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ISSN -1817 -2695



## Study of the Hydrogen bonding between 1-heteroaryl-2-(1-methylpyridinium-2-yl)ethylene Cation (HME) and Some small molecules

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Received 30-3-2011, Accepted 26-3-2012

### Abstract

The theoretical calculations of trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene(I) cation and its complexes with HF, CH<sub>3</sub>OH and H<sub>2</sub>O respectively (II, III and IV) were carried out by quantum mechanical method. The optimized structures of the cation and its complexes (I,II,III and IV) were obtained by the density functional theory DFT at B3LYP5 level of theory using the basis set 6-31G in gas phase and various solvents . The study shows that the optimized structures of compounds (I, II, III and IV) have the global minimum energy. Global descriptors such as the dipole moment( $\mu$ ), molecular orbital energy of HOMO and LUMO levels,  $\Delta E$ , hardness( $\eta$ ), electronegativity(X)and electrophilicity( $\omega$ ) were determined and used to identify the differences in the stability and reactivity of the compounds. In general the calculated values lead to the conclusion that the stabilities of the compounds according to the values of hardness and energy gap are in sequence II>III>IV>I in various solvents and according sequence II>III>I>IV in gas phase. The theoretical calculations of UV-Visible for the cation and its complexes with HF, CH<sub>3</sub>OH and H<sub>2</sub>O were carried out by TD-B3LYP5 level of theory using the basis sets 6-31G(d,p) and 6-311G(d,p), and the results were compared with experimental data.

**Keywords:** Trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene cation (HME), Intermolecular Hydrogen Bonding( IHB ), DFT.

### Introduction

In the family of heterocyclic compounds, nitrogen - containing heterocycles are an important class of compounds in medicinal chemistry[1] . There has been a considerable interest in these compounds because it represents one of the most active classes of compounds , possessing a wide spectrum of biological activities like antibacterial , antimicrobial and antiviral, they are also useful as anti-inflammatory , intermediates for dyes and display anti-tumor properties[2-4].

Therefore the studying of the hydrogen intermolecular bonding between the cation

and some small molecules is very important, because as known to all, the boiling and melting points vapor pressure, solubility, density , viscosity, heat conductivity, heat expansion, dielectric constant, dipole moment, electro conductivity, ionization, another optical properties, spectra, acid-base, and biological activity of chemical compounds are contributing essentially to helix and to double-helix stability, depending on the presence of intermolecular hydrogen bond (IHB) and its thermodynamic parameters. For the directive synthesis of compounds,

the quantum chemical evaluation of the IHB effect on the electronic structure of molecules is of great interest[5-9]. A direct determination of the hydrogen bonding arrangement will require additional experimental work. However, computational chemistry has played an important role in identifying and quantifying hydrogen - bonding geometries, energies of pertinent model systems, building and testing potential models for predicting cation-donor interactions and hence drug-drug interactions[10-11].

#### Computational method

A full quantum mechanical geometry optimization was performed by using PC GAMESS computational program for calculation. The calculations were done at the density functional theory DFT/B3LYP5 level of theory using the basis set 6-31G

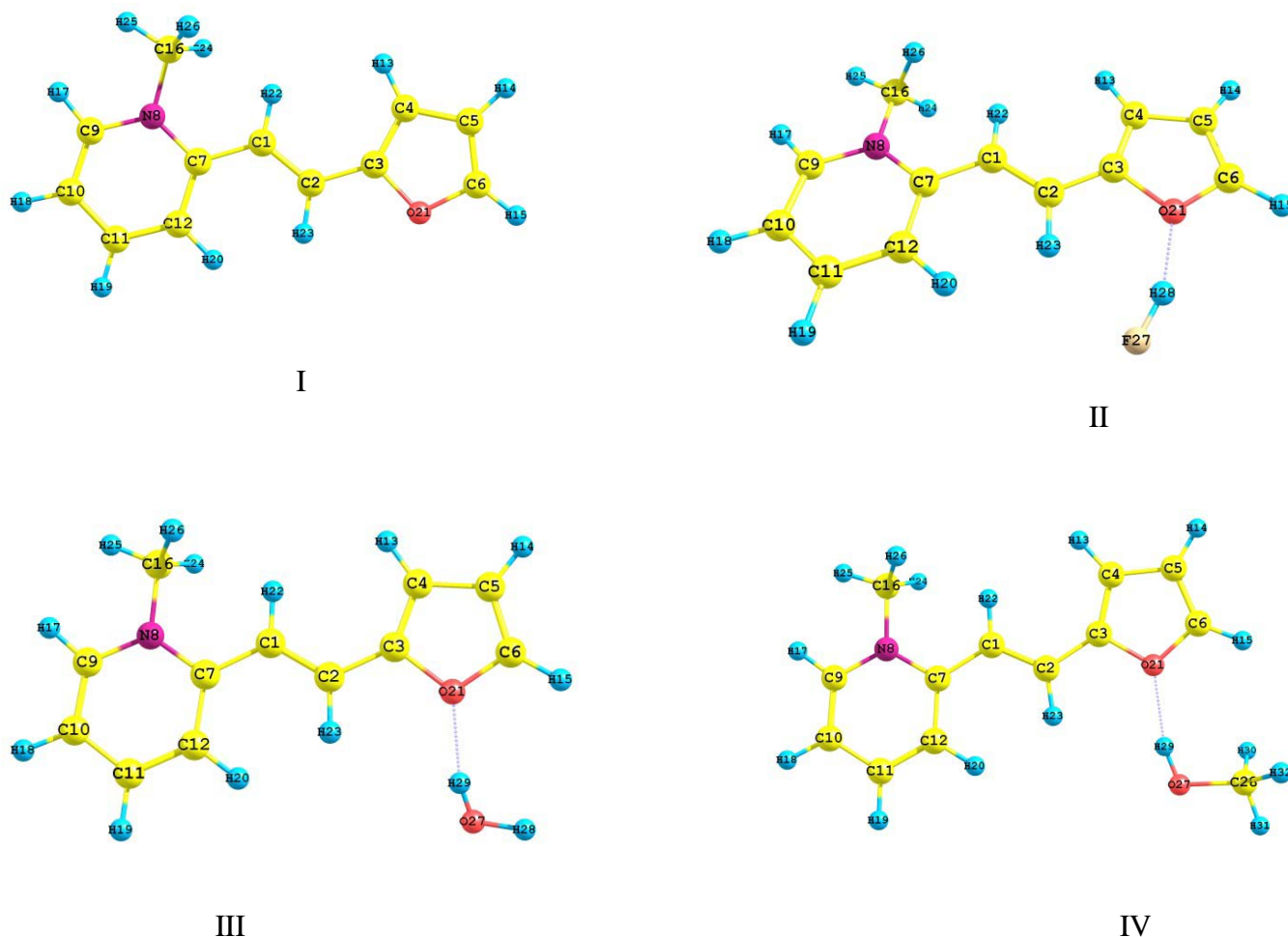
#### Results and Discussion

The trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene cation (compound I) possessing heteroaromatic moieties linked by a vinyl to strong electron withdrawing pyridinium ring. It belongs to the class of the so called push-pull (donor - acceptor, D-A)[13]. So that we here report hydrogen bonding forming between the cation and water, HF and

In this work, we attempt to study the interhydrogen bonding with different small molecules, electronic properties, and relative stabilities by performing density functional theory (DFT) at B3LYP5/ 6-31G level of theory. The purpose of this study was to investigate the effect of interhydrogen bonding on the properties of 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene cation, Therefore it is theoretically necessary to use an efficient set of methodologies which efficiently describe the red- and blue -shift effects.

[12]. Energy band gap ( $\Delta E$ ) calculation has been done using Chermcraft program, correlation drawing throughout the DPlot program. All calculations were performed on the Pentium (R)4/IPM-PC- CPU 3.000GHz.

methanol in various solvents such as water, chloroform and methanol and studying the effect of hydrogen bonding on the system properties. On other hand we attempt to examine the effect of the theory level in studying Uv-visible and results are agreement with the experimental values. The geometry optimized structures are visualized in Figure 1.



Figure(1) DFT-calculated optimized structures of the Cation(I), Cation-CH<sub>3</sub>OH, Cation-H<sub>2</sub>O and Cation-HF, in gas phase at B3LYP/6-31G method.

The total energy (the global minimum energy) and the system properties such as energy  $\Delta E_{\text{gap}}$  (hardness ( $\eta$ ), electronegativity ( $X$ ) and electrophilicity ( $\omega$ ) of the compounds (I, II, III and IV) are presented in Table 1; the calculated value of the total energy shows that the stabilities decrease for a molecule when transfers from polar solvents water and ethanol to nonpolar solvent (chloroform) due to the polarity of the molecules, which have positive charge. This faculty is surrounded by polar solvent molecules [14,15].

Moreover from Table 1; the molecule reactivity is related to the system properties, such as hardness ( $\eta$ ), electronegativity ( $X$ ) and electrophilicity ( $\omega$ ). The principle of

maximum hardness (PHM) is a qualitative tool to study the stability of the system, the system would be more stable if the global hardness related to energy gap  $\Delta E_{\text{gap}}$  is a maximum. So from Table 2, the cation (I) is less stable than complexes II, III and IV because of having less energy gap and hardness, while the complexes (II, III and IV) have high energy gap and hardness. The stabilities of the complexes in solvents H<sub>2</sub>O, CHCl<sub>3</sub> and CH<sub>3</sub>OH follow the sequence II > III > IV > I, whereas in gas phase the stabilities of the cation (I) and its complexes follow the sequence II > III > I > IV according to the values of hardness and energy gap in various solvents. [16,17].

The calculated values of global

reactivity index ( $\omega$  and  $X$ ) reflect the nucleophilicity power of compounds with or without interaction between solute cation and solvents. We obtain lower ( $\omega$  and  $X$ ) values for cation (I) in solvents which explain better propensity of cation (I) to be involved in the reaction with electrophiles

compared with the cation complexes HF, CH<sub>3</sub>OH and H<sub>2</sub>O which causes decrease nucleophilicity of cation(I). The calculations in gas phase how decrease electrophilicity when transport from cation(I) to its complexes. [17,18].

**Table 1** Electronic properties of the studied molecules, The Total energy,  $\Delta E$ , Global hardness ( $\eta$ ), Electronegativity( $X$ ), Electrophilicity( $\omega$ ) and dipole moment ( $\mu$ ) in gas phase and various solvents, at B3LYP5/6-31G method .

In gas phase						
Compounds	*Total Energy (A.U)	$\Delta E$ (ev)	$\eta$ (ev)	$X$ (ev)	$\omega$ (ev)	$\mu$ (Debye)
Cation I	-593.70792	3.15382	1.57691	7.68047	23.25155	5.417
Cation-HF II	-694.09226	3.28444	1.64222	7.81188	18.58017	5.224
Cation- H <sub>2</sub> O III	-670.07146	3.18375	1.59188	7.57026	18.0036	2.734
Cation-CH <sub>3</sub> OH IV	-709.32750	2.69122	1.34561	7.49543	20.87583	4.804

Continue

In H <sub>2</sub> O Solvent						
Compounds	*Total Energy (A.U)	$\Delta E$ (ev)	$\eta$ (ev)	$X$ (ev)	$\omega$ (ev)	$\mu$ (Debye)
Cation I	-593.77840	3.37968	1.68984	4.49263	5.97208	8.248
Cation-HF II	-694.16891	3.46403	1.73201	4.61372	6.14500	8.724
Cation- H <sub>2</sub> O III	-670.14354	3.42594	1.71297	4.56202	6.07483	8.893
Cation-CH <sub>3</sub> OH IV	-709.40326	3.41505	1.70752	4.60228	6.20226	8.479

In CH <sub>3</sub> OH Solvent						
<i>Compounds</i>	Total Energy (A.U)	$\Delta E$ (ev)	$\eta$ (ev)	X (ev)	$\omega$ (ev)	$\mu$ (Debye)
Cation I	-593.77676	3.37423	1.68711	4.55250	6.14223	8.155
Cation-HF II	-694.16698	3.45587	1.72793	4.67495	6.32066	8.545
Cation-H <sub>2</sub> O III	-670.14146	3.42594	1.71297	4.62461	6.24266	8.691
Cation-CH <sub>3</sub> OH IV	-709.40204	3.40417	1.70208	4.67087	6.40892	8.418
In CHCl <sub>3</sub> Solvent						
<i>Compounds</i>	Total Energy (A.U)	$\Delta E$ (ev)	$\eta$ (ev)	X (ev)	$\omega$ (ev)	$\mu$ (Debye)
Cation I	-593.76335	3.31437	1.65718	5.11033	7.87946	7.407
Cation-HF II	-694.15195	3.40961	1.70480	5.25047	8.08523	7.666
Cation-H <sub>2</sub> O III	-670.12494	3.37695	1.68847	5.21510	8.05379	8.134
Cation-CH <sub>3</sub> OH IV	-709.38774	3.37151	1.68575	5.24231	8.15121	6.265

\*: denotes lower energy (stabilization) for the total energies calculated.

Continued

The results of calculations of dipole moments of the cation(I) and its complexes are listed in Table 1. In gas phase the cation(I) has the highest dipole moment compare with its complexes. On the other hand ,the cation possesses the lowest dipole moment

compared with its complexes in H<sub>2</sub>O and CH<sub>3</sub>OH solvents. However the complexe IV has lower dipole moment value compared with complexes II,III and cation(I).

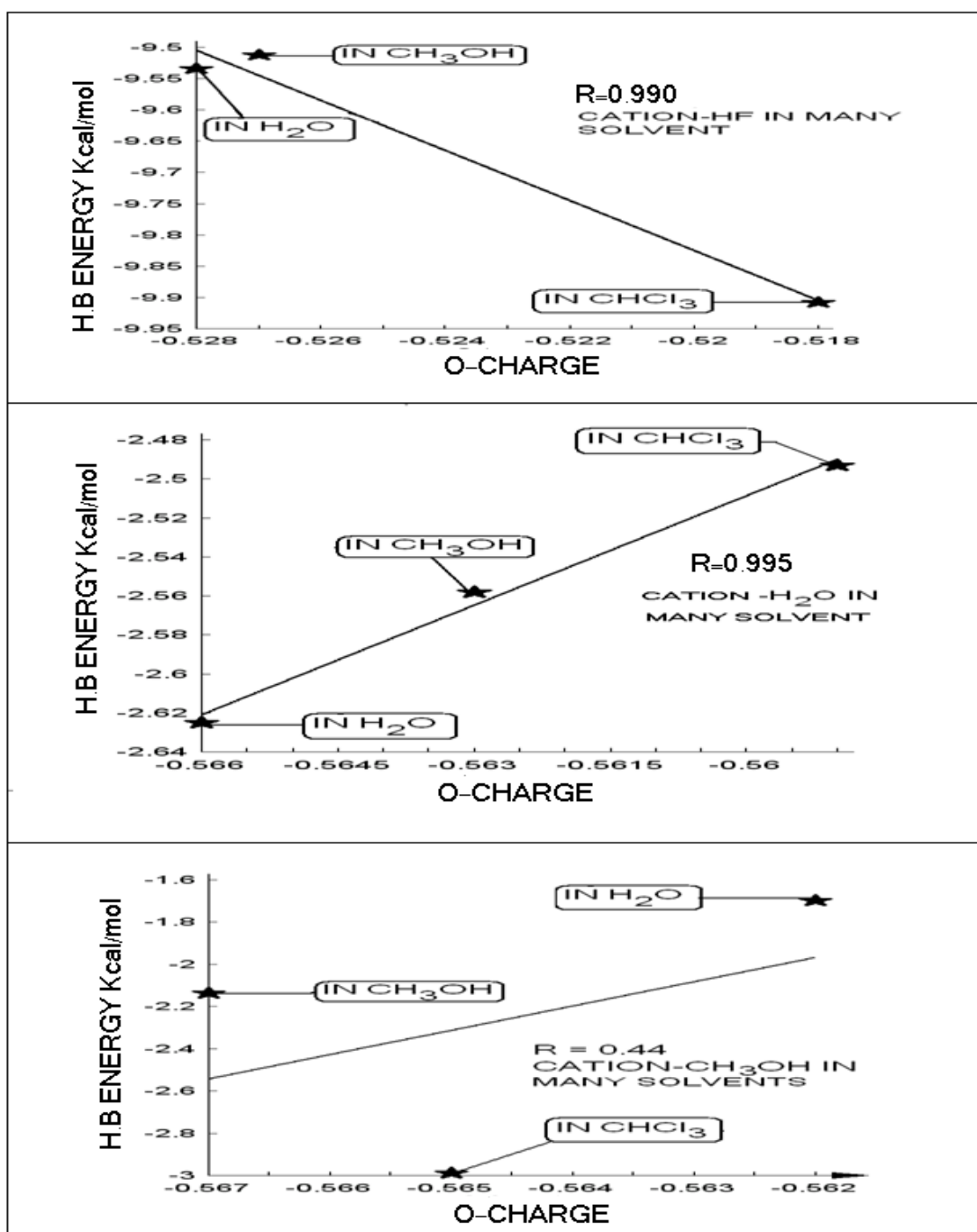


Figure 2 Correlation between the hydrogen bonding energy (kcal/mol) and O21-charge in complexes cation -HF, cation -H<sub>2</sub>O and cation -CH<sub>3</sub>OH in many solvents obtained by the B3LYP5/ 6-31G method

The Figure 2 show relationship between the complex hydrogen bonding energy and oxygen atom charge(atom no.21) in cation-H<sub>2</sub>O ,cation-HF and cation-CH<sub>3</sub>OH complexes in the various solvents, it found that the hydrogen bond energy in cation-

H<sub>2</sub>O and cation-HF, it influences by linearity correlate with the change of oxygen atom charge value which is proton acceptor with value of correlation coefficient equal 0.90 and 0.95 respectively. While this interpret reverse( Abnormal

behavior) with complex cation-CH<sub>3</sub>OH with value of  $r = 0.44$  Figure ( 2 ). In other words the figure (3) shows that there is an extremely relationship between hydrogen bond energy and oxygen atom charge in the studying complexes in every solvent in private. It influences by good linearity correlate with the change of oxygen atom charge value which is proton acceptor in

cation with value of correlation coefficients,  $r=0.98$  ,  $0.98$  and  $0.93$  respectively. Figure 4 shows the relationship between hydrogen bond and oxygen atom charge values in complexes under study in gas phase , the correlation coefficient in this case was found to be  $0.704$  [19].

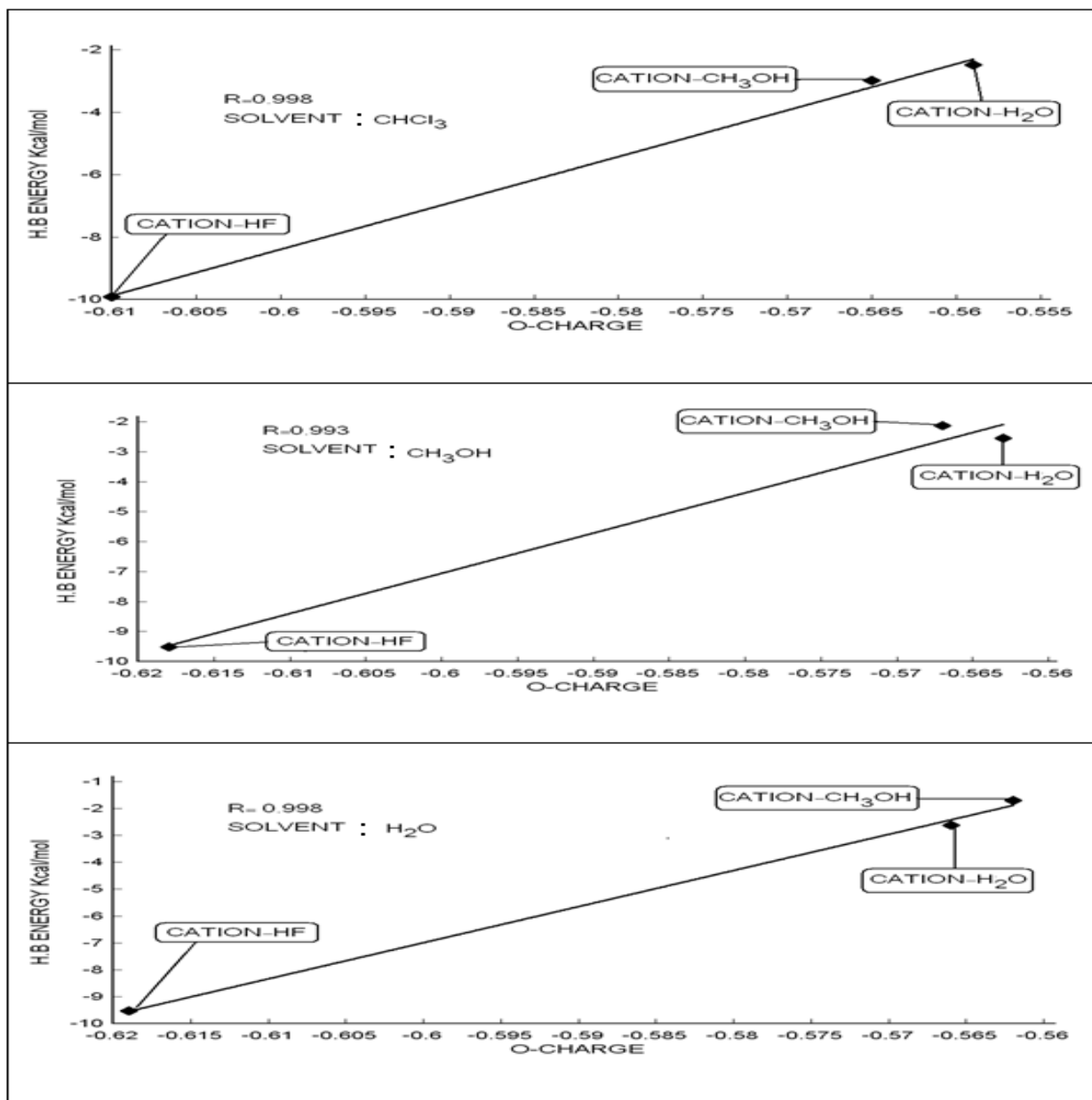


Figure 3 correlation between the hydrogen bonding energy(kcal/mol) and O21-charge in complexes cation –HF, cation –H<sub>2</sub>O and cation –CH<sub>3</sub>OH in one solvent (H<sub>2</sub>O), (CH<sub>3</sub>OH) and (CHCl<sub>3</sub>) obtained by the B3LYP5/6-31G method

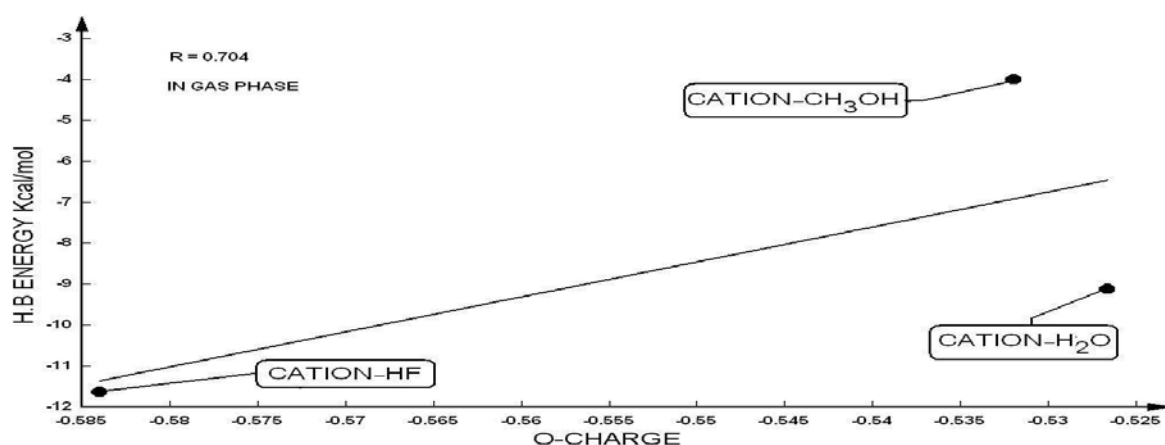


Figure 4 correlation between the hydrogen bonding energy(kcal/mol) and O21-charge in complexes cation –HF, cation –H<sub>2</sub>O and cation –CH<sub>3</sub>OH in gas phase obtained by the B3LYP5/6-31G method

From Table 2, we can see slight changes in the bond lengths and angles of compounds. Also the effect of the hydrogen bonding on the ring leads to redistribution of electron cloud in the ring of the compounds[20], slight change in the angle value (3-21-6) of compound(I) compared with complexes(II,III and IV). The great change of angle(3-21-6) value in the complex cation-HF compared with same angle in cation [18].

Among all the complex cations,the length

of hydrogen bond in complex cation-HF calculated in the gas phase and different solvent is the shortest as shown in Table 2 [Bond length of H28-O21 is 1.61-1.79Å ]with the highest energy(energy from -9.51 to -11.63 kcal/mol).This energy is less than those calculated for hydrogen bond between fluoride ion and hydrogen fluoride which is equal to 47.3 kcal/mol [21] and it is also higher than those of system (hydrogen fluoride-aliphatic carbonyl)which to fall upon between - 4.823 and -1.74 kcal/mol [19].

Table 2 selected structural parameters of the optimized cation and complexes in different solvents, bond distance(A°) X1- H --- X2 and bond angles(°) X1-H---X2. Obtained by the B3LYP5/6-31G method

Compound	In Gas Phase			
	Bond length(Å)		Bond angles(°)	
	Definition	value	Definition	value
Cation I	R( 1- 2)	1.370	A( 3- 21- 6)	107.2
Cation-HF II	R( 28- 21)	1.79160	A( 27- 28- 21)	146.30786
	R( 1- 2)	1.365	A( 3- 21- 6)	107.4
Cation-H <sub>2</sub> O III	R( 29- 21)	2.37167	A( 27- 29- 21)	143.69658
	R( 1- 2)	1.371	A( 3- 21- 6)	107.1
Cation-CH <sub>3</sub> OH IV	R( 29- 21)	2.04274	A( 27- 29- 21)	157.06526
	R( 1- 2)	1.371	A( 3- 21- 6)	107.6

Continue



Compound	In H <sub>2</sub> O Solvent			
	Bond length(Å)		Bond angles(°)	
	Definition	value	Definition	value
Cation I	R( 1- 2)	1.363	A( 3- 21- 6)	107.1
Cation-HF II	R( 28- 21)	1.67796	A( 27- 28- 21)	161.046263
	R( 1- 2)	1.360	A( 3- 21- 6)	107.6
Cation-H <sub>2</sub> O III	R( 29- 21)	1.923155	A( 27- 29- 21)	164.587021
	R( 1- 2)	1.362	A( 3- 21- 6)	107.3
Cation-CH <sub>3</sub> OH IV	R( 29- 21)	1.975993	A( 27- 29- 21)	161.834646
	R( 1- 2)	1.362	A( 3- 21- 6)	107.2

Compound	In CH <sub>3</sub> OH Solvent			
	Bond length(Å)		Bond angles(°)	
	Definition	value	Definition	value
Cation I	R( 1- 2)	1.363	A( 3- 21- 6)	107.1
Cation-HF II	R( 28- 21)	1.619773	A( 27- 28- 21)	160.874299
	R( 1- 2)	1.359	A( 3- 21- 6)	107.6
Cation-H <sub>2</sub> O III	R( 29- 21)	1.959736	A( 27- 29- 21)	164.595901
	R( 1- 2)	1.361	A( 3- 21- 6)	107.2
Cation-CH <sub>3</sub> OH IV	R( 29- 21)	1.926642	A( 27- 29- 21)	166.737360
	R( 1- 2)	1.362	A( 3- 21- 6)	107.3

Compound	In CHCl <sub>3</sub> Solvent			
	Bond length(Å)		Bond angles(°)	
	Definition	value	Definition	value
Cation I	R( 1- 2)	1.364	A( 3- 21- 6)	107.0
Cation-HF II	R( 28- 21)	1.654055	A( 27- 28- 21)	158.257150
	R( 1- 2)	1.360	A( 3- 21- 6)	107.5
Cation-H <sub>2</sub> O III	R( 29- 21)	1.955612	A( 27- 29- 21)	164.920632
	R( 1- 2)	1.363	A( 3- 21- 6)	107.2
Cation-CH <sub>3</sub> OH IV	R( 29- 21)	1.865926	A( 27- 29- 21)	173.603956
	R( 1- 2)	1.363	A( 3- 21- 6)	107.5

Continued

The max wavelenghtes of all compounds have been calculated by TD-B3LYP5/6-31G(d,p) and TD-B3LYP5/ 6-311G(d,p) theory levels using theory DFT as shown in table 3. From figure 5,we can note good correlation( $r=0.997$ ) between the experimental and theoretical max wavelength obtained by TD-B3LYP5 6-311G(d,p) level for cation Trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene in

solvents  $\text{CH}_3\text{OH}$ ,  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  ,so this level of theory is excellent to predict max absorption of the compounds,while the correlation coefficient is 0.381 between experimental and theoretical max wavelength calculated by the level TD-B3LYP5/6-31G(d,p) of the theory for cation trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene as shown in figure 6.

**Table 3 Absorbance maxima of the cation(I) and its complexes in different solvents obtained by the B3LYP5/ 6-31G(d,p) and B3LYP5/6-311G(d,p) method.**

Compounds	Basis set	$\lambda_{\text{max}}$ nm			
		Gas Phase	$\text{H}_2\text{O}$	$\text{CH}_3\text{OH}$	$\text{CHCl}_3$
Cation I	6-311G(d,p)	399.16	380.53	376.26	380.69
	6-31G(d,p)	395.60	376.61	377.16	382.27
	EXP*	-----	381.06	399.08	381.95
Cation-HF II	6-311G(d,p)	389.61	373.15	373.77	377.92
	6-31G(d,p)	386.21	369.11	369.68	374.00
Cation- $\text{H}_2\text{O}$ III	6-311G(d,p)	400.21	376.41	376.26	380.69
	6-31G(d,p)	396.46	372.31	372.22	376.73
Cation- $\text{CH}_3\text{OH}$ IV	6-311G(d,p)	395.71	378.20	379.27	382.44
	6-31G(d,p)	392.16	374.07	375.14	379.00

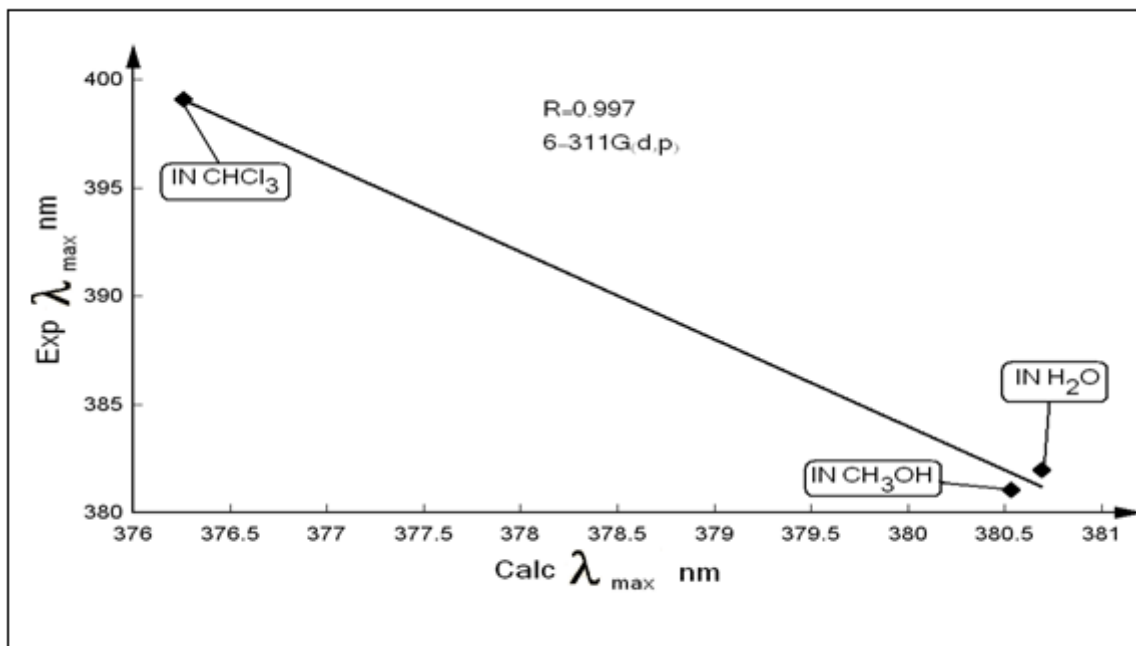
\*From ref 13

From table(3),the calculated max wavelength in gas phase and different solvents for complex II by using TD-B3LYP5/6-31G(d,p) and TD-B3LYP5/ 6-311G(d,p) theory levels are shifted to low wavelength compared with the max wavelength of cation(I). Similar result can be shown for max wavelength which calculated by TD-B3LYP5/ 6-31G(d,p) theory level of complexes III and IV excepting the max wavelength of complex III in gas phase, which is shifted to high wavelength compared with max wavelength of cation (I).

The calculated max wavelength for

complex III by TD-B3LYP5/ 6-311G(d,p) theory level they aren't shifted in  $\text{CHCl}_3$  and  $\text{CH}_3\text{OH}$  solvents while undergo red shift in gas phase compared with max wavelength of cation (I). In addition the calculated max wavelength by TD-B3LYP5/ 6-311G(d,p) theory level of complex IV  $\text{CHCl}_3$  and  $\text{CH}_3\text{OH}$  solvents appear red shift compared with max wavelength of cation (I). On other hand we notice that the complexes cation- $\text{CH}_3\text{OH}$ , cation- $\text{H}_2\text{O}$  and cation-HF appeared red shift when transfers from polar solvents ( $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$ ) to less polar solvent ( $\text{CH}_3\text{Cl}$ ) in both levels of theory[22,23,24].

Fig



Correlation between the experimental and theoretical max wavelength of the cation (I) in different solvents obtained by the B3LYP5/6-311G(d,p) method.

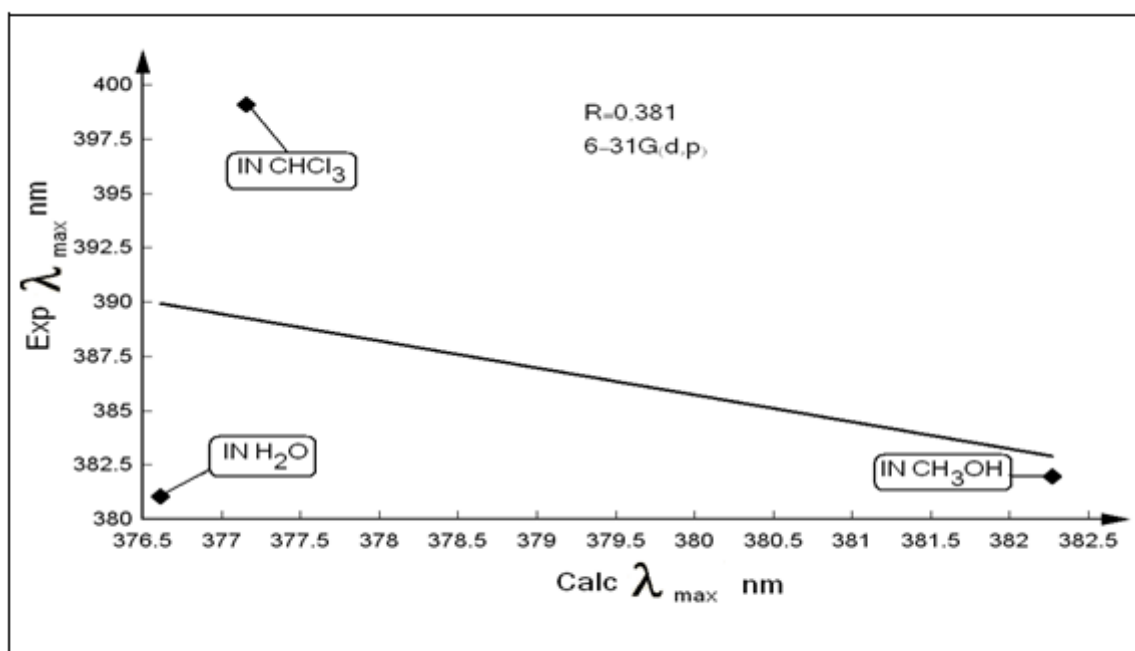


Figure 6 Correlation between the experimental and theoretical max wavelength of the cation (I) in different solvents obtained by the B3LYP5/6-31G(d,p) method.

### Conclusions:

The quantum chemical calculations can be successfully used for the prediction of geometry optimization (minimized energy), relative stabilities, electronic properties.(HOMO & LUMO) and bond

distance and bond angles. The method adopted here for calculation is density functional theory DFT/ B3LYP5 level of theory using the basis set 6-31G which proved to be good to give the optimized

geometry and minimized energy for the compounds under study. The structural, electronic properties such as hardness( $\eta$ ), electronegativity( $X$ ), electrophilicity( $\omega$ ) of the compounds (I, II, III, IV) shown the compound (I) more stable than compounds (II, III).. The results show that the stabilities of compounds in solvents H<sub>2</sub>O, CHCl<sub>3</sub> and CH<sub>3</sub>OH are II>III>IV>I and follow the sequence II> III> I > IV in gas phase according to the values of hardness and energy gap. and angles of compounds.The calculated showed strong relationship between complex hydrogen bond energy and oxygen atom charge value which proton acceptor in furan moiety in cation-H<sub>2</sub>O and cation-HF,in the H<sub>2</sub>O,CHCl<sub>3</sub> and CH<sub>3</sub>OH solvents,while the relationship between

complex hydrogen bond energy and oxygen atom charge value which proton acceptor in furan moiety seems feeble in the cation-CH<sub>3</sub>OH,within the same solvents which are mentioned above.In other word the calculation shows that there is an extremely relationship between complex hydrogen bond energy and oxygen atom charge value which proton acceptor in furan moiety in the studied complexes in every solvent in private . From the theoretical calculation it is found that TD-B3LYP5/6-311 G(d,p) level of theory best from TD-B3LYP5/6-31G(d,p) level of theory to predict max wavelength of trans 1-furan-2-yl(1-methylpyridinium-2-yl)ethylene cation.

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