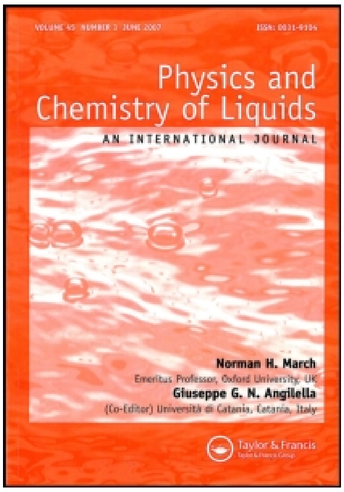


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Conformational behaviour of 1,2-dichloroethane and 1,2-dibromoethane: ^{1}H-NMR, IR, refractive index and theoretical studies

R. K. Sreeruttun[a]; P. Ramasami[a]
[a] Department of Chemistry, University of Mauritius, Réduit, Mauritius

To cite this Article Sreeruttun, R. K. and Ramasami, P.(2006) 'Conformational behaviour of 1,2-dichloroethane and 1,2-dibromoethane: ^{1}H-NMR, IR, refractive index and theoretical studies', Physics and Chemistry of Liquids, 44: 3, 315 — 328
To link to this Article: DOI: 10.1080/00319100600594547
URL: http://dx.doi.org/10.1080/00319100600594547

Physics and Chemistry of Liquids
Vol. 44, No. 3, June 2006, 315–328

Conformational behaviour of 1,2-dichloroethane and 1,2-dibromoethane: ^{1}H-NMR, IR, refractive index and theoretical studies

R. K. SREERUTTUN and P. RAMASAMI*

Department of Chemistry, University of Mauritius, Réduit, Mauritius

(*Received 16 January 2006; in final form 23 January 2006*)

Experimental and theoretical methods have been used to study the energy difference between the *gauche* and the *trans* conformational isomers of 1,2-dihaloethanes (XCH_2CH_2X, $X = Cl$ and Br). Nuclear magnetic resonance (NMR) analysis, infrared (IR) spectra and refractive index of solutions of 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE) in environments of varying polarity have been investigated. Molecular mechanics (MM2) calculations, semiempirical methods (AM1, PM3, MNDO, MNDO-d), *ab initio* methods (HF, MP2) and density functional theory (B3LYP, MPW1PW91) have been performed to study the relative energies of the two stable conformations of the 1,2-dihaloethanes. The solvent effect has been studied using the Onsager and IPCM models. The basis sets 6-31G(d), 6-31+G(d) and 6-311++G(d,p) were used in the *ab initio* and density functional theory (DFT) calculations. All calculations have been done on a PC, using facilities available from ChemOffice 2000 and Gaussian 98W. The results obtained show that there is a satisfactory correlation between experimental findings and theoretical predictions.

Keywords: Conformational isomers; 1,2-Dihaloethane; NMR analysis; IR spectra; Refractive index; Theoretical studies

1. Introduction

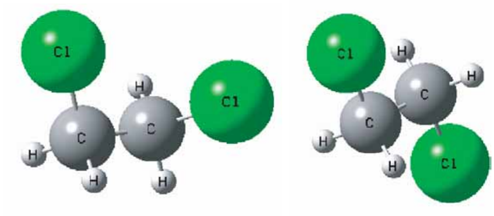
1,2-Dichloroethane (DCE) and 1,2-dibromoethane (DBE) are 1,2-disubstituted ethanes (XCH_2CH_2X), and these molecules have been excellent prototypes [1–17] for conformational studies. Conformational studies are generally done so as to investigate the relative stabilities of the conformers [18]. 1,2-Disubstituted ethanes are characterised by having two conformers namely the *gauche* and the *trans* forms with the *trans* conformer being more stable. The difference in energy associated with the *gauche* to *trans* rotation is termed as ΔE_{t-g}.

The relative stability of the *gauche* and *trans* conformers of 1,2-disubstituted ethane depends on various factors including the substituent X and the medium. The substituent effect can be illustrated with 1,2-difluoroethane where the *gauche* conformer is more

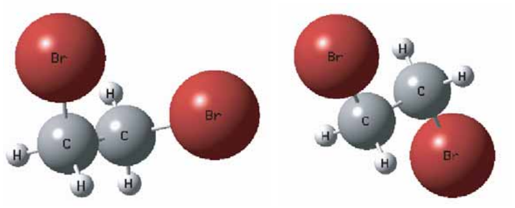
---

*Corresponding author. Tel.: 230 257 0315. Fax: 230 465 6928. Email: p.ramasami@uom.ac.mu

Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online
DOI: 10.1080/00319100600594547



gauche-DCE *trans*-DCE



gauche-DBE *trans*-DBE

Figure 1. *Gauche* and *trans* isomers of 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE).

stable than the *trans* conformer [5]. The effect of the medium can be illustrated using DBE where ΔE_{t-g} depends on dielectric constant of the solvent [8].

Therefore, we were interested in the conformational behaviour of DCE and DBE to investigate substituent and medium effects. There have not been many investigations where experimental studies have been correlated with theoretical findings [19]. This article reports experimental investigations of DCE and DBE in liquid phase and organic solvents by ^{1}H-NMR, infrared (IR) and refractive index. Theoretical calculations have also been done in the gas phase, liquid phase and organic solvents.

2. Experimental

2.1. *Solute*

DCE and DBE of analytical grade were purchased from BDH and they were used without any further purification.

2.2. *Solvent*

The solvent carbon tetrachloride (CCl_4) was purchased from BDH and the solvents chloroform ($CHCl_3$), acetone $(CH_3)_2CO$, acetonitrile (CH_3CN) and dimethylsulphoxide (DMSO) were purchased from Fischer Chemicals. All the solvents were of analytical grade and they were used without any further purification. Deuterated solvents were used for ^{1}H-NMR spectroscopy.

2.3. *Nuclear magnetic resonance (NMR) spectroscopy*

NMR spectra of 10% v/v solutions of DCE and DBE in the five solvents were recorded with a Bruker Spectrospin Avance DPX, Dual 5 mm, ^{1}H–^{13}C-NMR spectrometer operating at 250 MHz. All the ^{1}H-NMR spectra were done using acquisition parameter D1 being 0.01 s and the number of scans being 16. In the spectrum, the symmetrical ^{13}C-satellite patterns, which are usually found at the baseline of the main peak, were recorded. As a standard, the "downfield" half of the symmetric ^{13}C-satellite patterns was taken into consideration. The proton–proton coupling constants were analysed using simulation package DNMR [20], treating the spectrum as half of a AA′BB′ pattern and reasonable ^{13}C-satellite patterns had been simulated to obtain the vicinal coupling constants.

2.4. *IR spectroscopy*

The IR spectra of liquid DCE and DBE in the pure form and then dissolved in the different solvents were collected at 2 cm^{-1} resolution over a range of 4000–700 cm^{-1} in absorbance mode, using a Thermo Nicolet Avatar 320 FTIR spectrometer. The background scan was air in case of the pure form, but the solvent was taken in case of mixtures.

2.5. *Refractive index measurement*

The refractive indices, n_D, of DCE and DBE solutions of different concentrations in the various solvents were determined with a 60/70 Abbe Refractometer (BS) connected with a water circulator (HAAKE G. Fisons/044) at different temperatures (10–40°C). The measurements of index of refraction were made using sodium (Na) yellow light.

3. Theoretical methods

All the calculations were performed using the Gaussian 98W [21] and ChemOffice 2000 of programs [22] using a desktop computer.

3.1. *Molecular mechanics*

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

3.2. *Semiempirical methods*

Semiempirical methods such as AM1, PM3, MNDO, MNDO-d methods were performed using MOPAC available in ChemOffice 2000 to obtain the relative enthalpy of formation of the *gauche* and the *trans* conformers of DCE and DBE. The geometry of the *gauche* conformation of the 1,2-dihaloethanes was optimised using the minimum dihedral angle obtained from the MM2 calculations. The difference in the enthalpy of formation of each rotamer was approximated to be the ΔE_{t-g}.

3.3. Ab initio *methods*

Ab initio calculations were performed using the Gaussian 98W software. *Ab initio* methods such as HF and MP2 levels of theory (Onsager Models) were used to obtain equilibrium 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. 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 (Dipole and Sphere) Model, i.e., SCRF = Dipole, 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.

3.4. *Density functional methods*

The methods B3LYP/6-31+G(d) and MPW1PW91/6-31G(d) used were available in Gaussian 98W. In these methods, the Isodensity PCM model, i.e. SCRF = IPCM, 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.

4. Results and discussion

4.1. *NMR spectroscopy*

The chemical shifts (δ) of the protons in the NMR spectra of the 1,2-dihaloethanes are given in the table 1. It is found that the δ value slightly changes in different chemical environments. All the protons in the molecule have approximately the same chemical shift value. A singlet is observed in the spectrum because the molecules undergo rapid changes in their conformations and thus NMR cannot detect the protons, which are experiencing different chemical environments which will lead to a change in the chemical shift value.

The spectra are considered as half of an AA′BB′ pattern, the proton–proton coupling constants are determined using the DNMR simulation package [20]. The coupling–coupling constants ($J_{AB'}$, J_{AB} and J_t) obtained were used to evaluate the fractional population of the *gauche* (f_1) and the *trans* (f_2) rotamers and then the energy difference

Table 1. Chemical shifts values of the main peak in the ^{1}H-NMR spectra of the two 1,2-dihaloethanes in different solvents.

Solvent	Chemical shift (δ) for DCE (ppm)	Chemical shift (δ) for DBE (ppm)
CCl_4	3.6635	3.3694
$CDCl_3$	3.7353	3.6578
$(CD_3)_2CO$	3.8701	3.7174
CD_3CN	3.8103	3.7372
DMSO-d_6	3.8927	3.8318

Table 2. The coupling constants, fractional populations and the energy difference between the two conformers of DCE in different solvents obtained at 300 K.

Solvent	$J_{AB'}$ (Hz)	J_{AB} (Hz)	f_1	f_2	J_t (Hz)	ΔE_{t-g} (kJ mol^{-1})
CCl_4	5.8	9.3	0.221	0.557	13.9	−2.30
$CDCl_3$	5.8	8.4	0.246	0.507	12.7	−1.80
$(CD_3)_2CO$	7.0	6.0	0.367	0.267	13.3	0.79
CD_3CN	7.0	6.0	0.367	0.267	13.3	0.79
DMSO-d_6	6.0	6.0	0.333	0.333	11.9	N.A.

Table 3. The coupling constants, fractional populations and the energy difference between the two conformers of DBE in different solvents obtained at 300 K.

Solvent	$J_{AB'}$ (Hz)	J_{AB} (Hz)	f_1	f_2	J_t (Hz)	ΔE_{t-g} (kJ mol^{-1})
CCl_4	4.9	12.2	0.112	0.776	14.7	−4.83
$CDCl_3$	6.0	11.0	0.188	0.623	15.3	−2.98
$(CD_3)_2CO$	6.0	10.0	0.212	0.576	14.6	−2.49[a]
CD_3CN	6.0	9.0	0.238	0.524	13.9	−1.97
DMSO-d_6	5.2	9.1	0.249	0.501	14.5	−1.74[a]

[a] Literature values [7] are −3.56 and −1.72 kJ mol^{-1}.

ΔE_{t-g} was calculated [7]. These energy differences for DCE and DBE in the different solvents are given in tables 2 and 3.

It is observed that as the polarity of the solvents increases, the values of the fractional population of the *gauche* rotamer of DCE and DBE also increase. This is due to the *gauche* conformer being more polar than the *trans* one. This implies that the *gauche* conformation is able to overcome the energy barrier in a polar environment or it may be that the energy barrier is being reduced which favours *gauche* conformer to exist in a bigger population as compared in a non-polar solvent (CCl_4). Moreover, it is observed that the energy barrier between the two conformers decreases as the polarity increases.

4.2. *IR spectroscopy*

The IR spectra of the pure liquid DCE and DBE are shown in figures 2 and 3 respectively. In these spectra, corresponding peaks of *trans* and *gauche* conformational isomers have been well resolved. The *trans* peak (1232 cm^{-1} for DCE and 1185 cm^{-1} for DBE) has a higher intensity compared to that of the *gauche* one (1284 cm^{-1} for DCE and 1244 cm^{-1} for DBE). The area under these peaks can be used to estimate the fractional population of a particular rotamer.

In figure 4, it is observed that the peaks assigned to DCE in the region 1350–1100 cm^{-1} have different intensities. In that region the *trans* conformer has a vibrational mode at a wavenumber 1232.64 cm^{-1} whereas the *gauche* conformer has a vibration mode at wavenumbers 1313.72 cm^{-1} and 1284.57 cm^{-1}. Similarly there are three IR active peaks which come at 1276.48 cm^{-1} (*gauche′*), 1244.52 cm^{-1} (*gauche*) and 1185.38 cm^{-1} (*trans*) as can be seen from figure 4. However, the peak at 1429.25 cm^{-1} (figure 2) for DCE has a higher intensity compared to that of DBE which comes at 1418.57 cm^{-1} (figure 3).

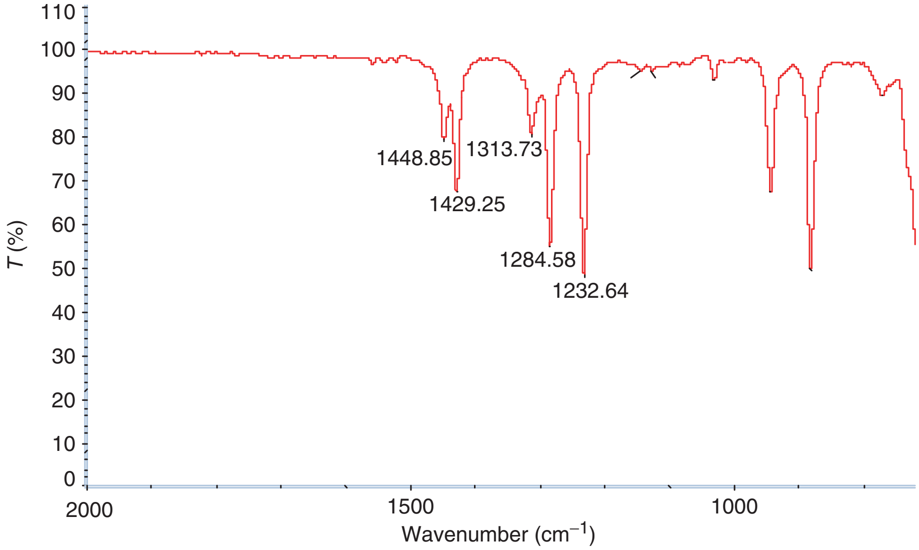


Figure 2. IR spectrum of DCE at room temperature (295 K).

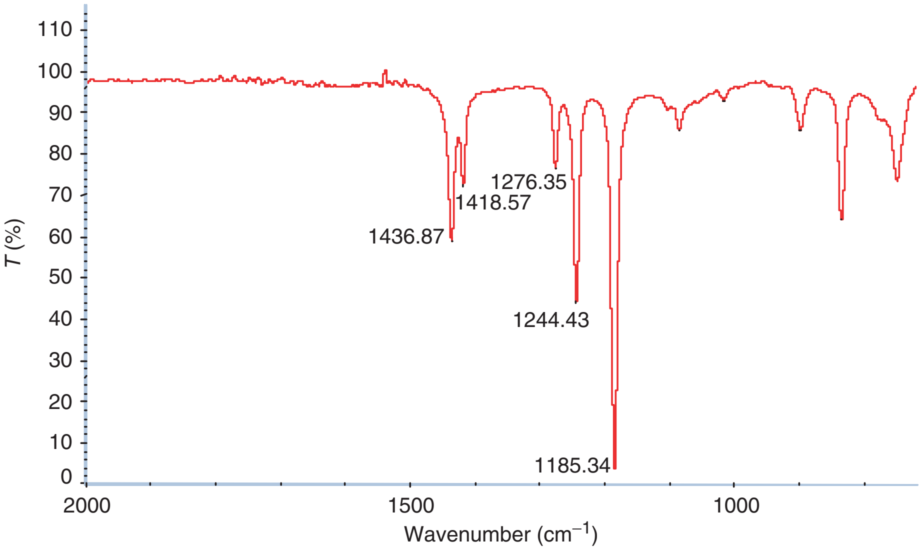


Figure 3. IR spectrum of DBE at room temperature (295 K).

The IR spectra of both DCE and DBE over the range 1350–1100 cm^{-1} in the five solvents are shown in figures 5 and 6 respectively. It is observed that as the dielectric constant of the solvent increases there is indeed a preferential stabilisation of the *gauche* isomer.

The value of ΔE_{t-g} can be calculated from the areas under the corresponding peaks of the *trans* and the *gauche* rotamers at a particular temperature and it is reported

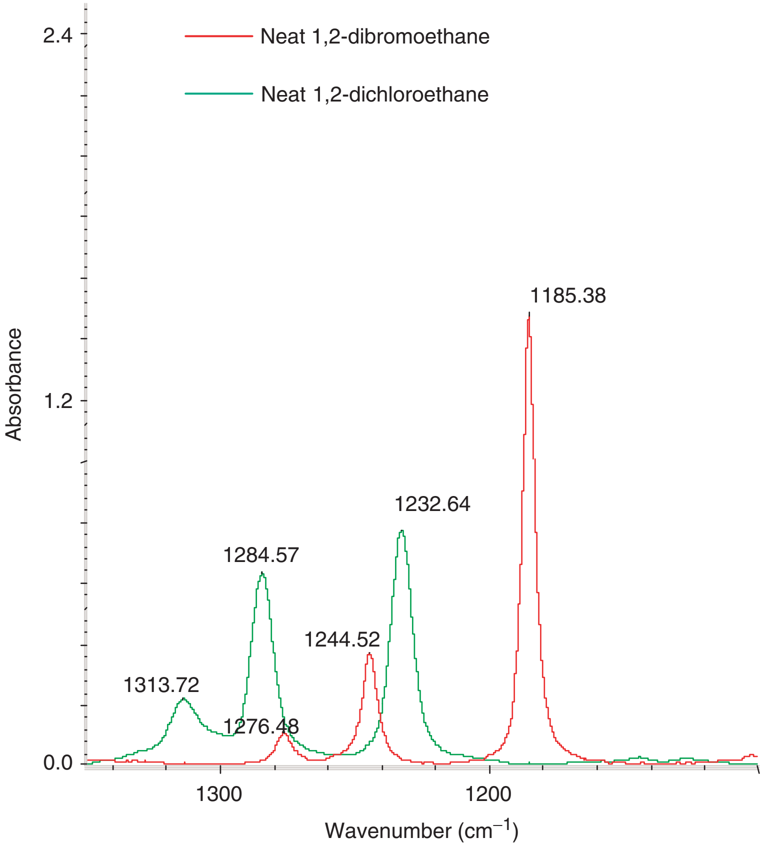


Figure 4. IR spectra of DCE and DBE as pure liquid (neat) at room temperature (295 K).

for DCE and DBE in pure liquid and mixtures in tables 4–6. It is assumed that the molar absorptivity ratio $\varepsilon_t/\varepsilon_g$ is independent of the environment [12].

4.3. *Dipole moment*

The Debye equation is:

$$P = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right) \tag{1}$$

where N_A is Avogadro's number, α is the molecular polarisability, k is the Boltzmann constant, T is temperature in Kelvin and P is the molar polarisation.

The molar polarisation is also given by:

$$P = \left(\frac{(\varepsilon/\varepsilon_0) - 1}{(\varepsilon/\varepsilon_0) + 2}\right)\frac{M}{\rho} \tag{2}$$

where $\varepsilon/\varepsilon_0$ is given as the dielectric constant of polar materials, M is the molar mass, and ρ is the density of the material.

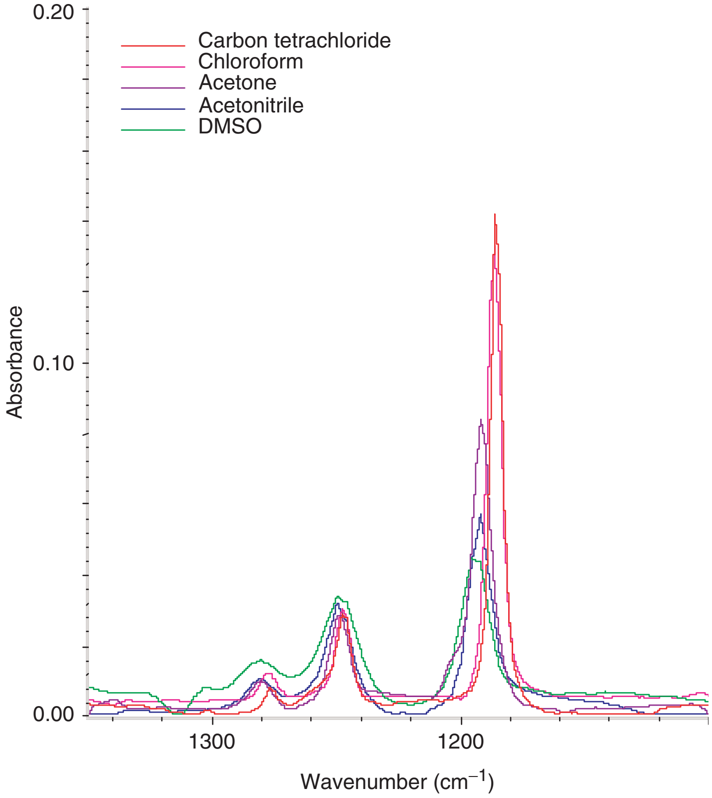


Figure 5. IR spectra of DBE in different solvents at room temperature (295 K).

Maxwell's theory shows that for materials composed of molecules with no permanent dipole moment the dielectric constant is given by:

$$\frac{\varepsilon}{\varepsilon_0} = n_{\mathrm{D}}^2 \tag{3}$$

where n_{D} is the refractive index of the material. Combining equations (1)–(3), we obtain:

$$\left(\frac{n_{\mathrm{D}}^2 - 1}{n_{\mathrm{D}}^2 + 2}\right)\frac{M}{\rho} = \frac{N_{\mathrm{A}}}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right) \tag{4}$$

A graph of $[(n_{\mathrm{D}}^2 - 1)/(n_{\mathrm{D}}^2 + 2)](M/\rho)$ is plotted against $1/T$ to obtain the dipole moment and polarisability. The plot of the molar polarisation for pure DCE and DBE against the reciprocal of temperature is given in figure 7. The average dipole moments for DCE and DBE are 0.552 and 0.587 D respectively and these are used to calculate the fractional populations in the *gauche* and *trans* forms. The value of $\Delta E_{\mathrm{t-g}}$ was then calculated and these are reported for DCE and DBE in table 7. The molecular polarisability for DCE and DBE are 6.44×10^{-34} and 8.76×10^{-34} mL mol^{-1} respectively in pure form.

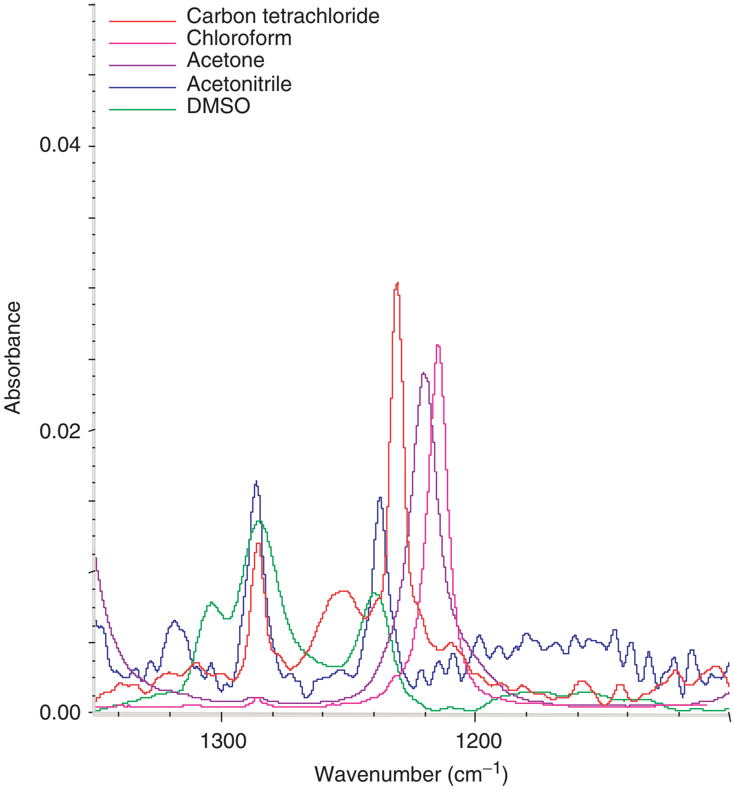


Figure 6. IR spectra of DCE in different solvents at room temperature (295 K).

Table 4. Energy difference associated with *gauche* to *trans* rotation of 1,2-dihaloethane in liquid phase at room temperature (295 K) with IR spectroscopic method.

1,2-dihaloethane	Area$_t$ (unit^2)	Area$_g$ (unit^2)	ΔE_{t-g} (kJ mol^{-1})
DBE	10.058	3.166	−8.13[a]
DCE	3.076	2.179	−1.67[a]

[a] Literature values [12] are −6.7 and −0.05 kJ mol^{-1} respectively.

Table 5. Energy difference associated with *gauche* to *trans* rotation of DCE in solution phase at room temperature (295 K) with IR spectroscopic method.

Solvent	Area$_t$ (unit^2)	Area$_g$ (unit^2)	ΔE_{t-g} (kJ mol^{-1})
CCl_4	0.139	0.066	−2.64[a]
$CHCl_3$	N.A	N.A	N.A
$(CH_3)_2CO$	N.A	N.A	N.A
CH_3CN	0.049	0.088	0.62[a]
DMSO	0.092	0.177	0.79

[a] Literature values [12] are −2.5 and −1.2 kJ mol^{-1} respectively.

N.A: The peak areas estimated for DCE in acetone and chloroform do not give a reasonable data as the area at the *gauche* peak is relatively very small compared to that of the *trans* peak, figure 6.

Table 6. Energy difference associated with *gauche* to *trans* rotation of DBE in solution phase at room temperature (295 K) with IR spectroscopic method.

Solvent	Area$_t$ (unit^2)	Area$_g$ (unit^2)	ΔE_{t-g} (kJ mol^{-1})
CCl_4	0.955	0.242	-8.66^a
$CHCl_3$	0.912	0.256	-8.41
$(CH_3)CO$	0.891	0.282	-8.12
CH_3CN	0.655	0.369	-6.70^a
DMSO	0.580	0.434	-6.01

[a] Literature values [12] are −9.1 and −6.4 kJ mol^{-1} respectively.

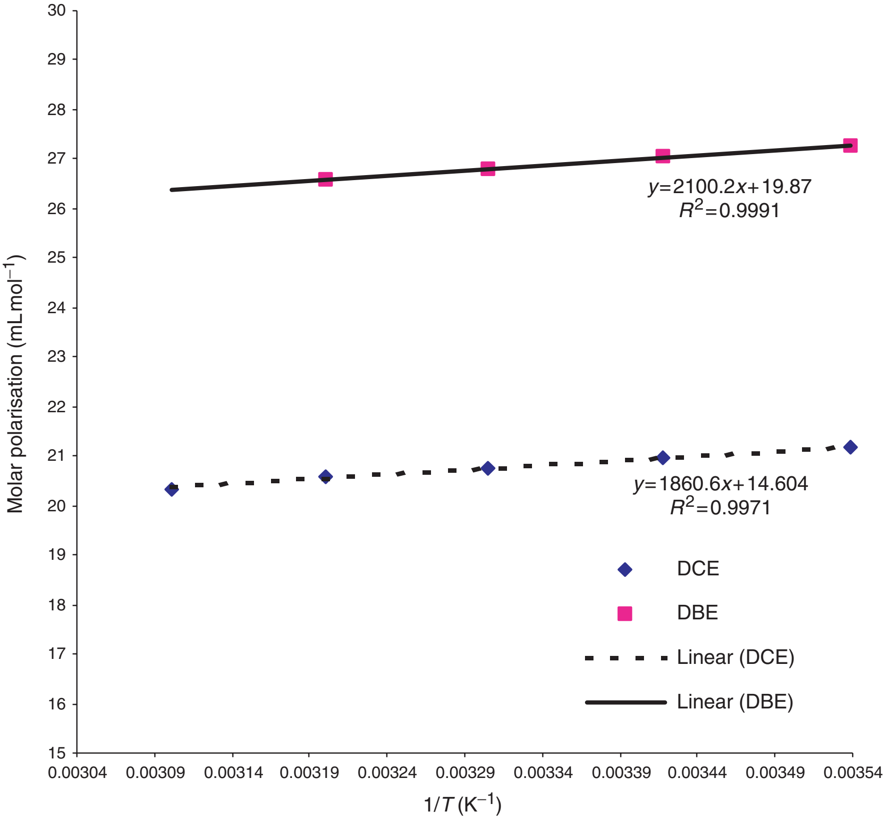


Figure 7. Plot of molar polarisation (*P*) of neat DCE and DBE against reciprocal of temperature.

Equation (4) may be modified for a binary mixture and may be written as:

$$\frac{n_D^2 - 1}{n_D^2 + 2} \times \frac{(x_1 M_1 + x_2 M_2)}{(x_1 \rho_1 + x_2 \rho_2)} = \frac{N_A}{3\varepsilon_0}\left(\alpha + \frac{\mu^2}{3kT}\right) \tag{5}$$

This equation was used to obtain ΔE_{t-g} for DBE in tetrachloromethane and it is also reported in table 7. The parameter could not be evaluated for DCE as the refractive index of the solvent (CCl_4) is higher than that of the solute (DCE).

Table 7. Energy difference associated with *gauche* to *trans* rotation of 1,2-dihaloethane at room temperature from dipole moment calculation.

1,2-Dihaloethane	ΔE_{t-g} (kJ mol^{-1})
Pure DCE	−10.51
Pure DBE	−10.12
DBE in CCl_4	−9.61

Table 8. Energy difference associated with the *gauche* to *trans* rotation of DCE and DBE with the MM2 method.

1,2-Dihaloethane	Energy of *trans* rotamer (kJ mol^{-1})	Energy of *gauche* rotamer (kJ mol^{-1})	ΔE_{t-g} (kJ mol^{-1})
DCE	21.6652	26.3195	−4.65
DBE	24.6224	27.6019	−2.98[a]

[a] Literature value [7] is −5.89 kJ mol^{-1}.

It is interesting to point out that the value of ΔE_{t-g} for DCE and DBE in polar solvents have not been solved as the equations separating the polarisability of the solvent and that of the solute is still unknown.

4.4. *Theoretical methods*

MM2 calculations. The total mechanical energies of DCE and DBE in the gas phase are obtained using MM2 calculations for varying dihedral angle and the ΔE_{t-g} for DCE and DBE are reported in table 8. The minimum *gauche* conformation for DCE occurs at dihedral angle of 62° whereas that for DBE occurs at dihedral angle of 65°.

In the gas phase the expected trend in the energy difference associated to the *gauche* to *trans* rotation shows a decrease in magnitude because when the size of the halogen increases the strain energy of the *gauche* conformer increases and in this way the energy barrier is bound to decrease.

Semiempirical methods. The semiempirical computational results for DCE and DBE in the gas phase are reported in tables 9 and 10 respectively.

ΔE_{t-g} for DCE obtained by semiempirical methods is in agreement with molecular mechanics but were overestimated for DBE.

***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 11 and 12 respectively.

***Ab initio* and DFT result for the 1,2-dihaloethanes in solution phase.** The SCF energy for the *trans* and *gauche* forms of the 1,2-dihaloethanes in solution phase were obtained. The results of the *ab initio* and the DFT computations for different levels

Table 9. Semiempirical results for the energy difference associated with the *gauche* to *trans* rotation of DCE.

	Enthalpy of formation of the rotamer of DCE		
Semiempirical method	*trans*-DCE ($\mathrm{kJ\,mol^{-1}}$)	*gauche*-DCE ($\mathrm{kJ\,mol^{-1}}$)	$\Delta E_{\mathrm{t-g}}$ ($\mathrm{kJ\,mol^{-1}}$)
AM1	−141.6222	−138.5374	−3.08[a]
MNDO	−152.4183	−147.1092	−5.31[a]
MNDO-d	−130.7634	−126.0845	−4.68
PM3	−103.4109	−100.8539	−2.56[a]

[a] Literature values [12] are −3.1, −5.3 and −2.6 $\mathrm{kJ\,mol^{-1}}$ respectively.

Table 10. Semiempirical results for the energy difference associated with the *gauche* to *trans* rotation of DBE.

	Enthalpy of formation of the rotamer of DBE		
Semiempirical method	*trans*-DBE ($\mathrm{kJ\,mol^{-1}}$)	*gauche*-DBE ($\mathrm{kJ\,mol^{-1}}$)	$\Delta E_{\mathrm{t-g}}$ ($\mathrm{kJ\,mol^{-1}}$)
AM1	−33.3710	−31.7740	−1.60[a]
MNDO	−56.2888	−51.8105	−4.48[a]
MNDO-d	−39.9696	−35.4035	−4.57
PM3	−14.3932	−9.9766	−4.42[a]

[a] Literature values [12] are −1.6, −4.5 and −4.4 $\mathrm{kJ\,mol^{-1}}$ respectively.

Table 11. Energy difference associated with *gauche* to *trans* rotation of DCE in the gas phase with different quantum chemical calculations.

Level of theory	SCF energy of *trans* rotamer (Hartree)	SCF energy of *gauche* rotamer (Hartree)	$\Delta E_{\mathrm{t-g}}$ ($\mathrm{kJ\,mol^{-1}}$)
B3LYP/6-31+G(d)	−999.023237	−999.020430	−7.37
MPW1PW91/6-31G(d)	−999.014627	−999.012123	−6.57
HF/6-31+G(d)	−997.032861	−997.029738	−8.20
HF/6-311++G(d, p)	−997.105088	−997.101950	−8.24
MP2/6-311++G(d, p)	−997.684534	−997.682220	−6.07

Table 12. Energy difference associated with *gauche* to *trans* rotation of DBE in the gas phase with different quantum chemical calculations.

Level of theory	SCF energy of *trans* rotamer (Hartree)	SCF energy of *gauche* rotamer (Hartree)	$\Delta E_{\mathrm{t-g}}$ ($\mathrm{kJ\,mol^{-1}}$)
B3LYP/6-31+G(d)	−5222.072842	−5222.069590	−8.54
MPW1PW91/6-31G(d)	−5222.334085	−5222.331523	−6.72
HF/6-31+G(d)	−5217.879880	−5217.876275	−9.46
HF/6-311++G(d, p)	−5222.829201	−5222.824878	−11.34
MP2/6-311++G(d, p)	−5223.381418	−5223.378069	−8.79

of theory and $\Delta E_{\mathrm{t-g}}$ for DCE and DBE in the gas phase are reported in tables 13 and 14 respectively.

In liquid state both the Onsager models (HF and MP2) and the IPCM models predict reasonable values of $\Delta E_{\mathrm{t-g}}$ because the results obtained are consistent with the expected

Table 13. Energy difference in kJ mol^{-1} associated with the *gauche* to *trans* rotation of DCE in solution phase with different quantum chemical calculations.

Solvent	Dielectric constant	B3LYP/ 6-31+G(d)	MPW1PW9/ 6-31G(d)	HF/ 6-31+G(d)	HF/ 6-311++G(d, p)	MP2/ 6-311++G(d, p)
CCl_4	2.23	−6.09	−10.57	−5.19	−5.04	−4.54
$CHCl_3$	4.90	−5.22	−5.97	−3.16	−3.08	−2.81
DCE	10.42	−3.74	−3.48	−2.06	−1.99	−2.01
$(CH_3)_2CO$	20.70	−3.28	−2.28	−1.51	−1.46	−1.62
CH_3CN	36.64	−3.06	−1.73	−1.26	−1.22	−1.44
DMSO	46.70	−3.00	−1.57	−1.19	−1.15	−1.39

Table 14. Energy difference in kJ mol^{-1} associated with the *gauche* to *trans* rotation of DBE in solution phase with different quantum chemical calculations.

Solvent	Dielectric constant	B3LYP/ 6-31+G(d)	MPW1PW9/ 6-31G(d)	HF/ 6-31+G(d)	HF/ 6-311++G(d, p)	MP2/ 6-311++G(d, p)
CCl_4	2.64	−1.79	−6.65	−3.91	−2.48	2.64
$CHCl_3$	2.19	−1.31	−4.67	−2.12	−1.19	2.19
DBE	2.18	−1.31	−4.65	−2.10	−1.18	2.18
$(CH_3)_2CO$	1.85	−0.99	−2.99	−0.62	−0.11	1.85
CH_3CN	1.80	−0.95	−2.73	−0.39	0.06	1.80
DMSO	1.79	−0.94	−2.66	−0.33	0.10	1.79

trend. As the dielectric constant of the solution increases the energy difference tends to decrease for DCE and DBE.

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 tends to decrease for both DCE and DBE. However the B3LYP hybrid functional overestimates the value of ΔE_{t-g} for DBE.

5. Conclusions

This article illustrates the conformational changes in DCE and DBE by experimental and theoretical methods. The energy barrier associated with the *gauche* and *trans* forms of the 1,2-dihaloethanes was obtained in different environments. The results obtained from the different methods are in agreement and some of the results compare satisfactorily with literature values. Furthermore, the results support theoretical investigations which are becoming increasingly important.

Acknowledgements

The authors gratefully acknowledge the stimulating discussion with Prof. Luther Erickson and the University of Mauritius Research Fund for supporting this work.

References

[1] D.E. Brown, B. Beagley. *J. Mol. Struct.*, **38**, 167 (1977).
[2] K.B. Wiberg, M.A. Murcko. *J. Am. Chem. Soc.*, **110**, 8029 (1988).

[3] A. Chung-Phillips. *J. Comp. Chem.*, **13**, 874 (1992).
[4] D.A. Dixon, N. Matsuzawa, S.C. Walker. *J. Phys. Chem.*, **96**, 10740 (1990).
[5] (a) A. Chung-Phillips, K.A. Jebber. *J. Chem. Phys.*, **102**, 7080 (1995); (b) S. Wolfe. *Acc. Chem. Res.*, **5**, 102 (1972); (c) N.L. Allinger, D. Hindman, H. Honig. *J. Am. Chem. Soc.*, **99**, 3282 (1977); (d) J.-H. Lii, K.-H. Chen, T.B. Grindley, N. Allinger. *J. Comp. Chem.*, **24**, 1490 (2003).
[6] M.A. Murcko, H. Castejon, K.B. Wiberg. *J. Phys. Chem.*, **100**, 16162 (1996).
[7] L.E. Erickson, K.F. Morris. *J. Chem. Educ.*, **75**, 900 (1998).
[8] N. Hansen, F. Temps, H. Mäder, N.W. Larsen. *Phys. Chem. Chem. Phys.*, **1**, 3219 (1999).
[9] T. Tanuma, J. Irisawa, K. Onishi. *Report Res. Lab. Asahi Glass Co., Ltd*, **50**, 89 (2000).
[10] E.M. Nolan, R.G. Linck. *J, Phys. Chem. A*, **106**, 533 (2002).
[11] Yu-Lin Lan, L.L. Koh, H.H. Huang. *J. Chem. Soc., Perkin. Trans.*, **2**, 175 (1993).
[12] B.D. Wladkowski, S.J. Broadwater. *J. Chem. Educ.*, **79**, 230 (2002).
[13] B.L. McClain, D. Ben-Amotz. *J. Phys. Chem. B*, **106**, 7882 (2002).
[14] N.S. Zefirov. *Tetrahedron*, **33**, 2719 (1997).
[15] A. Horn, P. Klaeboe, B. Jordanov, C.J. Nielson, V. Aleksa. *J. Mol. Struct.*, **695**, 77 (2004).
[16] J. Liang, M. Schwartz, H.L. Paige. *J. Fluorine Chemistry*, **61**, 31 (1993).
[17] K.B. Wiberg, T.A. Keith, M.J. Frisch, M. Murcko. *J. Phys. Chem.*, **99**, 9072 (1995).
[18] L. Radom, J. Baker, P.M.W. Gill, R.H. Nobes, N.V. Riggs. *J. Mol. Struct.*, **126**, 271 (1985).
[19] W.R. Carper, M. Zandler, G.J. Mains. *J. Phys. Chem.*, **97**, 9091 (1993).
[20] H.J. Reich. WinDNMR: Dynamic NMR Spectra for Windows, Version 7.1, *J. Chem. Educ. Sofware* 3D2 (2001).
[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, 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, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople. *GAUSSIAN 98W*, Gaussian Inc., Pittsburgh, PA (2001).
[22] ChemOffice Pro, CambridgeSoft Corporation http://www.cambridgesoft.com, UK (1999).