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RESEARCH ARTICLE

A DFT Study on Tautomer Stability of 4-Hydroxyquinoline Considering Solvent Effect and NBO Analysis

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Abstract: Computational calculations at B3LYP/6-311++G (d,p) level were employed in the study of the predominant tautomeric of 4-hydroxyquinoline derivatives (5-H, 5-NO_2, 5-Cl, 5-OH, 5-CH_3, 6-NO_2, 6-Cl, 6-OH, 6-CH_3, 7-NO_2, 7-Cl, 7-OH, 7-CH_3, 8-NO_2, 8-Cl, 8-OH, 8-CH_3,) in the gas phase and selected solvents (benzene (non-polar solvent), tetrahydrofuran (THF) (polar aprotic solvent) and water (protic solvent)). The tautomers were also optimized in solvents according to the polarisable continuum method (PCM). For electron withdrawing and releasing derivatives the order of stability is X1 >X2 >X3 and X1 form is a more stable and dominant form. An exception in the gas phase is X2 isomer of (8-OH) which has two forms. In one, the hydrogen bond between hydroxyl substituted with nitrogen isn't formed, but in another it is formed. If the hydrogen bond is formed, X2 isomer is more stable than X1. In addition variation of dipole moments and charges on atoms in the solvents are studied.

Keywords: DFT study, NBO analysis, PCM model, 4-Hydroxyquinoline, Tautomerism

Introduction

The word quinoline in fact is derived from the word quinine, which in turn is derived from quina, a Spanish version of a local South American name for the bark of quinine-containing Cinchona species. The subsequent importance of quinoline is linked with malaria in the several successful antimalarial drugs such as chloroquine, which is also used in treatment of amoebic dysentery. Also the most general synthesis of these drugs has been through the 4-hydroxyquinoline. Apart from these, quinolines occur in plants as secondary metabolites (alkaloids) with quinine being the best known[1]. Among the bifunctional molecules, hydroxyquinolines have been widely studied from both experimental and theoretical viewpoints[2]. Early in 1968, Mason *et al.*[3] had investigated the excited-state properties of 7- hydroxyquinolines (7-HQ) and pointed out that the OH group is more acidic and the ring nitrogen atom more basic in the excited state than in the ground state. 7-HQ has also been the subject of some theoretical investigations. The triple-proton-transfer reactions in the ground and first excited states of 7-HQ in methanol solution have been studied by using HF, MP2, CIS and CASSCF methods[4]. Tokay *et al.* studied tautomerism of 2-, 3- or 4-hydroxyquinoline derivatives along with their thio and azo analogs[5]. Shchavlev *et al.* studied rotation barriers, tautomerism, intramolecular hydrogen bond and solvent effects in 8-hydroxyquinoline by DFT computational[6]. Theoretical studies on proton transfer reactions of 8-hydroxyquinoline monomers and dimers have done and it implied that the hydrogen bond played an important role in depressing the activation energy of reaction[7]. In the present paper we studied tautomerism of 4-hydroxyquinoline in the gas phase and solution using polarisable continuum method (PCM) at the B3LYP/6-311++G (d,p) level of theory.

Experimental

All these calculations were carried out on a corei7 computer by means of GAUSSIAN09 program package. First, all the compound's structures were drawn using Gauss View 03 and optimized in GAUSSIAN09. The tautomers were also optimized in solvents according to the polarisable continuum method of Tomasi and co-workers, which exploits the generating polyhedra procedure[8-11] to build the cavity in the polarisable continuum medium, where the solute is accommodated. Atomic charges in all the structures were obtained using the Natural Population Analysis (NPA) method within the Natural Bond Orbital (NBO) approach[12-14].

Results and Discussion

Structures and numbers of 4-hydroxyquinoline derivatives are depicted in Figure 1 and 2. The results of energy comparisons tautomers in the gas phase and different solvents are given in Table 1. In solvent phase X2 isomer is dominant. The order of stability in solvent phase is X1 >X2 >X3. X1 and X2 isomers are both *N*-amins, as it expected they are more stable than X3 isomers which is imine. In the gas phase X1 isomer is also dominant, with the exception of X2 isomer of (8-OH) form that is optimized to two forms which is depicted in Figure 2. At the first form, hydrogen bond between hydroxyl substituted (OH) with nitrogen isn't formed then we consider it as X2 form.

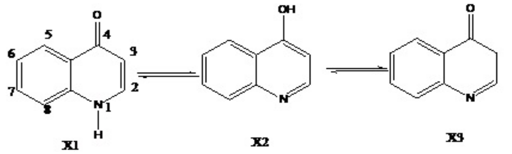

Figure 1. Tautomeric forms of 4-hydroxy quinoline.

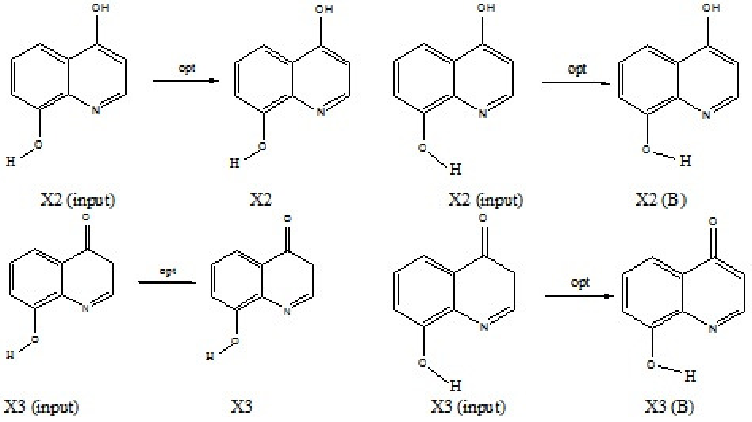

Figure 2. Stationary Structure and optimized of X1, X2, X3 with 8-OH situation

Table 1. Total energies at B3LYP/6-311++G(d,p) in the gas phase and solvents

C-R	Tautomer	Gas(1.0)	Benzene(2.2)	THF(7.9)	Water(78.54)
5-H	X1	-477.2877453	-477.2961726	-477.3021367	-477.3049159
	X2	-477.2816309	-477.2870899	-477.290546	-477.292516
	X3	-477.265782	-477.2712432	-477.274696	-477.2761871
5-NO_2	X1	-681.8341753	-681.8467459	-681.8557466	-681.859961
	X2	-681.8304161	-681.8386952	-681.8438853	-681.8460108
	X3	-681.8131533	-681.8218036	-681.8274844	-6818298817
5-Cl	X1	-936.8982053	-936.9072757	-936.9138317	-936.9168042
	X2	-936.8937659	-936.8993989	-936.9029489	-936.9043978
	X3	-936.8778688	-936.8838108	-936.8876389	-936.889226
5-CH_3	X1	-516.6115067	-516.6189948	-516.6242409	-516.6266708
	X2	-516.6037536	-516.6089159	-516.6122544	-516.613722
	X3	-516.5903093	-516.5952858	-516.5984212	-516.5997726
5-OH	X1	-552.5498916	-552.5578293	-552.5633784	-552.5658462
	X2	-552.5302909	-552.5369148	-552.5412133	-552.5430067
	X3	-552.5258144	-552.5312048	-552.5345845	-552.535965
6-NO_2	X1	-681.849861	-681.8612292	-681.8692131	-681.8729173
	X2	-681.8444538	-681.8523581	-681.8573956	-681.8594943
	X3	-681.8260318	-681.8341119	-681.8392801	-681.8414311
6-Cl	X1	-936.9090792	-936.917665	-936.9237708	-936.9265152
	X2	-936.9039818	-936.909358	-936.9127584	-936.914154
	X3	-936.8871807	-936.8926042	-936.8960195	-936.8974222
6-CH_3	X1	-516.6149904	-516.6234023	-516.6293534	-516.6321269
	X2	-516.6088008	-516.6142604	-516.61776	-516.6192888
	X3	-516.5936713	-516.5991912	-516.6026813	-516.6041887
C6-OH	X1	-552.5350491	-552.5452791	-552.5521995	-552.5552048
	X2	-552.5295309	-552.5368536	-552.5414488	-552.543323
	X3	-552.5137838	-552.5210603	-552.5255349	-552.527338
7-NO_2	X1	-681.8485593	-681.8589573	-681.8660425	-681.8691386
	X2	-681.8433271	-681.8511364	-681.8561379	-681.858232
	X3	-681.8248417	-681.8325341	-681.8373812	-681.8393728
7-Cl	X1	-936.9097793	-936.9181033	-936.9239211	-936.9265048
	X2	-936.9043448	-936.9097021	-936.9131172	-936.9145326
	X3	-936.8879896	-936.8933757	-936.8967526	-936.8981348
7-CH_3	X1	-516.6156274	-516.6241515	-516.6302146	-516.6330483
	X2	-516.610003	-516.6154843	-516.61776	-516.6205267
	X3	-516.5944621	-516.6000944	-516.6036699	-516.6052182
7-OH	X1	-552.5366461	-552.5470699	-552.554143	-552.5572149
	X2	-552.5308576	-552.5381364	-552.5426477	-552.5444694
	X3	-552.5159576	-552.523576	-552.5283221	-552.5302579
8-NO_2	X1	-681.8524071	-681.8604231	-681.8657324	-681.8679972
	X2	-681.8336558	-681.8426087	-681.8484754	-681.8509664
	X3	-681.8159934	-681.8246576	-681.8301925	-681.8324876
8-Cl	X1	-936.9102968	-936.91728	-936.9221247	-936.9242687
	X2	-936.9003076	-936.9064727	-936.9104637	-936.9121332
	X3	-936.8832317	-936.8892072	-936.8930222	-936.8945926
8-CH_3	X1	-516.6150235	-516.6233332	-516.6292595	-516.6320312
	X2	-516.6098154	-516.6147717	-516.6179225	-516.6192913
	X3	-516.5931177	-516.5982474	-516.6015069	-516.6029196
8-OH	X1	-552.5362293	-552.5455198	-552.5519222	-552.5547455
	X2	-552.5239723	-552.5325723	-552.5380869	-552.5403496
	X2(B)	-552.5376213	-552.5430497	-552.5464555	-552.5478522
	X3	-552.5074838	-552.5160866	-552.5215156	-552.5237662
	X3(B)	-552.5202238	-552.5258915	-552.5294623	-552.5309337

The energy stability is X1 >X2 >X3. At second form, the hydrogen bond between them is formed. In this case X2(B) isomer with substituted energy between X1, X2(B) with 0.878 kcal mol^{-1} is more dominant than X1. Then the stability order is X2(B) >X1 >X3. It is to mention that because of the solvent effect on the hydrogen bond only X2(B) is more predominant than X1 in gas phase. Although, the hydrogen bond of X2(B) causes more stability and negative energy than X2(A) in solvent phase, but this change is not that much to stabilize X2(B) form than X1 in solvent phase. Definitely in X3 form the hydrogen bond is formed, but given the fact that there is a large difference in energy stability of X3 with X1, X2. The hydrogen bond effect also can not compensate this difference and no change happens in the stability of X3 form compared to X1 and X2. The difference of (E2-E1) between X2 and X1 forms in gas phase is belonged to derivates with this subsisted situation (5-OH), (6-CH_3), (7-OH), (8-NO_2) and their energy is 12.299, 3.884, 3.630, 11.766 respectively on the basis of (kcal mol^{-1}). Solvent effects are relevant to the tautomers stability phenomena, since polarity differences among the tautomers can induce significant changes in their relative energies in solution, PCM/B3LYP calculations were used to analyze the solvent effects on tautomerism of 4-hydroxyquinoline. It is important to stress that the PCM model does not consider the presence of explicit solvent molecules; hence specific solute–solvent interactions are not described and the calculated solvation effects arises only from mutual solute-solvent electrostatic polarization. Calculated dipole moments for the Xs are presented in Table 2. The solvent represented by a polarizable continuum is found to show significant effect on the dipole moments of the individual solute conformers. The dipole moments increase by changing the gas phase to the solution. For all conforms, the most obtained dipole moment is seen in water solvent and gas phase. The biggest difference of dipole moment of all conforms belongs to X1 with substituent situation (5-NO_2) is 14.3963D, 4.3972D for water solution and gas phase respectively. For all conforms with substituent situation (5-R), (6-R) the most dipole moment belongs to X1 with R=NO_2, in (7-R) it belongs to X2 with R=NO_2, but in (8-R) it belongs to X2 with R=OH. We have examined the charge distribution of tautomers in the solvent as well as gas phase by using calculated NBO charges (Table 3,4 & 5). The decrease of negative charge was observed on (N) atom in X1 form when the phase is changed from gas phase to polar solvent. With the exception of the X1 with substituent situation (8-OH) and all X2 and X3 isomers, the phase is changed from gas to polar solvent the negative charge on N increases.

Table 2. Calculated dipole moments in the gas phase and solvents

C-R	Tautomer	Gas	Benzene	THF	Water
5-H	X1	6.2321	7.6598	8.7957	9.3584
	X2	2.6005	3.1475	3.5613	3.7602
	X3	1.451	1.6685	1.8307	1.9075
5-NO_2	X1	9.9991	12.0424	13.6239	14.3963
	X2	2.9567	3.2832	3.509	3.6143
	X3	5.31	6.169	6.7924	7.0771
5-Cl	X1	7.3173	9.0429	10.417	11.0766
	X2	1.7747	2.0978	2.3356	2.4437
	X3	2.6787	3.2056	3.6016	3.7854
5-CH_3	X1	5.6115	6.9293	7.9792	8.4993
	X2	2.8697	3.5039	3.9931	4.2309
	X3	0.9581	1.0932	1.1929	1.2409
5-OH	X1	6.6742	8.1693	9.3536	9.9196
	X2	3.506	4.258	4.827	5.089

Contd…

	X3	1.9678	2.3459	2.6319	2.7657
6-NO_2	X1	9.5081	11.3729	12.8312	13.5491
	X2	6.2037	7.1799	7.9096	8.2528
	X3	5.886	6.8419	7.5547	7.8872
6-Cl	X1	7.1479	8.7072	9.934	10.517
	X2	3.2454	3.828	4.2547	4.4489
	X3	2.6072	3.0687	3.4035	3.5559
6-CH_3	X1	6.0299	7.4474	8.5841	9.151
	X2	2.6301	3.1865	3.6112	3.8168
	X3	1.3757	1.55	1.6804	1.7431
6-OH	X1	5.2436	6.513	7.5306	8.0205
	X2	3.6682	4.3917	4.9364	5.186
	X3	0.3808	0.4894	0.5724	0.61
7-NO_2	X1	5.54	6.6605	7.5598	7.9939
	X2	7.6709	8.8954	9.8018	10.2241
	X3	4.5309	5.2187	5.7194	5.9471
7-Cl	X1	5.4069	6.6817	7.7001	8.1879
	X2	4.3562	5.1484	5.7335	6.0025
	X3	1.4499	1.7371	1.9431	2.0356
7-CH_3	X1	6.5437	8.0462	9.2412	9.8338
	X2	2.2407	2.7344	3.1175	3.3018
	X3	2.0031	2.2998	2.5184	2.6221
7-OH	X1	5.1298	6.3782	7.3825	7.8667
	X2	2.0543	2.473	2.7897	2.9358
	X3	2.8032	3.2931	3.6557	3.8228
8-NO_2	X1	0.896	1.3667	1.7776	1.9846
	X2	7.1056	8.3267	9.259	9.7053
	X3	3.0084	3.4425	3.7557	3.9026
8-Cl	X1	4.4466	5.5925	6.522	6.9721
	X2	4.2436	5.0948	5.7366	6.0335
	X3	0.2256	0.3447	0.4328	0.4721
8-CH_3	X1	6.6548	8.1798	9.3817	9.9748
	X2	2.2092	2.6537	2.9851	3.143
	X3	2.0008	2.3178	2.553	2.6647
8-OH	X1	6.6527	8.1272	9.3013	9.8676
	X2	2.1459	2.6713	3.0909	3.22906
	X2(B)	3.8466	4.5561	5.0822	5.3247
	X3	2.224	2.5142	2.7196	2.8136
	X3(B)	1.7186	2.0908	2.3685	2.4952

Table 3. Calculated NBO charge for 5-H and 5-R positions

	e=	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4
C-R	Atom	X_1				X_2				X_3			
5-H	N1	-0.541	-0.536	-0.529	-0.525	-0.468	-0.497	-0.519	-0.529	-0.458	-0.48	-0.495	-0.502
	C2	0.0637	0.0746	0.085	0.088	0.087	0.0836	0.0813	0.08	0.174	0.183	0.189	0.192
	C3	-0.332	-0.348	-0.359	-0.366	-0.34	-0.342	-0.342	-0.342	-0.556	-0.56	-0.566	-0.567
	C4	0.472	0.4713	0.469	0.471	0.375	0.3797	0.383	0.385	0.556	0.568	0.575	0.58
	C5	-0.142	-0.152	-0.161	-0.166	-0.174	-0.18	-0.184	-0.185	-0.139	-0.14	-0.145	-0.147
	C6	-0.216	-0.222	-0.225	-0.225	-0.2	-0.206	-0.21	-0.212	-0.201	-0.21	-0.209	-0.21

Contd...

	C7	-0.17	-0.177	-0.18	-0.18	-0.192	-0.196	-0.199	-0.2	-0.167	-0.17	-0.167	-0.168
	C8	-0.237	-0.236	-0.234	-0.232	-0.183	-0.193	-0.201	-0.205	-0.191	-0.2	-0.204	-0.206
5-NO_2	N1	-0.537	-0.532	-0.524	-0.519	-0.463	-0.488	-0.505	-0.514	-0.457	-0.48	-0.49	-0.495
	C2	0.0685	0.0791	0.091	0.097	0.094	0.0918	0.0901	0.09	0.185	0.195	0.202	0.205
	C3	-0.322	-0.338	-0.347	-0.351	-0.326	-0.325	-0.323	-0.322	-0.553	-0.56	-0.564	-0.565
	C4	0.4648	0.4714	0.469	0.468	0.383	0.386	0.3868	0.389	0.563	0.573	0.579	0.583
	C5	0.1801	0.1684	0.158	0.153	0.145	0.1386	0.1334	0.132	0.144	0.141	0.138	0.137
	C6	-0.225	-0.228	-0.228	-0.228	-0.198	-0.198	-0.198	-0.198	-0.194	-0.2	-0.199	-0.2
	C7	-0.158	-0.162	-0.164	-0.164	-0.185	-0.188	-0.19	-0.19	-0.16	-0.16	-0.153	-0.151
	C8	-0.226	-0.221	-0.214	-0.21	-0.164	-0.168	-0.17	-0.172	-0.176	-0.18	-0.182	-0.182
5-Cl	N1	-0.542	-0.539	-0.533	-0.53	-0.468	-0.494	-0.513	-0.522	-0.459	-0.48	-0.493	-0.499
	C2	0.0623	0.0707	0.079	0.084	0.09	0.0872	0.0854	0.085	0.179	0.187	0.193	0.195
	C3	-0.328	-0.346	-0.357	-0.362	-0.336	-0.336	-0.335	-0.335	-0.555	-0.56	-0.564	-0.565
	C4	0.471	0.4778	0.48	0.481	0.382	0.3843	0.3859	0.388	0.553	0.567	0.576	0.58
	C5	0.0364	0.0296	0.024	0.021	0.017	0.0133	0.0109	0.01	0.012	0.011	0.01	0.01
	C6	-0.251	-0.255	-0.257	-0.257	-0.235	-0.239	-0.241	-0.241	-0.22	-0.22	-0.227	-0.227
	C7	-0.16	-0.164	-0.166	-0.167	-0.18	-0.184	-0.187	-0.186	-0.155	-0.16	-0.155	-0.154
	C8	-0.241	-0.239	-0.235	-0.232	-0.185	-0.192	-0.197	-0.2	-0.194	-0.2	-0.202	-0.203
5-CH_3	N1	-0.543	-0.54	-0.534	-0.53	-0.471	-0.501	-0.523	-0.533	-0.461	-0.48	-0.499	-0.505
	C2	0.062	0.071	0.08	0.085	0.084	0.0826	0.0805	0.08	0.173	0.181	0.187	0.19
	C3	-0.331	-0.346	-0.358	-0.364	-0.344	-0.346	-0.346	-0.345	-0.552	-0.56	-0.561	-0.563
	C4	0.4709	0.4695	0.467	0.466	0.379	0.3827	0.3861	0.388	0.553	0.564	0.57	0.573
	C5	0.0426	0.0353	0.029	0.025	0.034	0.0339	0.034	0.034	0.047	0.045	0.044	0.044
	C6	-0.223	-0.231	-0.234	-0.234	-0.216	-0.223	-0.228	-0.23	-0.206	-0.21	-0.214	-0.215
	C7	-0.161	-0.169	-0.172	-0.172	-0.181	-0.186	-0.189	-0.19	-0.158	-0.16	-0.16	-0.16
	C8	-0.258	-0.257	-0.255	-0.252	-0.201	-0.212	-0.221	-0.225	-0.209	-0.22	-0.221	-0.223
5-OH	N1	-0.53	-0.525	-0.519	-0.515	-0.46	-0.49	-0.512	-0.523	-0.451	-0.47	-0.49	-0.497
	C2	0.0772	0.0861	0.095	0.1	0.089	0.0866	0.0854	0.085	0.171	0.182	0.189	0.192
	C3	-0.33	-0.343	-0.351	-0.355	-0.342	-0.343	-0.342	-0.341	-0.546	-0.55	-0.557	-0.558
	C4	0.4716	0.4701	0.467	0.464	0.369	0.3759	0.3813	0.384	0.556	0.566	0.573	0.576
	C5	0.3886	0.381	0.373	0.369	0.349	0.347	0.3459	0.346	0.397	0.396	0.393	0.393
	C6	-0.276	-0.286	-0.291	-0.294	-0.26	-0.269	-0.275	-0.278	-0.254	-0.26	-0.265	-0.267
	C7	-0.146	-0.153	-0.156	-0.157	-0.177	-0.183	-0.187	-0.188	-0.141	-0.14	-0.143	-0.143
	C8	-0.285	-0.284	-0.28	-0.277	-0.203	-0.214	-0.221	-0.225	-0.225	-0.23	-0.237	-0.239

Table 4. Calculated BO charge for 6-R and 7-R positions

	e=	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4
C-R	Atom	X1				X2				X3			
6-NO_2	N1	-0.54	-0.53	-0.523	-0.518	-0.47	-0.48	-0.51	-0.52	-0.46	-0.482	-0.5	-0.501
	C2	0.065	0.077	0.089	0.095	0.103	0.092	0.103	0.103	0.193	0.205	0.214	0.218
	C3	-0.32	-0.33	-0.342	-0.346	-0.34	-0.32	-0.33	-0.33	-0.56	-0.566	-0.57	-0.572
	C4	0.473	0.477	0.477	0.477	0.388	0.381	0.399	0.402	0.558	0.572	0.581	0.585
	C5	-0.12	-0.12	-0.122	-0.124	-0.15	-0.16	-0.14	-0.14	-0.13	-0.123	-0.12	-0.12
	C6	0.056	0.055	0.054	0.054	0.072	-0.2	0.068	0.067	0.069	0.069	0.067	0.067
	C7	-0.16	-0.16	-0.164	-0.165	-0.19	0.068	-0.19	-0.19	-0.15	-0.151	-0.15	-0.147
	C8	-0.22	-0.22	-0.215	-0.212	-0.17	-0.14	-0.18	-0.18	-0.18	-0.187	-0.19	-0.19
6-Cl	N1	-0.54	-0.54	-0.531	-0.528	-0.46	-0.49	-0.51	-0.52	-0.46	-0.478	-0.49	-0.499
	C2	0.067	0.075	0.083	0.088	0.087	0.085	0.084	0.084	0.176	0.185	0.192	0.195
	C3	-0.33	-0.35	-0.36	-0.364	-0.33	-0.34	-0.33	-0.33	-0.56	-0.563	-0.57	-0.568

Contd…

	C4	0.471	0.477	0.48	0.48	0.376	0.379	0.382	0.383	0.558	0.571	0.58	0.584
	C5	-0.17	-0.18	-0.185	-0.189	-0.2	-0.21	-0.21	-0.21	-0.17	-0.169	-0.17	-0.172
	C6	-0.05	-0.05	-0.056	-0.057	-0.03	-0.04	-0.04	-0.04	-0.04	-0.043	-0.04	-0.045
	C7	-0.19	-0.2	-0.199	-0.201	-0.21	-0.22	-0.22	-0.22	-0.19	-0.19	-0.19	-0.189
	C8	-0.22	-0.22	-0.212	-0.21	-0.17	-0.17	-0.18	-0.18	-0.17	-0.18	-0.18	-0.185
6-CH_3	N1	-0.54	-0.54	-0.528	-0.524	-0.47	-0.5	-0.52	-0.53	-0.46	-0.479	-0.49	-0.5
	C2	0.067	0.075	0.084	0.089	0.083	0.08	0.078	0.077	0.169	0.177	0.183	0.186
	C3	-0.33	-0.35	-0.362	-0.367	-0.34	-0.34	-0.34	-0.34	-0.56	-0.561	-0.56	-0.566
	C4	0.465	0.471	0.468	0.466	0.374	0.377	0.383	0.384	0.555	0.569	0.576	0.579
	C5	-0.14	-0.15	-0.162	-0.167	-0.18	-0.18	-0.19	-0.19	-0.14	-0.143	-0.14	-0.145
	C6	-0.04	-0.04	-0.042	-0.041	-0.03	-0.03	-0.03	-0.03	-0.03	-0.027	-0.03	-0.027
	C7	-0.17	-0.18	-0.178	-0.179	-0.19	-0.19	-0.19	-0.2	-0.17	-0.17	-0.17	-0.169
	C8	-0.23	-0.23	-0.227	-0.225	-0.18	-0.19	-0.2	-0.2	-0.18	-0.191	-0.2	-0.198
6-OH	N1	-0.54	-0.53	-0.524	-0.519	-0.46	-0.49	-0.51	-0.52	-0.46	-0.476	-0.49	-0.498
	C2	0.065	0.074	0.082	0.087	0.075	0.071	0.069	0.068	0.075	0.17	0.176	0.178
	C3	-0.34	-0.35	-0.363	-0.369	-0.33	-0.34	-0.34	-0.34	-0.33	-0.561	-0.56	-0.566
	C4	0.466	0.466	0.463	0.461	0.364	0.368	0.373	0.376	0.364	0.568	0.575	0.578
	C5	-0.23	-0.24	-0.248	-0.252	-0.27	-0.27	-0.28	-0.28	-0.27	-0.226	-0.23	-0.225
	C6	0.305	0.304	0.304	0.303	0.321	0.319	0.318	0.317	0.321	0.315	0.315	0.315
	C7	-0.21	-0.22	-0.222	-0.224	-0.23	-0.23	-0.24	-0.24	-0.23	-0.216	-0.22	-0.218
	C8	-0.21	-0.21	-0.212	-0.21	-0.16	-0.17	-0.18	-0.19	-0.16	-0.178	-0.18	-0.187
7-NO_2	N1	-0.54	-0.53	-0.524	-0.519	-0.46	-0.48	-0.5	-0.51	-0.45	-0.475	-0.49	-0.496
	C2	0.07	0.082	0.094	0.1	0.094	0.092	0.091	0.091	0.185	0.195	0.202	0.206
	C3	-0.33	-0.34	-0.35	-0.353	-0.32	-0.32	-0.32	-0.32	-0.56	-0.565	-0.57	-0.571
	C4	0.468	0.47	0.469	0.468	0.377	0.381	0.384	0.386	0.557	0.57	0.579	0.583
	C5	-0.13	-0.14	-0.145	-0.148	-0.16	-0.16	-0.16	-0.16	-0.14	-0.136	-0.14	-0.137
	C6	-0.21	-0.21	-0.208	-0.208	-0.2	-0.2	-0.2	-0.2	-0.19	-0.187	-0.19	-0.186
	C7	0.086	0.085	0.084	0.084	0.068	0.068	0.067	0.066	0.088	0.09	0.09	0.091
	C8	-0.19	-0.18	-0.176	-0.171	-0.14	-0.14	-0.14	-0.14	-0.16	-0.159	-0.16	-0.16
7-Cl	N1	-0.54	-0.54	-0.533	-0.529	-0.47	-0.5	-0.52	-0.53	-0.46	-0.48	-0.49	-0.5
	C2	0.066	0.075	0.083	0.087	0.093	0.089	0.088	0.087	0.181	0.19	0.196	0.199
	C3	-0.33	-0.35	-0.358	-0.363	-0.34	-0.34	-0.34	-0.34	-0.56	-0.563	-0.57	-0.568
	C4	0.471	0.478	0.48	0.481	0.378	0.385	0.388	0.389	0.555	0.569	0.577	0.581
	C5	-0.13	-0.13	-0.141	-0.144	-0.16	-0.16	-0.16	-0.16	-0.12	-0.127	-0.13	-0.129
	C6	-0.24	-0.24	-0.246	-0.247	-0.22	-0.23	-0.23	-0.23	-0.22	-0.227	-0.23	-0.229
	C7	-0.01	-0.01	-0.017	-0.018	-0.04	-0.04	-0.04	-0.04	-0.01	-0.01	-0.01	-0.01
	C8	-0.26	-0.26	-0.257	-0.255	-0.19	-0.2	-0.21	-0.21	-0.22	-0.222	-0.23	-0.228
7-CH_3	N1	-0.54	-0.54	-0.53	-0.525	-0.47	-0.5	-0.52	-0.53	-0.46	-0.48	-0.49	-0.5
	C2	0.066	0.074	0.084	0.089	0.086	0.084	0.081	0.081	0.174	0.182	0.188	0.191
	C3	-0.33	-0.35	-0.361	-0.365	-0.35	-0.35	-0.35	-0.35	-0.55	-0.561	-0.56	-0.566
	C4	0.465	0.472	0.469	0.467	0.379	0.382	0.385	0.387	0.553	0.566	0.573	0.576
	C5	-0.13	-0.14	-0.153	-0.158	-0.17	-0.17	-0.18	-0.18	-0.13	-0.133	-0.14	-0.137
	C6	-0.22	-0.22	-0.223	-0.223	-0.19	-0.2	-0.2	-0.21	-0.2	-0.209	-0.21	-0.212
	C7	-0.01	-0.01	-0.008	-0.008	-0.03	-0.03	-0.02	-0.02	-0	0.004	0.007	0.009
	C8	-0.22	-0.22	-0.217	-0.215	-0.17	-0.18	-0.19	-0.2	-0.18	-0.184	-0.19	-0.191
7-OH	N1	-0.54	-0.54	-0.532	-0.528	-0.48	-0.51	-0.53	-0.54	-0.46	-0.484	-0.5	-0.504
	C2	0.063	0.073	0.082	0.087	0.091	0.087	0.084	0.082	0.181	0.188	0.194	0.196
	C3	-0.33	-0.35	-0.36	-0.366	-0.35	-0.35	-0.35	-0.35	-0.55	-0.56	-0.56	-0.565
	C4	0.472	0.472	0.47	0.468	0.38	0.384	0.387	0.388	0.551	0.561	0.568	0.571
	C5	-0.12	-0.13	-0.14	-0.145	-0.15	-0.16	-0.16	-0.17	-0.12	-0.123	-0.13	-0.128
	C6	-0.29	-0.29	-0.288	-0.286	-0.23	-0.24	-0.25	-0.25	-0.25	-0.254	-0.26	-0.26
	C7	0.343	0.342	0.343	0.342	0.328	0.327	0.327	0.327	0.348	0.352	0.355	0.357
	C8	-0.29	-0.3	-0.298	-0.297	-0.28	-0.29	-0.29	-0.29	-0.28	-0.279	-0.28	-0.281

Table 5. Calculated NBO charge for 8-R position

	e=	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4	1.0	2.2	7.6	78.4
C-R	Atom	X1				X2				X3			
8-NO_2	N1	-0.541	-0.532	-0.524	-0.52	-0.457	-0.483	-0.504	-0.516	-0.452	-0.474	-0.49	-0.497
	C2	0.0724	0.081	0.09	0.094	0.103	0.1	0.0981	0.098	0.195	0.2051	0.212	0.2157
	C3	-0.318	-0.329	-0.336	-0.34	-0.331	-0.333	-0.331	-0.33	-0.559	-0.565	-0.57	-0.571
	C4	0.4717	0.475	0.477	0.477	0.381	0.387	0.3918	0.395	0.561	0.5733	0.581	0.5845
	C5	-0.099	-0.099	-0.099	-0.1	-0.155	-0.153	-0.149	-0.145	-0.128	-0.126	-0.12	-0.122
	C6	-0.217	-0.219	-0.219	-0.22	-0.194	-0.199	-0.203	-0.205	-0.19	-0.192	-0.19	-0.193
	C7	-0.155	-0.151	-0.147	-0.15	-0.176	-0.174	-0.171	-0.17	-0.162	-0.16	-0.16	-0.157
	C8	0.0633	0.067	0.071	0.073	0.103	0.092	0.0838	0.08	0.097	0.089	0.083	0.082
8-Cl	N1	-0.543	-0.539	-0.533	-0.53	-0.457	-0.485	-0.505	-0.516	-0.449	-0.471	-0.49	-0.493
	C2	0.0698	0.078	0.086	0.089	0.094	0.092	0.0898	0.089	0.184	0.1932	0.2	0.2027
	C3	-0.329	-0.344	-0.355	-0.36	-0.335	-0.336	-0.335	-0.334	-0.558	-0.564	-0.57	-0.569
	C4	0.4719	0.479	0.481	0.482	0.377	0.381	0.3844	0.386	0.559	0.5722	0.581	0.5846
	C5	-0.145	-0.152	-0.159	-0.16	-0.178	-0.181	-0.181	-0.181	-0.147	-0.148	-0.15	-0.149
	C6	-0.203	-0.208	-0.209	-0.21	-0.188	-0.194	-0.197	-0.198	-0.188	-0.191	-0.19	-0.193
	C7	-0.196	-0.199	-0.199	-0.2	-0.212	-0.215	-0.217	-0.217	-0.189	-0.189	-0.19	-0.189
	C8	-0.06	-0.06	-0.059	-0.06	-0.028	-0.034	-0.04	-0.042	-0.035	-0.039	-0.04	-0.044
8-CH_3	N1	-0.542	-0.537	-0.528	-0.52	-0.476	-0.496	-0.512	-0.521	-0.463	-0.479	-0.49	-0.496
	C2	0.0645	0.075	0.085	0.09	0.089	0.084	0.0807	0.08	0.178	0.1849	0.19	0.1932
	C3	-0.329	-0.345	-0.355	-0.36	-0.341	-0.342	-0.342	-0.341	-0.556	-0.562	-0.57	-0.567
	C4	0.467	0.472	0.47	0.469	0.377	0.38	0.382	0.384	0.555	0.5684	0.576	0.5789
	C5	-0.148	-0.159	-0.168	-0.17	-0.184	-0.19	-0.194	-0.196	-0.148	-0.153	-0.16	-0.157
	C6	-0.208	-0.215	-0.217	-0.22	-0.192	-0.198	-0.203	-0.204	-0.193	-0.199	-0.2	-0.203
	C7	-0.183	-0.189	-0.191	-0.19	-0.206	-0.212	-0.215	-0.216	-0.18	-0.182	-0.18	-0.181
	C8	-0.033	-0.028	-0.023	-0.02	0.02	0.015	0.0106	0.008	0.012	0.0092	0.007	0.0056
		X1				X2				X2(B)			
8-OH	N1	-0.61	-0.664	-0.707	-0.73	-0.448	-0.479	-0.503	-0.516	-0.515	-0.53	-0.54	-0.547
	C2	0.0669	0.075	0.084	0.089	0.085	0.08	0.0772	0.077	0.09	0.0874	0.086	0.0853
	C3	-0.334	-0.348	-0.358	-0.36	-0.335	-0.338	-0.338	-0.339	-0.34	-0.34	-0.34	-0.337
	C4	0.4692	0.471	0.468	0.467	0.373	0.377	0.3805	0.384	0.382	0.3848	0.387	0.3881
	C5	-0.174	-0.185	-0.196	-0.2	-0.209	-0.217	-0.221	-0.222	-0.216	-0.221	-0.22	-0.225
	C6	-0.197	-0.202	-0.203	-0.2	-0.181	-0.187	-0.19	-0.191	-0.173	-0.181	-0.19	-0.189
	C7	-0.271	-0.273	-0.273	-0.27	-0.296	-0.297	-0.297	-0.296	-0.255	-0.263	-0.27	-0.271
	C8	0.3171	0.32	0.325	0.327	0.358	0.353	0.3479	0.345	0.334	0.3279	0.323	0.3211
		X3				X3(B)							
8-OH	N1	-0.442	-0.466	-0.483	-0.49	-0.498	-0.51	-0.518	-0.521				
	C2	0.1719	0.179	0.184	0.187	0.181	0.19	0.1966	0.199				
	C3	-0.557	-0.562	-0.566	-0.57	-0.556	-0.561	-0.565	-0.567				
	C4	0.5584	0.57	0.577	0.58	0.557	0.569	0.5767	0.58				
	C5	-0.173	-0.178	-0.181	-0.18	-0.174	-0.178	-0.18	-0.182				
	C6	-0.182	-0.187	-0.19	-0.19	-0.179	-0.185	-0.188	-0.19				
	C7	-0.261	-0.259	-0.255	-0.25	-0.221	-0.224	-0.226	-0.228				
	C8	0.3481	0.345	0.343	0.342	0.328	0.323	0.3198	0.318				

Conclusion

1. In gas phase and solution at B3LYP/6-311++G (d,p) type DFT calculations yield the following results which estimates the stability of those tautomers is X1 >X2 >X3. X1 is the most stable form, but in gas phase, (8-OH) subsisted is an exception that it has two forms. At the first one, hydrogen bond in hydroxyl substituent (OH) with nitrogen is not formed and then the stability order is X1 >X2 >X3. The second form, the hydrogen bond is formed between them then the stability order is X2 >X1 >X3 and X2 isomer is dominant form. In all forms with increase of polarity, the total energy of all compounds is more negative.
2. The charges on all eight positions were affected by substituents and solvents.
3. The dipole moments of all compounds are affected by solvent. With increase of the polarity of solvents the dipole moments of the tautomers were increased.

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