Conformation stability, halogen and solvent effects on CO stretching of 4-chloro-3-halogenobenzaldehydes

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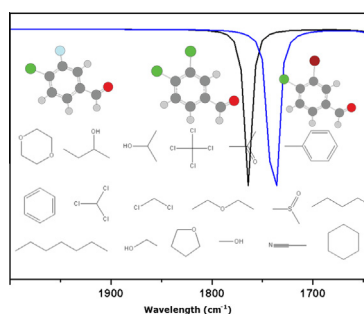# Conformation stability, halogen and solvent effects on C=O stretching of 4-chloro-3-halogenobenzaldehydes

Mahir Tursun, Cemal Parlak *

Department of Physics, Dumlupınar University, Kütahya 43100, Turkey

HIGHLIGHTS

- Effects of halogen and solvent on conformer and C=O stretching of CFB, CCB and CBB.
- Carbonyl vibrations were correlated with the KBM, AN, Swain and LSER equations.
- DFT method was used to predict structural and vibrational parameters.
- Conformational energy barrier is independent of the solvent for CFB.
- Theoretical frequencies exhibit good linear correlations with the KBM.

GRAPHICAL ABSTRACT

ABSTRACT

The effects of halogen and solvent on the conformation and carbonyl stretching of 4-chloro-3-halogeno-benzaldehydes [C_7H_4ClXO; X = F (CFB), Cl (CCB) or Br (CBB)] were investigated using the density functional theory (DFT) method. The B3LYP functional was used by the 6-311+G(3df,p) basis set in combination with the polarizable continuum model (PCM). Computations were focused on the *cis* and *trans* isomers of the compounds in 18 different polar or non-polar organic solvents. The theoretical frequencies of the solvent-induced C=O stretching vibrations were correlated with the empirical solvent parameters such as the Kirkwood–Bauer–Magat (KBM) equation, the solvent acceptor number (AN), Swain parameters and the linear solvation energy relationships (LSER). The present work explores the effect of both the halogen and medium on the conformational preference and C=O vibrational frequency. The findings of this work can be useful to those systems involving changes in the conformations analogous to the compounds studied.

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Introduction

Benzaldehyde is used as a food or flavoring additive and can be found in many foods, including baked goods, frozen dairy, fruit juice, gelatin pudding, alcoholic or non-alcoholic beverages, hard or soft candies, and chewing gum. It is also employed in dyes, perfumes, deodorants, drugs, shave gels, bath soaps, etc. as artifi-cial flavoring, and as an additive for one or more types of tobacco products. Furthermore, it is used as a solvent for oils, resins, and cellulose fibers [1]. It is the simplest aromatic aldehyde with CHO functional group. Functional group found in aldehyde and ketone is closely related to the class of carbonyl group i.e., the elec-tron-rich double bonded C=O. The difference is in the attachment of the carbonyl group. When this group is directly bonded to, at least, one hydrogen atom the compound is said to be an aldehyde, but when directly bonded to carbon atom it is described as ketone.

Aldehydes are of interest to researchers around the world due to presence of electron-rich, unsaturated C=O group, participating

* Corresponding author. Tel.: +90 (274) 265 20 31/3116; fax: +90 (274) 265 20 14.

E-mail address: cemal.parlak@dpu.edu.tr (C. Parlak).

in some addition reactions. Aromatic aldehydes are the chief precursor to large number of organic compounds with potential pharmaceutical activity. Substituted benzaldehydes are used in applications designed to increase the oxygen affinity of human hemoglobin and, to inhibit the sickle erythrocytes [2]. They are employed in the synthesis of bioactive materials, which have wide applications in dyes, cosmetics, textiles and pharmaceuticals [3], and of chalcones [4,5]. Literature has also revealed the ample examples of CFB being used as a starting material in the organic synthesis [6,7].

Solvent effects on vibrational frequencies and intensities are well known [8–11]. The characteristic IR stretching vibrations of solute structures are studied extensively. There are numerous works for the solvent influence on frequencies of some groups [10–16]. In this context, the structures bearing the carbonyl moiety have been extensively investigated due to their dipolarity and hydrogen bond accepting nature [10–14]. Furthermore, several empirical approaches attempt to characterize the solvent influences on vibrational frequencies such as KBM [17,18], AN [19], Swain [20] and LSER [21] equations. We also reported the solvent effect studies on the vibrational frequencies of some organic compounds [22–24]. But, they were conducted without empirical approaches or correlations for the solvent influence.

Recently, we have set out the experimental and theoretical investigations to study the conformations and vibrational modes of CFB. It is seen that CFB prefers the *cis* isomer while the chloro- and bromo-analogs prefer the *trans* in the gas phase. The conformational preference and rotational barrier remain qualitatively unaffected when HF/aug-cc-pVDZ, MP2/aug-cc-pVDZ or B3LYP/6-311+G(3df,p) are used [25]. In continuation with our interests in the investigation of substituted benzaldehydes, the prime objective of this study was to use DFT method in conjunction with the B3LYP/6-311+G(3df,p) method to examine the solvent and halogen effects on the conformation and C=O stretching of CFB, CCB and CBB. Further, the frequencies of carbonyl stretch vibrations were correlated with the KBM, AN, Swain and LSER solvent scales. We hereby report the findings of our research.

Computational methodology

All the computations were performed using Gaussian 09 program package [26] and GaussView [27] was used for visualization of the structures. For all the computations, *cis* and *trans* conformers in C_s symmetry of the compounds were optimized in the various solvents using the B3LYP functional in conjunction with the 6-311+G(3df,p) basis set. 18 different solvents were employed to investigate the solute–solvent interactions. The PCM [28], which is the default in Gaussian 09, was used to study the solvent effects. Harmonic vibrational frequencies were also computed by the same functional and basis set to confirm the nature of the ground state structures. Mole fractions of individual conformers were calculated as described earlier [22,29,30].

The KBM model is given with the following equation:

$$\frac{v_0 - v_s}{v_0} = A\frac{\varepsilon - 1}{2\varepsilon + 1} = Af(\varepsilon)$$

Here, v_0 and v_s are vibrational frequencies of the solute in the gas phase and solvent, respectively. ε is dielectric constant of the solvent and A is a constant depending upon the dimensions and electrical properties of the vibrating solute dipole [17,18]. This equation can be modified into a generalized form as $v_s = v_0 - C(\varepsilon - 1)/(2\varepsilon + 1)$, where the C equals to Av_0. When the correlation between v_s and $f(\varepsilon)$ is linear, the slope is C and v_0 is the intercept.

The equation of solvent AN is stated as;

$$v = v_0 + K\text{AN}$$

where, v_0 is the vibrational frequency of a solute in hexane and K is the sensitivity of vibrational frequency (v) to the solvent AN [19].

The model equation of Swain is shown as;

$$v = v_0 + aA_j + bB_j$$

v is the vibrational frequency of a solute in presence of a solvent. v_0 represents the predicated value for *n*-heptane as a reference solvent. A_j is a measure of the solvent hydrogen-bond donor (HBD) acidity whereas B_j is measure of the solvent hydrogen-bond acceptor (HBA) basicity. The coefficients a and b represent the sensitivity of solute to a solvent change [20].

LSER model equation is given as follows:

$$v = v_0 + (s\pi^* + d\delta) + a\alpha + b\beta$$

Here, v is the vibrational frequency of solute in a solvent. v_0 is the regression value of v in cyclohexane as a reference solvent. π^* is an index of solvent dipolarity/polarizability. δ is a discontinuous polarizability correction term for poly-chlorinated aliphatic hydrocarbon and aromatic solvents. α and β are measures of the solvent HBD acidity and HBA basicity, respectively. The regression coefficients s, d, a and b can provide quantitative measures of the relative contribution of the indicated parameters [21]. The KBM, AN, Swain and LSER parameters of the solvents used in the present study are presented in Table S1 [31,32].

Results and discussion

The results of the electronic computations on the conformers of the investigated compounds are reported and discussed in detail. Further, the solvent effect for the C=O stretching of the compounds is also analyzed together with several approaches.

Conformational stability

Free and relative free energies and mole fractions for the optimized geometries of the two conformers of 4-chloro-3-halogeno-benzaldehydes in solutions are listed in Tables 1–3. Solvent-induced carbonyl frequency vs. energy plots for the compounds are depicted in Figs. 1a and S1. There is a linear correlation noticed between the frequency and energy values (R^2 = 0.99972, 0.99971 and 0.99959 for CFB, CCB and CBB, respectively).

In the case of gas phase of CFB, the *cis* isomer was more stable than the *trans*. Similarly, for the computed free energies of CFB in the solution, the *cis* form is more stable than the *trans* by 0.2259–0.2736 kcal/mol (Table 1). According to the calculations of mole fractions of the individual conformers, CFB prefers *cis* and *trans* isomers in the solutions with approximate probabilities of 59–61% and 41–39%, respectively.

Turning to CCB, in the gas phase, the *trans* conformer was more stable than the *cis*. The computed free energies in solutions, however, indicate that the *cis* conformer is more stable by 0.220–0.1255 kcal/mol. On the basis of the calculations of the mole fractions of the individual conformers, CCB prefers *cis* and *trans* conformers with approximate probabilities of 51–55% and 49–45%, respectively (Table 2).

Moving to the computed free energies of CBB in the gas phase, the *trans* form was more stable than the *cis*. Similarly, the computed free energies in non-polar solvents show that the *trans* form is more stable than the *cis* by 0.0044–0.0860 kcal/mol. The Br-compound prefers *trans* and *cis* forms with approximate probabilities of 54–51% and 46–49%, respectively. However, the free energies in polar solvents reveal that the *cis* form is more stable than the other by 0.0157–0.0521 kcal/mol and the compound prefers *cis* and *trans* forms with approximate probabilities of 51–52% and 49–48% correspondingly (Table 3).

Table 1
Free energy, relative free energy and mole fraction of CFB.

Solvent	Free energy (Hartree)		Relative free energy (kcal/mol)		Mol fraction (%)	
	Cis	Trans	Cis	Trans	Cis	Trans
n-Hexane	−904.533538	−904.533178	0	0.2259	59.43	40.57
Cyclohexane	−904.533789	−904.533417	0	0.2334	59.74	40.26
Diethylether	−904.535931	−904.535497	0	0.2723	61.31	38.69
Toluene	−904.534346	−904.533953	0	0.2466	60.27	39.73
Tetrahydrofuran	−904.536935	−904.536505	0	0.2698	61.21	38.79
Benzene	−904.534199	−904.533811	0	0.2435	60.14	39.86
Tetrachloromethane	−904.534135	−904.53375	0	0.2416	60.07	39.93
1,4-Dioxane	−904.534108	−904.533723	0	0.2416	60.07	39.93
Acetonitrile	−904.538113	−904.537737	0	0.2359	59.84	40.16
Dichloromethane	−904.537175	−904.536751	0	0.2661	61.05	38.95
Chloroform	−904.536156	−904.535720	0	0.2736	61.36	38.64
2-Butanol	−904.537716	−904.537314	0	0.2523	60.50	39.50
2-Propanol	−904.537838	−904.537443	0	0.2479	60.32	39.68
Ethanol	−904.537972	−904.537585	0	0.2428	60.12	39.88
Methanol	−904.538082	−904.537704	0	0.2372	59.89	40.11
Acetone	−904.537873	−904.537481	0	0.2460	60.24	39.76
n-Heptane	−904.533595	−904.533232	0	0.2278	59.51	40.49
Dimethylsulfoxide	−904.538191	−904.537821	0	0.2322	59.68	40.32

Table 2
Free energy, relative free energy and mole fraction of CCB.

Solvent	Free energy (Hartree)		Relative free energy (kcal/mol)		Mol fraction (%)	
	Cis	Trans	Cis	Trans	Cis	Trans
n-Hexane	−1264.888454	−1264.888419	0	0.0220	50.93	49.07
Cyclohexane	−1264.888696	−1264.888646	0	0.0314	51.33	48.67
Diethylether	−1264.890779	−1264.890612	0	0.1048	54.42	45.58
Toluene	−1264.889237	−1264.889152	0	0.0533	52.25	47.75
Tetrahydrofuran	−1264.891758	−1264.891568	0	0.1192	55.02	44.98
Benzene	−1264.889094	−1264.889018	0	0.0477	52.01	47.99
Tetrachloromethane	−1264.889032	−1264.888955	0	0.0483	52.04	47.96
1,4-Dioxane	−1264.889006	−1264.888934	0	0.0452	51.91	48.09
Acetonitrile	−1264.892906	−1264.892738	0	0.1054	54.44	45.56
Dichloromethane	−1264.891990	−1264.891801	0	0.1186	54.99	45.01
Chloroform	−1264.890998	−1264.890824	0	0.1092	54.60	45.40
2-Butanol	−1264.892536	−1264.892336	0	0.1255	55.28	44.72
2-Propanol	−1264.892638	−1264.892459	0	0.1123	54.73	45.27
Ethanol	−1264.892768	−1264.892594	0	0.1092	54.60	45.40
Methanol	−1264.892876	−1264.892707	0	0.1060	54.47	45.53
Acetone	−1264.892673	−1264.892495	0	0.1117	54.70	45.30
n-Heptane	−1264.888509	−1264.888471	0	0.0238	51.01	48.99
Dimethylsulfoxide	−1264.892982	−1264.892818	0	0.1029	54.34	45.66

Table 3
Free energy, relative free energy and mole fraction of CBB.

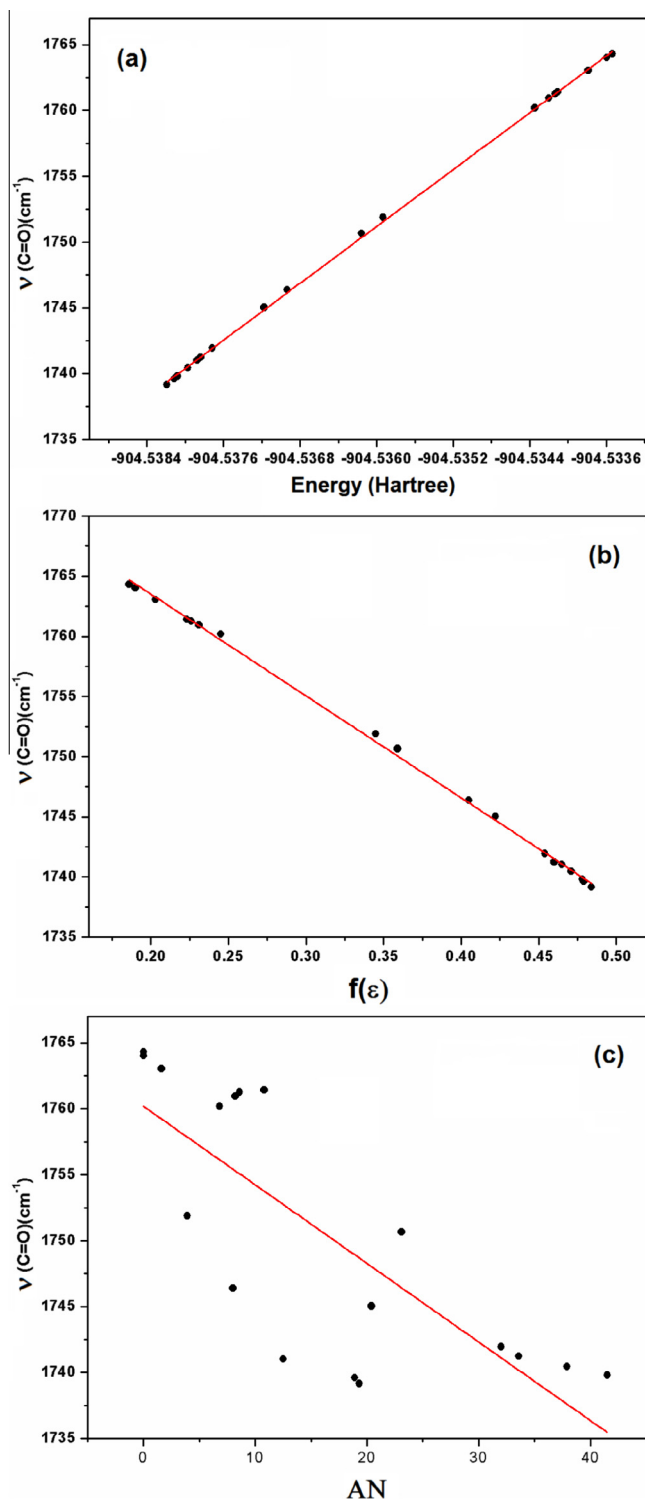| Solvent	Free energy (Hartree)		Relative free energy (kcal/mol)		Mol fraction (%)	
	Cis	Trans	Cis	Trans	Cis	Trans
n-Hexane	−3378.807658	−3378.807799	0.0885	0	46.27	53.73
Cyclohexane	−3378.807896	−3378.808025	0.0809	0	46.59	53.41
Diethylether	−3378.809954	−3378.809976	0.0138	0	49.42	50.58
Toluene	−3378.808425	−3378.808527	0.0640	0	47.30	52.70
Tetrahydrofuran	−3378.810944	−3378.810919	0	0.0157	50.66	49.34
Benzene	−3378.808285	−3378.808395	0.0690	0	47.09	52.91
Tetrachloromethane	−3378.808228	−3378.808338	0.0690	0	47.09	52.91
1,4-Dioxane	−3378.808202	−3378.808313	0.0697	0	47.06	52.94
Acetonitrile	−3378.812161	−3378.812079	0	0.0515	52.17	47.83
Dichloromethane	−3378.811192	−3378.811149	0	0.0270	51.14	48.86
Chloroform	−3378.810177	−3378.810184	0.0044	0	49.81	50.19
2-Butanol	−3378.811747	−3378.811680	0	0.0420	51.78	48.22
2-Propanol	−3378.811874	−3378.811802	0	0.0452	51.91	48.09
Ethanol	−3378.812013	−3378.811936	0	0.0483	52.04	47.96
Methanol	−3378.812128	−3378.812049	0	0.0496	52.09	47.91
Acetone	−3378.811911	−3378.811837	0	0.0464	51.96	48.04
n-Heptane	−3378.807714	−3378.807851	0.0860	0	46.37	53.63
Dimethylsulfoxide	−3378.812242	−3378.812159	0	0.0521	52.20	47.80

Fig. 1. Plot of the optimized energy (a), KBM (b), and AN (c) parameters vs. the carbonyl frequency of CFB.

former. The mole fractions for the most stable conformers of CFB and CCB increase from gas to polar solvent whereas the mole fractions of CBB decrease.

The computed carbonyl bond lengths and dipole moments of the compounds are listed in Table 4. The relationships between the carbonyl bond lengths and stretching frequencies are shown in Fig. S2. It was noticed that these C=O bond lengths show good and linear correlations with the carbonyl frequencies of the compounds (R^2 = 0.99999, 0.99911 and 0.99961 for CFB, CCB and CBB, respectively). These C=O bond lengths increase with the decrease of v(C=O) frequencies.

Plots of the dipole moments vs. the carbonyl vibrations are shown in Fig. S3. There are good and linear correlations between the carbonyl frequencies and dipole moments (R^2 = 0.99986, 0.99898 and 0.99961/0.99922 for CFB, CCB and CBB (non-polar/polar), respectively). In the gas phase, CFB, CCB and CBB have 3.11–1.00, 3.03–1.14 and 3.00–1.20 Debye dipole moments (*cis–trans*) correspondingly. The dipole moment is expected to be larger in solution than in the corresponding gas phase (Table 4). The dipole moment increases gradually from lower to higher dielectric and it is in agreement with the literature data [22–23]. It also increases by the decrease of the v(C=O) frequencies.

Carbonyl stretching

The computed carbonyl stretching frequencies of the compounds are tabulated in Table 4. For the compounds/*n*-hexane, the carbonyl vibrations are computed at higher frequencies. This belongs to the free monomer state of carbonyl as no remarkable solute–solvent interactions occur in the inert solvent *n*-hexane. Interestingly, these bands were found at lower frequencies in polar solvents such as dimethylsulfoxide, acetonitrile and methanol.

Figs. 1b and S4 demonstrate the carbonyl frequency vs. the parameter of KBM equation. As seen from Table 5 and Fig. 1b, there is linear correlation between the v(C=O) and $f(\varepsilon)$. The negative slopes indicate that these frequencies are red-shifted by the increase in dielectric constant of the solvent employed. Although the specific and non-specific solvent effects collectively contribute to solute–solvent interactions, the KBM only considers the solvent dielectric constants. Also, the vibrational frequencies depend on the dielectric constant of the solvent. These facts conclude a good relationship between the KBM parameter and v(C=O) frequencies. The current results confirm that the PCM model is suitable to predict dielectric-induced solvent effect on the vibrational frequencies. Similar studies were reported for the KBM equation with both theoretical [16,33] and experimental data [11]. The AN equations are given in Table 5. Figs. 1c and S5 illustrate the plots of the v(C=O) vs AN data, which shows the poor correlation of the data. The results show that AN has no major role in the determination of vibrational shift in solution.

The Swain equations for the v(C=O) are also listed in Table 5. The solvent effects are divided into two species by Swain. One is the anion-solvating tendency of the solvent (acidity), and the other is the cation-solvating tendency of the solvent (basicity). This means the specific solute–solvent interactions are only considered. Even tough the correlations of the Swain equation for the v(C=O) are poor, they are better than those noticed with AN. It is probable that both the Lewis acidity and basicity for the solvent are considered in Swain equation, but the AN only considers the Lewis acidity of the solvent into account. The negative signs for A_j and B_j represent that the solvent HBD acidity and HBA basicity lead to red-shift of the v(C=O). The ratios of these coefficients are almost equal to 2. This implies that the red-shift of the C=O band induced by the solvent acidity is larger than the one induced by the solvent basicity.

Further, the LSER values are given in Table 5. The results of LSER having the poor correlations exhibit better correlations than the

Conformational energy barrier is independent on the solvent for the F-compound whereas it is dependent on the solvent for the Cl- and Br-compounds. In addition, there is halogen effect on the conformations. In the gas phase, CFB prefers the *cis* conformation while CCB and CBB prefer the *trans* conformation, but the *cis* form, except CBB in non-polar solvents, is the most stable conformer of the compounds in the solutions. On the other hand, for Br-compound in non-polar solvents, the *trans* form is the most stable con-

Table 4
Dipole moment, carbonyl stretching and bond length of the compounds.

Solvent	CFB			CCB			CBB		
	Dipole moment	C=O bond length	v(C=O)	Dipole moment	C=O bond length	v(=O)	Dipole moment	C=O bond length	v(C=O)
n-Hexane	3.49	1.209	1764.30	3.41	1.208	1765.16	1.32	1.209	1765.36
Cyclohexane	3.53	1.209	1763.04	3.45	1.209	1763.91	1.33	1.209	1764.13
Diethylether	3.86	1.211	1751.88	3.79	1.210	1752.80	1.41	1.211	1753.32
Toluene	3.61	1.209	1760.19	3.53	1.209	1761.07	1.35	1.209	1761.40
Tetrahydrofuran	4.03	1.212	1746.38	3.96	1.211	1747.36	3.93	1.211	1747.32
Benzene	3.59	1.209	1760.95	3.51	1.209	1761.82	1.35	1.209	1762.11
Tetrachloromethane	3.58	1.209	1761.27	3.50	1.209	1762.15	1.34	1.209	1762.43
1,4-Dioxane	3.57	1.209	1761.41	3.49	1.209	1762.29	1.34	1.209	1762.56
Acetonitrile	4.24	1.213	1739.62	4.18	1.212	1740.67	4.17	1.213	1740.01
Dichloromethane	4.07	1.212	1745.03	4.00	1.212	1746.04	3.98	1.212	1745.67
Chloroform	3.90	1.211	1750.66	3.82	1.211	1751.61	1.42	1.211	1752.15
2-Butanol	4.17	1.212	1741.94	4.11	1.212	1744.21	4.08	1.212	1742.31
2-Propanol	4.19	1.212	1741.23	4.13	1.212	1742.27	4.11	1.212	1741.61
Ethanol	4.22	1.213	1740.45	4.15	1.212	1741.49	4.13	1.212	1740.83
Methanol	4.24	1.213	1739.80	4.18	1.212	1740.85	4.15	1.212	1740.19
Acetone	4.20	1..212	1741.02	4.14	1.212	1742.05	4.11	1.212	1741.40
n-Heptane	3.50	1.209	1764.02	3.42	1.209	1764.87	1.32	1.209	1765.08
Dimethylsulfoxide	4.26	1.213	1739.16	4.20	1.213	1740.22	4.18	1.213	1739.55

Table 5
Solvent equations for the carbonyl stretching vibrations of the compounds.

Compound	KBM equation	R^2	AN equation	R^2
CFB	$1780.44 - 84.67f(\varepsilon)$	0.99888	$1760.19 - 0.6AN$	0.58225
CCB	$1781.05 - 83.47f(\varepsilon)$	0.99814	$1761.03 - 0.58AN$	0.57478
CBB	$1782.23 - 87.38f(\varepsilon)$	0.99689	$1761.37 - 0.62AN$	0.58582
	LSER equation		Swain equation	
CFB	$1763.79 - 22.78\pi^* + 9.09\delta - 7.79\alpha - 6.87\beta$	0.82966	$1765.6 - 28.19A_j - 13B_j$	0.73402
CCB	$1764.65 - 22.93\pi^* + 9.17\delta - 7.56\alpha - 6.4\beta$	0.83007	$1766.43 - 27.96A_j - 12.9B_j$	0.73379
CBB	$1764.96 - 23.28\pi^* + 9.46\delta - 8.28\alpha - 7\beta$	0.83258	$1766.85 - 29.25A_j - 13.2B_j$	0.73063

results found by the Swain equation. In the LSER model, there are not only the specific interaction parameters such as α and β, but also the non-specific interaction parameter as π^*. The negative π^* coefficients inform that red-shift of the v(C=O) is observed by non-specific solvent effects. The π^* coefficients having the biggest absolute values among the others prove that non-specific solvent effects are dominant in the compound/solvent interactions. The coefficients α and β are also negative, in agreement with the case of A_j and B_j in Swain equation. This states the same influence with regard to the red-shift of the carbonyl vibrations by the solvent HBD acidity and HBA basicity. The α coefficients are bigger than the β factors. The carbonyl vibrations of the compounds are more susceptible to the solvent HBD acidity than the HBA basicity. The poor correlations obtained by the LSER and Swain equations verify that the PCM model neglects specific solvent effects.

Conclusions

We have undertaken a theoretical research, using DFT, to study the effects of halogen and solvent on the conformation and C=O stretching of 4-chloro-3-halogenobenzaldehyde. The results can be useful for analyzing the conformations involving these analogous. The important conclusions drawn for this research work are;

(i) Conformational energy barrier is dependent on the solvent employed for CCB and CBB whereas it is independent for CFB.

(ii) It is worth to note that the compounds have large dipole moments and this is an essential criterion for drug–receptor interaction [33,34].

(iii) From lower to higher dielectric, the dipole moments increase while the frequencies of the solvent-induced C=O stretching vibrations decrease.

(iv) The solvent-induced C=O frequencies decrease inversely with the dipole moment and bond length whereas they increase when approaching the more stable energy.

(v) For the solvent-induced C=O stretching frequencies, it has been noticed that the Swain and LSER parameters with the theoretical data have poor correlations. Interestingly, the KBM model the used theoretical values shows a good correlation. No linear relationships are observed with AN model. The LSER model employed the experimental values is a powerful tool for the study of solvent effect [10,11,33,35,36]. However, the PCM technique has not perfectly captured the solvent effects found in the experiments, and reflects non-specific interactions. The experimental data will facilitate developments in upgrading of theoretical modeling.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.01.023.

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