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Carbonyl stretching vibrations of 5-halogen-2-thiophenecarboxaldehydes: KBM, AN, SWAIN and LSER parameters

5-halojen-2-tiyofenkarboksaldehitlerin karbonil gerilme titreşimleri: KBM, AN, SWAIN ve LSER parametreleri

Cemal PARLAK[1]*, *Özgür ALVER*[2]

[1]Department of Physics, Science Faculty, Ege University, Izmir, Turkey.
cemal.parlak@ege.edu.tr
[2]Department of Physics, Science Faculty, Anadolu University, Eskisehir, Turkey.
ozguralver@anadolu.edu.tr

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* Corresponding author/Yazışılan Yazar
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Abstract

Halogen and solvent influence on the conformational stability and carbonyl stretching vibration of 5-Halogeno-2-thiophene-carboxaldehydes (C_5H_3XOS; X=F, Cl or Br) were investigated by the density functional theory using the B3LYP functional, 6-311+G(3df,p) basis set and polarizable continuum model. Calculations were performed by the cis and trans forms of the compounds in eighteen different solvents. The carbonyl stretching frequencies were correlated with some solvent parameters such as the Kirkwood-Bauer-Magat equation, the solvent acceptor number, Swain parameters and the linear solvation energy relationships. The findings of this research will be useful for thiophenecarboxaldehydes.

Keywords: 5-Halogeno-2-thiophenecarboxaldehyde, DFT, Solvent effect

Öz

5-halojen-2-tiyofenkarboksaldehitlerin (C5H3XOS; X=F, Cl veya Br) yapısal denge ve karbonil gerilme titreşimleri üzerindeki çözücü ve halojen etkileri yoğunluk fonksiyoneli teorisi ile B3LYP fonksiyoneli, 6-311+G(3df,p) baz seti ve kutuplanabilir süreklilik modeli kullanılarak incelendi. Hesaplamalar on sekiz farklı çözücü içinde moleküllerin cis ve trans konformasyonları ele alınarak yürütüldü. Çözücü içindeki karbonil gerilme titreşim frekansları Kirkwood-Bauer-Magat denklemi, çözücü akseptör sayısı, Swain parametreleri ve lineer çözünme enerji ilişkisi gibi çözücü skalaları ile incelendi. Bu çalışmanın sonuçları tiyofen-karboksaldehit türevleri için faydalı olacaktır.

Anahtar kelimeler: 5-Halojen-2-tiyofenkarboksaldehit, YFT, Çözücü etkisi

1 Introduction

Polymers of thiophenes have intense interest in literature due to their electrical properties and durability [1]. Thiophenes are well known to exhibit various biological activities such as anti-inflammatory agents [2], anti-HIV or some inhibitors [3] and anti-breast cancer [4]. Further, aldehydes are of interest to researchers around the world due to presence of electron-rich, unsaturated C=O group, participating in some addition reactions. For T2C, the cis form is defined as having the heaviest (generally nonhydrogen) atom of a substituent group cis to the ring sulfur atom. Experimental and theoretical results for 2TC indicated that the cis form was found to be more stable than the trans [5]-[8].

Organic synthesis is typically carried out in solvents. Molecular properties are strongly solvent dependent. Many interesting reactions take place in the liquid phase. For example, biochemical reactions generally occur in the aqueous environment. Rates of chemical reactions can vary many orders of magnitude depending on the solvent. In this sense, nature and effect of the solute-solvent interaction on the vibrational spectrum are well known [9]-[13]. There are numerous examples of the solvent effect on some group frequencies. The carbonyl has been extensively investigated due to its polarity and hydrogen bond accepting nature [12]-[15]. Furthermore, the empirical approaches such as the Kirkwood-Bauer-Magat (KBM) [16],[17], solvent acceptor number (AN) [18], Swain [19] and linear solvation energy relationships (LSER) [20] have characterized the solvent effect on vibrational frequency.

It is clear that the computational description of solvent effects is crucial. The prime objective of the present work was to use density functional theory (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 the compounds [X=F (5F-2TC), Cl (5C-2TC) and Br (5B-2TC)]. Further, the frequencies of carbonyl stretch vibrations were correlated with the KBM, AN, Swain and LSER solvent scales.

2 Calculations

Gaussian 09 was used for the calculations [21]. Computations in solutions, without imposing symmetry, were performed by B3LYP/6-311+G(3df,p). The polarizable continuum model. (PCM) was used to evaluate solvent effect. Harmonic vibrational frequencies, scaled by 0.9683, were calculated by the same level to confirm the nature of the ground state structure. Mole fractions of the individual isomers were computed as described earlier [22]. As described earlier, the C=O frequencies were correlated by KBM, AN, Swain and LSER scales to evaluate the solvent effect [9]. KBM, AN, Swain and LSER parameters of the solvents are given in Table 1.

3 Results and discussion

Results of the electronic computations on the isomers of the investigated compounds are reported and discussed in detail. Further, solvent effect for the carbonyl stretching of the compounds is also analysed together with several approaches.

3.1 Conformational stability

Mole fractions for the optimized geometries of the two forms of the compounds investigated in solutions are given in Table 2. There is a linear correlation between the solvent-induced carbonyl frequency and energy values (R^2=0.99951, 0.99906 and 0.99805 for 5F-2TC, 5C-2TC and 5B-2TC, respectively).

In the case of 5F-2TC in solution, the computed free energies show that the cis form is more stable by 1.64-1.84 kcal/mol. On the basis of the mole fraction computations of individual isomers, 5F-2TC prefers cis and trans forms with approximate probabilities of 94-96% and 4-6% correspondingly (Table 2).

Moving to the free energies calculated of 5C-2TC and 5B-2TC in solution, similarly, the cis form is more stable than trans by 1.42-1.60 and 1.41-1.59 kcal/mol. Both Cl- and Br-compounds prefer cis and trans forms with approximate probabilities of 92-94% and 6-8% correspondingly. The calculated carbonyl bond lengths and dipole moments of the compounds are listed in Table 3.

It was noticed that these C=O bond lengths show good and linear correlations with the carbonyl frequencies of the compounds (R^2=0.99940, 0.99936 and 0.99882 for 5F-2TC, 5C-2TC and 5B-2TC correspondingly). These C=O bond lengths increase with the decrease of ν(C=O) frequencies.

There are good and linear correlations between the carbonyl frequencies and dipole moments (R^2 = 0.99960, 0.99908 and 0.99908, respectively). The dipole moments increase gradually in the solutions. It also increases by the decrease of the ν(C=O) frequencies.

3.2 Carbonyl stretching

The carbonyl stretching frequencies of the compounds are tabulated in Table 3. For the n-hexane or n-heptane, 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. The C=O bond lengths increase with the polarity of the solvent. Hence, carbonyl stretching frequencies should decrease. It is clearly observed in Table 3 that this requirement is substantially fulfilled for the compounds.

Table 1: Solvent parameters.

Solvent	f(ε)	AN	π*	δ	α	β	A_j	B_j
n-Hexane	0.186	0.00	-0.04	0.0	0.00	0.00	0.01	-0.01
n-Heptane	0.190	0.00	0.00	0.0	0.00	0.00	0.00	0.00
Cyclohexane	0.203	1.60	0.00	0.0	0.00	0.00	0.02	0.06
1.4-dioxane	0.223	10.80	0.55	0.0	0.00	0.37	0.19	0.67
Tetrachloromethane	0.226	8.60	0.28	0.5	0.00	0.10	0.09	0.34
Benzene	0.231	8.20	0.59	1.0	0.00	0.10	0.15	0.59
Toluene	0.245	6.80	0.54	1.0	0.00	0.11	0.13	0.54
Diethylether	0.345	3.90	0.27	0.0	0.00	0.47	0.12	0.34
Chloroform	0.359	23.10	0.58	0.5	0.20	0.10	0.42	0.73
Tetrahydrofuran	0.405	8.00	0.58	0.0	0.00	0.55	0.17	0.67
Dichloromethane	0.422	20.40	0.82	0.5	0.13	0.10	0.33	0.80
2-Butanol	0.454	32.00	0.40	0.0	0.69	0.80	-	-
2-Propanol	0.460	33.60	0.48	0.0	0.76	0.84	0.59	0.44
Acetone	0.465	12.50	0.62	0.0	0.08	0.48	0.25	0.81
Ethanol	0.471	37.90	0.54	0.0	0.86	0.75	0.66	0.45
Methanol	0.478	41.50	0.60	0.0	0.98	0.66	0.75	0.50
Acetonitrile	0.479	18.90	0.75	0.0	0.19	0.40	0.37	0.86
Dimethylsulfoxide	0.484	19.30	0.76	0.0	1.00	0.00	0.34	1.08

Table 2: Mole fraction of the compounds.

Solvent	5F-2TC Mole fraction (%)		5C-2TC Mole fraction (%)		5B-2TC Mole fraction (%)	
	Trans	Cis	Trans	Cis	Trans	Cis
n-hexane	5.86	94.14	8.30	91.70	8.44	91.56
n-heptane	5.85	94.15	8.28	91.72	8.38	91.62
Cyclohexane	5.82	94.18	8.25	91.75	8.30	91.70
1-4-dioxane	5.77	94.23	8.23	91.77	8.18	91.82
Tetrachloromethane	5.76	94.24	8.26	91.74	8.20	91.80
Benzene	5.75	94.25	8.17	91.83	8.17	91.83
Toluene	5.73	94.27	8.17	91.83	8.13	91.87
Diethylether	5.33	94.67	7.71	92.29	7.31	92.69
Chloroform	5.25	94.75	7.63	92.37	7.20	92.80
Tetrahydrofuran	4.96	95.04	7.20	92.80	6.84	93.16
Dichloromethane	4.85	95.15	7.11	92.89	6.70	93.30
2-butanol	4.57	95.43	6.68	93.32	6.52	93.48
2-propanol	4.51	95.49	6.63	93.37	6.52	93.48
Acetone	4.48	95.52	6.59	93.41	6.48	93.52
Ethanol	4.43	95.57	6.51	93.49	6.44	93.56
Methanol	4.36	95.64	6.41	93.59	6.46	93.54
Acetonitrile	4.34	95.66	6.39	93.61	6.39	93.61
Dimethylsulfoxide	4.29	95.71	6.32	93.68	6.43	93.57

As can be shown from Tables 3-4, the carbonyl frequencies scaled are inversely proportional to dielectric constant of the solvent. For KBM, there is linear correlation between the carbonyl stretching frequency and f(ε). Negative slope means that the frequency is red-shifted by the increase in dielectric constant. Though both the specific and non-specific solvent effects contribute to interactions, KBM only pays regard to the dielectric constant. The results verify that PCM is very successful in determining the effects of solvent on the vibrational frequency. For the AN, however, there are poor correlations and it has no major act in the detection of the frequency shift in solution. Similar results were reported for the KBM and AN equations [9],[23],[24].

Swain divided the solvent effects into two species, the anion (acidity) and cation (basicity) solvating tendency of solvent. Therefore, specific solute-solvent interactions are only kept in view. Correlations of Swain equations are poor like AN (Table 4). Swain considers both Lewis acidity and basicity of solvent whereas Lewis acidity of solvent is only considered in AN. The negative signs for A_j and B_j mean that hydrogen-bond donor (HBD) acidity and hydrogen-bond acceptor (HBA) basicity of the solvent lead to red-shift of carbonyl stretching frequencies. Ratio of these coefficients is equal to about 2. Red-shift induced by acidity is larger than the one by basicity.

For multiparameter equation LSER, there are not only specific interaction parameters (α and β), but also non-specific interaction parameter (π*). Similarly, negative π* coefficients state that the red-shifts are observed by non-specific solvent effects. The π* or δ coefficients have the biggest absolute values among the others. It supports that the non-specific effects are dominant in the interactions. Further, the α and β are negative, in agreement with the Swain coefficients (Table 4). This informs the same influence with regard to the red-shifts by solvent HBD acidity and HBA basicity. The α coefficients are bigger than the β values and carbonyl stretching frequencies are more susceptible to HBD acidity than HBA basicity of solvent. The poor correlations of the LSER and Swain, when compared to KBM, verify that the PCM neglects specific solvent effects.

Table 3: Dipole moment (μ, Debye), carbonyl bond length (Å) and frequency (ν, cm^{-1}) of the compounds.

Solvent		5F-2TC			5C-2TC			5B-2TC	
	μ	Å	ν	μ	Å	ν	μ	Å	ν
n-hexane	4.09	1.2141	1675	4.07	1.2135	1676	4.07	1.2132	1677
n-heptane	4.10	1.2142	1675	4.08	1.2135	1676	4.08	1.2133	1676
Cyclohexane	4.13	1.2144	1673	4.11	1.2137	1675	4.12	1.2135	1675
1-4-dioxane	4.19	1.2148	1671	4.17	1.2141	1672	4.18	1.2138	1673
Tetrachloromethane	4.20	1.2148	1671	4.18	1.2141	1672	4.18	1.2139	1673
Benzene	4.21	1.2149	1671	4.19	1.2142	1672	4.20	1.2139	1672
Toluene	4.24	1.2151	1670	4.22	1.2143	1671	4.22	1.2141	1672
Diethylether	4.55	1.2169	1659	4.52	1.2161	1661	4.53	1.2159	1661
Chloroform	4.59	1.2172	1657	4.57	1.2164	1659	4.58	1.2161	1660
Tetrahydrofuran	4.75	1.2182	1651	4.73	1.2173	1653	4.74	1.2171	1654
Dichloromethane	4.81	1.2185	1650	4.78	1.2176	1651	4.79	1.2174	1652
2-butanol	4.93	1.2192	1645	4.90	1.2183	1647	4.92	1.2181	1647
2-propanol	4.95	1.2194	1644	4.93	1.2185	1646	4.94	1.2182	1646
Acetone	4.96	1.2194	1644	4.94	1.2186	1645	4.95	1.2183	1646
Ethanol	4.99	1.2196	1643	4.96	1.2187	1644	4.97	1.2184	1645
Methanol	5.01	1.2197	1642	4.99	1.2188	1644	5.00	1.2186	1644
Acetonitrile	5.02	1.2198	1642	5.00	1.2189	1643	5.01	1.2186	1644
Dimethylsulfoxide	5.04	1.2199	1641	5.01	1.2190	1643	5.03	1.2187	1643

Table 4: Solvent equations for the carbonyl stretching vibrations.

Compound	KBM	R^2	AN	R^2
5F-2TC	1697.17-114.21 f(ε)	0.99796	1669.89-0.80 AN	0.58468
5C-2TC	1698.04-112.68 f(ε)	0.99719	1671.08-0.79 AN	0.58076
5B-2TC	1698.61-112.79 f(ε)	0.99642	1671.69-0.80 AN	0.58665
	LSER		SWAIN	
5F-2TC	1674.49-30.40 π*+12.68 δ-10.68 α-9.16 β	0.83364	1677.07-38.27 A_j-17.25 B_j	0.73173
5C-2TC	1675.85-30.67 π*+12.53 δ-10.15 α-8.98 β	0.83371	1678.30-37.56 A_j-17.35 B_j	0.73307
5B-2TC	1676.18-29.72 π*+12.34 δ-10.95 α-8.94 β	0.83512	1678.69-37.98 A_j-16.81 B_j	0.72974

4 Conclusions

We have undertaken a theoretical research, by DFT, to study solvent and halogen effects on the conformational stability and carbonyl stretching of 5-halogeno-2-thiophene-carboxaldehydes. Results will be useful for analysing the conformations involving similar analogous. The important conclusions drawn for the present research are;

i. Energy barrier of conformation is independent on the solvent employed for the compounds.

ii. There is no halogen effect on conformations of the compounds.

iii. It is worth to note that the compounds have large dipole moments and this is an essential criterion for drug-receptor interaction [25].

iv. Solvent-induced carbonyl frequencies decrease inversely with the dipole moment, bond length and dielectric constant.

v. Swain and LSER parameters have poor correlations whereas KBM shows a good correlation. No linear relationships are observed with AN. Hence, PCM technique reflects non-specific interactions.

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