values of ΔE_{t-g}. As the dielectric constant of the solution increases the energy difference should decrease for the 1,2-dihaloethanes although this is not predicted by all methods.

Table (6): Energy difference (kJ/mol) associated with the gauche to trans rotation for DCE and DBE in liquid phase.

Solvent	Dielectric constant	HF 6-31+G (d)	HF 6-311++G (d,p)	MP2 6-311++G (d,p)	B3LYP 6-31G (d)	B3LYP 6-31+G (d)	MPW1PW9 6-31G (d)
DCE	10.42	-2.06	-1.99	-2.01	-3.88	-3.74	-3.48
DBE	2.18	-2.10	-1.18	-2.18	-4.16	-1.31	-4.65

Table (7): Gauche-trans energy difference (kJ/mol) for DCE and DBE in alcohols calculated by B3LYP level of theory and different basis sets.

Basis set	Methanol	Ethanol	Propanol	Butanol	Pentanol
Dielectric constant	32.7	24.5	20.1	17.8	13.9
1,2-dichloroethane					
6-31G	-3.56	-3.62	-3.66	-3.70	-3.77
6-31G (d)	-4.41	-4.46	-4.50	-4.54	-4.62
6-31+G (d, p)	-4.14	-4.20	-4.24	-4.28	-4.35
1,2-dibromoethane					
6-31G	-1.81	-1.83	-1.85	-1.87	-1.90
6-31G (d)	-3.93	-3.94	-3.95	-3.96	-3.98
6-31+G (d, p)	-3.82	-3.83	-3.85	-3.86	-3.88

The DFT method gives meaningful energy difference for the 1,2-dihaloethanes in alcohols but results from other *ab-initio* methods are more complex for interpretation. As the chain length of the alcohols increases, the dielectric constant decreases and this causes an increase in the magnitude of the energy difference. The interactions between the 1,2-haloethane and the alcohols that are polar have caused major influence on the stabilization of the gauche rotamer. Although the solvent effect is small, it can be predicted [**Wiberg (1995)**].

CONCLUSIONS

In this work the gauche and trans conformers have been studied in gas phase, liquid phase and linear alcohols as solvents. The study was an attempt to obtain the gauche-trans energy difference using molecular mechanics, *ab-initio* and DFT methods. The results obtained could be correlated with each other and some of the available data in literature. The usefulness of the results depends of the methods used as some of them gave information, which are more complex for valid interpretation. Our future work will involve other 1,2-dihalogenoethanes and mixed halogenoethanes.

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دراسة نظرية على ١ ، ٢ – ثنائى كلوروايثيان و١ ، ٢ – ثنائى برومواثيان

فى الحالة الغازية ، الحالة السائلة وفى الكحول كمذيب

يـتعلق البحـث الدراسـة الـنظرية لتشـكيلات جزيئات المركبين ١ ، ٢ – ثنائى كلوروايثـيان وكذلك ١ ، ٢ –ثانى برومواثيان وذلك فى حالتهم الغازية والسائلة وكذلك فى محاليلها الكحولية. فلقـد تم حساب الطاقات الكلية للتشكل المتقابل ترانس "trans " والتشكل المـــائل جـــوش "gauche" وطاقـة التنشـيط بينهما كما تم دراسة تأثير طول سلسلة الكحـولات $C_nH_{2n+1}OH$ كمذيبت على طاقات التنشيط وذلك لكلا الجزيئين. كما تم تعيين كثافة تواجد التشكلين معا وكذلك زاوية الالتواء فى حالة التشكل 'جوش' . ولقد إستخدمت فى الحسـابات طريقة الهندسة الجزيئية المتاحة ضمن حزمة برامج ChemOffice وكذلك طرق ميكانـيكا الكـم "اب انيشيو" و"دالة الكثافة" المدمجة ضمن حزمة برامج Gaussian 03W . ولقـد أظهـرت نتائج الحسابات بالطرق المختلفة توافقا قيما بينها كما أنها تتفق مع تلك القيم المنشـورة. ولقـد دلت النتائج أن طاقة التنشيط تقل قيمتها كلما زاد حجم ذرة الهالوجين كما أنها تزداد كلما ازداد طول سلسلة الكحول المذيب.