Book Chapter

Effect of Electronegativity on Structural, Spectrophotometric and Thermo-Chemical Properties of Fluorine and Chlorine Substituted Isoxazoles by DFT Method

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Abstract

The effect of electronegativity (F and Cl atom) on structural, spectrophotometric, thermo-chemical properties, and solvent effect on electronic absorption spectra of {3-(3,5-dichloro-2-hydroxyphenyl)-5-[(4-fluorophenyl)amino] isoxazol-4-yl}(phenyl)methanone (Ia) and {3-(3,5-dichloro-2-hydroxyphenyl)-5-[(4-chlorophenyl)amino] isoxazol-4-yl}(phenyl) methanone (Ib) were studied by DFT method using PBE1PBE functional with 6-311++g (d, p) basis set. The results show that the electronegativity of halogen group affect the bond length, atomic charges, excited wavelength, molecular orbital energy gap, vibration frequency, thermo-chemical parameters, and stability of compounds.

Keywords

DFT, Electronegativity, Stability, HOMO–LUMO Gap

Public Interest Statement

The work presented here shows how computational methods used for understanding the molecular problem more clearly and that helps to design the drug with better action. In particular, the results presented here demonstrate that the DFT method is good tool for studying the stability of isoxazole by computational technique. This is a very useful tool for synthesizing a target molecule because a single compound may generate toxic waste, require months of labor, and raw materials cost. So before synthesizing the drug, firstly design the molecule, understand the molecular properties by computational method, and minimize the chemical pollution by synthesizing lots of unusable drug.

Introduction

Isoxazole derivatives are five-member nitrogen–oxygen-containing heterocyclic compounds that play an important role in pharmacological activities such as anti-cancer [1], anti-tuberculosis [2,3], anti-inflammatory [4], cytotoxic [5], antimicrobial [6], anti-HIV [7], anti-diabetic [8], antipsychotic [9,10], and anticonvulsant [11].

The density functional theory (DFT) is a common method to study the electronic structures that helps for understanding the drug activity of molecules. FT-IR, FT-Raman spectra, NBO, HOMO–LUMO, and thermodynamic properties of 4-chloro-3-nitro benzaldehyde [12], pycolinaldehyde oxime [13] was satisfactorily analyzed by DFT. The spectral properties of heterocyclic compounds such as the valence shell photoelectron spectra, geometry optimization, X-ray, vibrational frequency analysis of purine, pyrimidine [14], heteroaromatic molecules [15], and substituted isoxazole [16,17] were studied using DFT calculation.

Thermodynamic properties (enthalpy, entropy, and Gibbs free energy) are important to understand the stability of molecule at different temperature and pressure that can easily explained using DFT (B3LYP/6-31G*) with the Gaussian 03 program [18,19].

In this work, a theoretical study of {3-(3,5-dichloro-2-hydroxyphenyl)-5-[(4-fluoro phenyl)amino]isoxazol-4-yl}(phenyl)methanone (Ia) and {3-(3,5-dichloro-2-hydroxyphenyl)-5-[(4-chlorophenyl)amino]isoxazol-4-yl}(phenyl)methanone (Ib) has been performed using DFT method in order to elucidate the effect of electronegativity on structural, spectrophotometric, and thermo-chemical properties.

Computational Details

All theoretical calculations performed with the Gaussian-03 package [20]. Full ground-state geometry optimizations and frequency were carried out at the DFT [21-25] using the

PBE1PBE functional [26,27] and the 6-311++g (d, p) basis set [28-32]. Electronic absorption spectra were computed as vertical electronic excitations from the ground state using TD-DFT [33-35] with PBE1PBE/6-311++g (d, p).

Results and Discussion

Geometry Optimization

The geometry optimization has started without symmetry constraints and after optimization; the structure converged to C_1 symmetrical species. The geometry was optimized in the lowest energy singlet ground state by DFT method with PBE1PBE function using 6-311++g (d, p) basis set in gas phase and the optimized structures of Ia and Ib shown in Figures 1 and 2, respectively.

Figure 1: Optimized structure of Ia in gas phase.

Figure 2: Optimized structure of Ib in gas phase.

The geometry was non-planer because of strong distortion between electron cloud of three aromatic rings and isoxazole ring. The optimized geometric parameters of Ia and Ib are recorded in supplementary information Tables S1 and S2, respectively.

Bond lengths of isoxazole ring were not largely affected by electronegativity of fluorine and chlorine substituent but the bond lengths of 16O–17N, 14C–15C, and 15C–16O were slightly more in Ia than Ib. The 9O–10H bond length was important in formation of metal complexes but the difference between 9O–10H bond length in Ia and Ib was very less i.e. 0.00014 Å (Table 1).

Table 1: Bond length and NBO atomic charges of Ia and Ib.

Type	Bond Length (Å)		Atoms	NBO atomic charges	
	Ia	Ib		Ia	Ib
16 O–17 N	1.40411	1.40355	9 O	−0.695	−0.694
17 N–13 C	1.30429	1.30435	10 H	0.500	0.500
13 C–14 C	1.44012	1.44027	13 C	0.209	0.208
14 C–15 C	1.39562	1.39489	14 C	−0.320	−0.318
15 C–16 O	1.32216	1.32195	15 C	0.608	0.607
15 C–31 N	1.34401	1.34522	16 O	−0.339	−0.338
31 N–32 H	1.01025	1.01047	17 N	−0.141	−0.139
14 C–18 C	1.44796	1.44871	18 C	0.544	0.545
18 C–19 O	1.23004	1.22974	19 O	−0.592	−0.591
13 C–3 C	1.47812	1.47802	31 N	−0.584	−0.584
9 O–10 H	0.98723	0.98709	32 H	0.427	0.428

Natural Bond Orbital Charges

The natural bond orbital (NBO) atomic charges have calculated in gas phase (Table 1). The atomic charge gives information about oxidation states of atoms in molecule, which gives important information for complex formation.

The carbon atoms connected to the high electronegative (F, Cl, O, and N) atoms were positive in nature. The 9O will provide the binding site for metal ion in formation of metal complex; as 9O contained the highest negative charge and the 10H contained highest positive charge.

Electronic Absorption Spectra

The electronic absorption spectra has computed as the lowest 10 vertical electronic excitations from the singlet ground state to singlet excited state using TD-DFT and the effect of solvent was simulated by IEFPCM (Table 2).

Table 2: Electronic absorption data in different solvent of Ia and Ib.

Excited state	Gas phase		Water phase		Ethanol phase		DMSO phase	
	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f
<i>Ia</i>								
1 st	379.31	0.0511	360.56	0.1977	360.45	0.2000	361.22	0.2101
2 nd	358.75	0.1055	318.13	0.0344	321.03	0.0328	320.33	0.0353
3 rd	302.59	0.0049	288.12	0.0099	289.13	0.0091	289.02	0.0106
4 th	295.23	0.0354	281.99	0.1544	280.70	0.1572	281.48	0.1690
5 th	282.49	0.0422	270.77	0.0726	271.43	0.1043	271.54	0.0942
6 th	268.00	0.1248	269.08	0.0828	269.39	0.0721	269.76	0.0827
7 th	266.38	0.0547	265.83	0.1495	267.15	0.1325	267.09	0.1574
8 th	263.04	0.2338	262.25	0.0272	262.33	0.0204	262.30	0.0237
9 th	260.46	0.0052	257.98	0.1501	257.90	0.1417	258.24	0.1395
10th	256.83	0.0044	252.09	0.4278	252.00	0.4434	252.47	0.4665
<i>Ib</i>								
1 st	380.67	0.0550	358.51	0.2333	359.53	0.2355	360.11	0.2472
2 nd	359.65	0.1249	317.61	0.0335	322.09	0.0308	321.26	0.0332
3 rd	303.14	0.0064	288.10	0.0108	289.45	0.0094	289.37	0.0110
4 th	295.99	0.0326	282.96	0.2655	281.51	0.2756	282.34	0.2921
5 th	284.14	0.0331	271.54	0.0726	272.35	0.1241	272.41	0.1144
6 th	270.98	0.4253	269.78	0.0941	270.00	0.0689	270.41	0.0775
7 th	267.85	0.0620	265.84	0.1524	267.88	0.1333	267.77	0.1608
8 th	264.60	0.0683	263.74	0.0345	263.81	0.0125	263.74	0.0152
9 th	262.39	0.0056	260.01	0.2014	259.90	0.1676	260.17	0.1667
10th	258.20	0.0078	254.20	0.4036	254.43	0.4355	254.93	0.4448

In both compounds, polarity of solvent affects wavelength and follows the same order, i.e. λ in DMSO > in water > in ethanol. Decrease in electronegativity increases the excited wavelengths in both phases because when electronegativity decreases the electron cloud slightly shifted toward HOMO and after that electron excited to LUMO by low energy.

Frontier Molecular Orbital

Highest occupied molecular orbital (HOMO) contains electrons and tends to donate these electrons such as an electron donor. On the other hand, lowest unoccupied molecular orbital (LUMO) contains free places and tends to accept electrons. The $\lambda_{\max}$ of compound formed due to excitation of electron from HOMO to LUMO. HOMO and LUMO in different phases for Ia and Ib shown in Figures 3 and 4, respectively.

Figure 3: HOMO and LUMO of Ia (Isodensity value = 0.02).

Figure 4: HOMO and LUMO of Ib (Isodensity value = 0.02).

In gas phase, HOMO was form due to non-bonding (n) and pi-bonding electron density (switched on benzene ring containing hydroxyl group) but in solvent phase, HOMO was form due to non-bonding (n) and pi-bonding electron density (switched on benzene ring containing halogen group). In both phases, LUMO was formed due to π^* bonding electron density (switched on isoxazole ring and benzene ring) and electron transition was mixed type (n to π^* and π to π^*).

The molecular orbital energy gap was very important to study the photo-physics and kinetic stability of isoxazole compounds. E (LUMO), E (HOMO), and molecular orbital energy gap of Ia and Ib were shown in Table 3 in different phases.

Table 3: Energy gap (a.u.) for Ia and Ib.

Solvent	E-LUMO	E-HOMO	Energy gap
<i>Ia</i>			
Gas phase	-0.093	-0.240	0.147
DMSO	-0.083	-0.238	0.155
Ethanol	-0.083	-0.238	0.155
Water	-0.082	-0.237	0.155
<i>Ib</i>			
Gas phase	-0.094	-0.240	0.146
DMSO	-0.084	-0.239	0.155
Ethanol	-0.084	-0.239	0.155
Water	-0.082	-0.237	0.155

The molecular orbital energy gap decreased with a decrease in electronegativity of halogen group and the lowest molecular orbital energy gap (0.146 a.u.) was found in Ib gas phase. The molecular orbital energy gap was lower in gas phase than in solvent phase and no significance effect shown by solvent.

A large HOMO–LUMO gap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying LUMO. Meanwhile, a molecule with a small frontier orbital gap is more polarizable, is generally associated with a high chemical reactivity, low kinetic stability, and is termed as soft molecule [36].

Vibration Mode

The IR spectral data of Ia and Ib were recorded in Table 4. The calculated IR frequencies were show the difference with reported [37] value. The suggested reason is the computational data obtained when the Ia and Ib molecules in isolated state of vacuum condition and the reported values in solid phase. The phenolic O–H stretching frequency increased with decrease in electronegativity of halogen group, due to which more electronegative fluorine atom in Ia attracted the electron cloud on oxygen atom toward itself and phenolic O–H stretching was less from electron interaction.

Table 4: IR spectral data of Ia and Ib.

Type	Vibration mode	Frequency (cm ⁻¹)		
		Ia	Ib	Reported
Isoxazole ring	N–O str.	1,014.75	1,015.32	850–800
	C=N str.	1,555.15	1,554.59	1,690–1,640
Amine	N–H Str.	3,589.04	3,584.64	3,400–3,200
Phenolic OH	O–H Str.	3,319.27	3,323.84	3,200–3,600
Carbonyl	C=O Str.	1,751.17	1,752.53	1,650–1,800

Thermo-Chemical Study

The thermo-chemical parameters were calculated to their ideal gas state at 298.15 K and 101.325 kPa for Ia and Ib, respectively. The thermodynamic parameters including total electronic energy (E_t), enthalpy ($H^\ominus$), entropy ($S^\ominus$), Gibbs free energy ($G^\ominus$), and standard heat capacity at constant volume ($C_v^\ominus$) were obtained from the Gaussian frequency output files (Table 5). The equations used for computing thermo-chemical data in Gaussian programs have derived from statistical thermodynamics [38]. The thermal energy (E_{thermal}) calculated as the sum of zero-point energy and thermal energy corrections for molecular translation (E_{trans}), rotation (E_{rot}), and vibration (E_{vib}). The enthalpy ($H^\ominus$) was obtained by adding RT to the total electronic energy (E_t) and thermal energy at 298.15 K and 101.325 kPa.

Table 5: Thermo-dynamical properties of I (a, b).

Properties	Thermo-dynamical properties	
	Ia	Ib
E_t (Hartree)	-2,200.1584	-2,560.4430
$H^\ominus$ (Hartree)	-2,199.3851	-2,559.9730
$G^\ominus$ (Hartree)	-2,199.4581	-2,559.7462
$C_v^\ominus$ (cal/mole-K)	83.292	83.970
$S^\ominus$ (cal/mole-K)	153.511	154.181

With decrease in electronegativity of halogen group, the values of E_t , $H^\ominus$, and $G^\ominus$ decreased and the value of $C_v^\ominus$ and $S^\ominus$ increased. It has known that the compounds with higher free energies are less stable than those with lower free energies. The Ib was more stable because it had low free energy i.e. -2559.7462 Hartree.

Conclusion

The DFT method reveals the useful information about the effect of solvent on electronic absorption spectra. There is less effect of electronegativity on structural, spectrophotometric, and thermochemical properties of fluorine- and chlorine-substituted isoxazoles. The chlorine (less electronegative)-substituted isoxazole (Ib) is soft molecule, more polarizable, high chemical reactivity, low kinetic stability, and high $\lambda_{\max}$ than Ia.

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Supplemental Material

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Table S1: Full geometry parameter of Ia.

#	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	C	----	----	----	----	----	----	4.452798	-1.431318	1.099516
2	C	1	----	----	1.382086	----	----	3.075738	-1.361708	1.004530
3	C	2	1		1.397135	120.056125	----	2.481565	-0.621173	-0.020434
4	C	3	2	1	1.406247	120.426968	-0.479239	3.276110	0.065870	-0.955421
5	C	4	3	2	1.402798	117.710470	1.567976	4.669166	-0.049797	-0.837694
6	C	5	4	3	1.384907	121.975184	-1.355191	5.260932	-0.787056	0.174348
7	H	2	1	6	1.082585	120.429447	177.816839	2.449900	-1.895296	1.708520
8	H	6	5	4	1.082753	120.033349	-179.354848	6.339952	-0.846577	0.241640
9	O	4	3	2	1.336873	123.180462	178.622448	2.766799	0.768184	-1.972567
10	H	9	4	3	0.987229	108.011815	48.857739	2.060679	1.357294	-1.613449
11	Cl	5	4	3	1.729089	118.893274	178.834871	5.674839	0.757519	-1.989480
12	Cl	1	2	3	1.738641	119.795319	179.538607	5.185048	-2.344943	2.384807
13	C	3	2	1	1.478123	116.677663	173.434406	1.011704	-0.717943	-0.142873
14	C	13	3	2	1.440120	132.186681	124.318323	-0.026415	0.280181	-0.144551
15	C	14	13	3	1.395617	102.588657	-175.002960	-1.189415	-0.490604	-0.177251
16	O	15	14	13	1.322159	109.895096	0.651558	-0.877726	-1.775498	-0.178680
17	N	13	3	2	1.304285	115.912624	-49.072503	0.517894	-1.925134	-0.141547
18	C	14	13	3	1.447956	129.069834	8.308636	0.094452	1.722547	-0.183883
19	O	18	14	13	1.230044	122.019273	26.696293	1.066479	2.282021	-0.689017
20	C	18	14	13	1.490902	119.644494	-153.508025	-0.986192	2.569242	0.397586
21	C	20	18	14	1.397996	121.659248	40.184742	-1.623498	2.226443	1.593714
22	C	20	18	14	1.397474	118.546736	-143.765401	-1.303934	3.774113	-0.235074
23	C	21	20	18	1.389616	120.052229	176.629069	-2.577370	3.075233	2.142090
24	H	21	20	18	1.085866	119.727866	-1.692445	-1.350324	1.308557	2.105541
25	C	22	20	18	1.387174	120.079220	-177.891287	-2.273602	4.607382	0.303124
26	H	22	20	18	1.084646	118.861076	1.887969	-0.778150	4.042161	-1.145106
27	C	23	21	20	1.391286	119.959021	0.755485	-2.909543	4.259514	1.491847
28	H	23	21	20	1.084828	119.856044	-178.666561	-3.054243	2.816546	3.081518
29	H	25	22	20	1.084812	119.901812	-179.197603	-2.527225	5.535806	-0.197398
30	H	27	23	21	1.085176	119.874438	179.695245	-3.658211	4.918938	1.918769

31	N	15	14	13	1.344013	130.953074	-176.657891	-2.482366	-0.131555	-0.252958
32	H	31	15	14	1.010251	113.756574	-6.130465	-2.631923	0.865807	-0.193731
33	C	31	15	14	1.406670	130.984506	178.286653	-3.653303	-0.908370	-0.317661
34	C	33	31	15	1.398450	116.204982	174.124844	-4.862648	-0.208407	-0.261100
35	C	33	31	15	1.396088	124.401464	-6.569345	-3.671598	-2.298440	-0.445850
36	C	34	33	31	1.384670	120.851110	179.322480	-6.073585	-0.876283	-0.330990
37	H	34	33	31	1.086348	119.807426	-0.625448	-4.856323	0.873386	-0.161919
38	C	35	33	31	1.389458	119.751411	-179.387476	-4.886825	-2.968703	-0.513405
39	H	35	33	31	1.079874	120.842924	0.560729	-2.751786	-2.862115	-0.494257
40	C	38	35	33	1.380904	119.724963	0.110082	-6.067045	-2.254124	-0.455487
41	H	36	34	33	1.083602	121.263424	-179.919007	-7.014539	-0.340517	-0.289115
42	H	38	35	33	1.083787	120.572067	180.000000	-4.916547	-4.047494	-0.613004
43	F	40	38	35	1.341843	119.352851	179.984082	-7.236376	-2.908968	-0.521712

Table S2: Full geometry parameter of Ib.

#	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	C	----	----	----	----	----	----	4.632788	-1.633226	1.099303
2	C	1	----	----	1.382136	----	----	3.263080	-1.467555	1.017123
3	C	2	1	----	1.397118	120.052791	----	2.711168	-0.705853	-0.015903
4	C	3	2	1	1.406254	120.434147	-0.430534	3.541416	-0.095475	-0.972814
5	C	4	3	2	1.402768	117.708225	1.474206	4.924077	-0.306952	-0.866587
6	C	5	4	3	1.384891	121.974100	-1.281128	5.473747	-1.065090	0.153714
7	H	2	1	6	1.082608	120.425277	177.838636	2.609227	-1.942041	1.737803
8	H	6	5	4	1.082761	120.031942	-179.373622	6.546574	-1.199602	0.211342
9	O	4	3	2	1.336901	123.191666	178.489272	3.071472	0.620054	-1.999691
10	H	9	4	3	0.987087	108.041079	48.927016	2.413209	1.265398	-1.646758
11	Cl	5	4	3	1.729018	118.891313	178.890355	5.970991	0.405291	-2.043950
12	Cl	1	2	3	1.738528	119.791832	179.547719	5.313085	-2.572669	2.394341
13	C	3	2	1	1.478016	116.688342	173.488795	1.236900	-0.698813	-0.120860
14	C	13	3	2	1.440273	132.172414	124.282787	0.273305	0.371595	-0.130675
15	C	14	13	3	1.394893	102.583342	-174.969565	-0.941799	-0.313405	-0.135425
16	O	15	14	13	1.321950	109.926453	0.592738	-0.724095	-1.617166	-0.116370
17	N	13	3	2	1.304348	115.957549	-49.125316	0.656865	-1.866727	-0.091548
18	C	14	13	3	1.448709	129.076341	8.422950	0.497116	1.801171	0.201239
19	O	18	14	13	1.229736	121.993526	26.817456	1.498832	2.278441	-0.731361

20	C	18	14	13	1.490525	119.603594	-153.439324	-0.511550	2.733800	0.377086
21	C	20	18	14	1.398021	121.616036	40.196388	-1.153425	2.459721	1.588424
22	C	20	18	14	1.397492	118.603023	-143.647799	-0.754532	3.945201	-0.275947
23	C	21	20	18	1.389620	120.061067	176.713205	-2.037766	3.383461	2.132197
24	H	21	20	18	1.085903	119.760447	-1.587452	-0.937370	1.535429	2.115862
25	C	22	20	18	1.387183	120.073239	-178.022598	-1.656725	4.853811	0.257676
26	H	22	20	18	1.084672	118.873035	1.807575	-0.225302	4.158265	-1.198461
27	C	23	21	20	1.391245	119.959972	0.813531	-2.297385	4.574651	1.461953
28	H	23	21	20	1.084811	119.849403	-178.657381	-2.517284	3.176882	3.083093
29	H	25	22	20	1.084819	119.883855	-179.157027	-1.853252	5.787263	-0.258926
30	H	27	23	21	1.085158	119.889506	179.649728	-2.992510	5.292669	1.884823
31	N	15	14	13	1.345225	130.917462	-176.824851	-2.207380	0.137847	-0.201043
32	H	31	15	14	1.010466	113.743017	-6.338537	-2.283417	1.144335	-0.153691
33	C	31	15	14	1.404239	130.980827	177.819937	-3.429788	-0.551767	-0.246199
34	C	33	31	15	1.398479	116.269285	174.555158	-4.585770	0.233487	-0.193040
35	C	33	31	15	1.395682	124.477934	-6.224002	-3.551401	-1.937936	-0.354241
36	C	34	33	31	1.383846	120.869718	179.230361	-5.841120	-0.346368	-0.246844
37	H	34	33	31	1.086516	119.831079	-0.696026	-4.502106	1.313558	-0.109591
38	C	35	33	31	1.388917	119.745909	-179.251658	-4.812747	-2.517069	-0.406225
39	H	35	33	31	1.080016	120.938034	0.666372	-2.676959	-2.570177	-0.399591
40	C	38	35	33	1.386400	120.417147	0.065467	-5.950667	-1.726884	-0.352832
41	H	36	34	33	1.083460	120.373981	-179.936271	-6.731391	0.269781	-0.206060
42	H	38	35	33	1.083615	119.660797	179.985300	-4.905563	-3.593419	-0.490352
43	Cl	40	38	35	1.736180	119.944853	-179.980915	-7.521339	-2.463790	-0.418265