

Some Aspects of 8-hydroxyquinoline in Solvents

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Abstract: The study of a UV-VIS spectrum of 8-hydroxyquinoline (8HQ) in different solvents can provide relevant information concerning the influence of the medium on the electronic structure of the solute or the nature and strength of the specific solvent-solute intra- or intermolecular interactions. The electronic absorption spectra of 8-hydroxyquinoline in various solvents have very different features due to dimeric or monomeric form in a particular environment. Thus, we have performed a quantum chemical semi-empirical PM3 calculations optimization of 8HQ and corresponding tautomer as single and dimeric form in free space and surrounded by the first solvation sphere. The dipole moment, polarizability and other physical parameters of these molecular systems were calculated. These results are useful tools in predicting optical properties of new materials which include hydroxyquinoline and explain the change in UV-VIS spectrum of 8HQ in different solvents.

Keywords: Intermolecular hydrogen bond; Electronic spectra; Solvent effect, PM3 semi-empirical method; Dipole moment.

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Introduction

8-hydroxyquinoline (8-HQ) (Figure 1) is a conjugated system and, in the same time, a bifunctional hydrogen bonding molecule, which in protic solvents simultaneously acts as an H donor at the O-H group and as an H acceptor at the N atom.

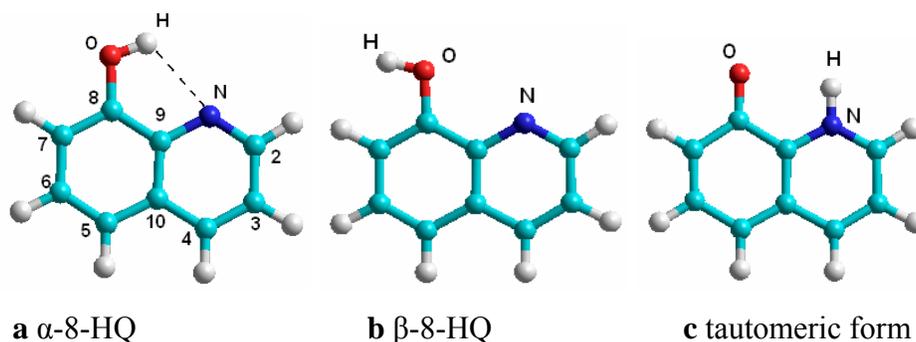


Figure 1. The structure of 8-hydroxyquinoline

The O-H and aza groups may be also involved in a keto-enol tautomeric equilibrium. Because of a too short distance between the OH group and the ring N atom,¹⁻⁵ the intramolecular and intermolecular hydrogen bonding induce the existence of many conformers of 8-HQ in different environments. In Figure 1 are shown two conformers named α -8-HQ (with intramolecular hydrogen bonding), Figure 1a, and β -8-HQ (without intra-molecular hydrogen bonding), Figure 1b. The tautomeric form of 8-HQ, supposed to be present in polar solvents, is presented in Figure 1c.

8-Hydroxyquinoline and its derivatives are widely used as chelating reagents in analytical chemistry and radiochemistry for metal ion extraction and fluorometric determination.⁶ 8-hydroxyquinolines are well known because can perform as structurally related subunits in important

biomolecules or biochemical process, which show strong cytotoxic and antimicrobial properties, and they represent the main component in some bactericide, fungicide and antimalarial drugs.^{7,8}

Experimentally it was found that hydroxyquinoline has analogous properties, such as an intense fluorescence in concentrated acids, lack of fluorescence in water or alkanes or formation of the hydrogen-bonded clusters with water, ammonium or alcohol molecules.¹⁻¹³ When presents dimeric form 8-HQ is soluble in non-polar solvents. Conjugated organic materials that are functionalized by electron-donor moiety coupled, through a π -conjugated bridge, to an electron-acceptor moiety, can exhibit large optical nonlinear (NLO) properties. The new materials exhibiting NLO effects are of great technological importance for use in application within electronics and photonics.

The study of absorption electronic spectra of molecules solved at very low concentration ($< 10^{-3}\text{M}$) can provide relevant information about the internal force field strength of solvent or various properties of the investigated molecules. The solvatochromic shifts are a measure of interactions between the solvent and the solute in the immediate vicinity of the solute. The interactions can be classified into: (i) non-specific solute – solvent association caused by polarity – polarizability effects; and (ii) specific solute – solvent association such as hydrogen bonding or electron donor–acceptor interactions.^{8, 14-17}

Although many chemical or physical phenomena are experimentally investigated in condensed phases, the great majority of quantum chemical calculations for the study of the structure, properties and spectroscopy deal with isolated molecules.

In the present work, the B3LYP/6-31+G levels of theory, from Gaussian 98 program¹⁸, and PM3 semi-empirical method,^{19,20} included in HyperChem software packages,²¹ for the molecular optimization of the 8-hydroxyquinoline structure in free space were used. The solvent effect of water, ethanol, chloroform and hexane was simulated using the explicit model „solvent box”.¹⁴⁻¹⁶ In „solvent box” model, we have simulated a cube of certain dimensions full of solvent molecules, and the molecule of 8-HQ has been introduced in its centre. The solvent molecules, in the „solvent box”, have a random distribution. The number of solvent molecules was assumed to be the first sphere of solvation, in according with Abe’s model.¹⁷ To simulate the first solvation spheres for 8-HQ, according to Abe’s model, the number of molecule of specific solvent was obtained according to the formula used earlier.¹⁶ The volume of 8-HQ and solvent molecules are a COSMO volume and were calculated with MOPAC program,²² PM6 semiempirical method.²³ The molecular systems build in this way have a great number of molecules and it have been optimized using the PM3 method. In order to investigate the influence of solvents on the physical properties of 8-HQ, the molecule has been „extracted” and „frozen” and on this structure a „single point” calculation has been done. The obtained results have been compared with those obtained in the case when the molecular structure has been optimized in free space.

Experimental

The 8-hydroxyquinoline was purchase from Aldrich Chemical Co. The solvents used in present work were: n-hexane, dioxane and chloroform from Merck and n-heptane from Fluka and they were spectroscopic grade products. The ethanol of 99.2 % purity was used without purification. The

electronic spectra were performed on a Hitachi-2001 UV-VIS spectrophotometer, (250-700 nm) using 10 mm quartz cells.

Results and discussions

The above mentioned solvents have been chosen because many experimental investigations evidence a kind of discontinuity in relation to the three fundamental indices of solvents: π^* dipolarity/polarizability parameter, α solvent hydrogen bond donor acidity and β solvent hydrogen bond acceptor basicity. Thus, the two absorption bands of 8-HQ are blue-shifted in solvents like n-hexane, dioxane, chloroform, ethanol and water, but it is not a monotone shift with solvent polarity. In the same time, the shifts on the 8-HQ bands in various solvents are very small in comparison with other substituted quinolines. As reported in the literature,¹⁻¹² the intramolecular hydrogen bonding plays an important role in the stability of predominant conformer α -8-HQ (Figure 1a) in water or ethanol. In chloroform solution was experimentally evidenced the 1:1 H₂O - 8-HQ adduct and the dimeric form of 8-HQ in alkane solutions. Same kind of dimer was marked out in crystal structure of 8-HQ.

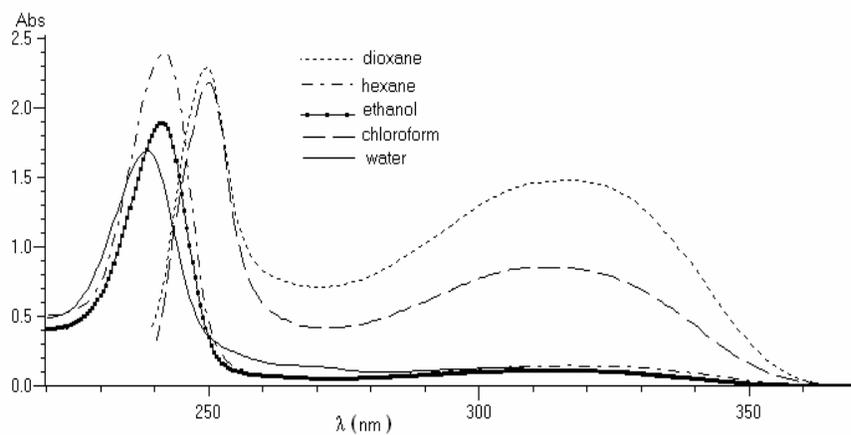


Figure 2. The UV-VIS spectra of the 8-hydroxyquinoline in some solvents.

The theoretical investigations on the 8-hydroxyquinoline structure in free space has been performed by the molecular optimization using B3LYP/6-31+G levels of theory from Gaussian 98¹⁸ program and compared with semi empirical PM3^{19, 20} method included in HyperChem²¹ modeling packages. The geometric parameters for 8-HQ conformers shown in Figure 1 are presented in Table 1 and compared with X-ray data.^{13, 24}

As can be seen the results are very similar for both conformers and there is a good agreement between experimental, semi-empirical PM3, or B3LYP/6-31+G high levels, calculated values. Calculations were performed starting from standard bonds lengths and bond angles. All geometries were fully optimized by minimizing the energy with respecting the geometrical variables without symmetry constraint, using the Polak–Ribiere minimization algorithm (RMS gradient 0.005 kcal/Åmol) and as convergence criterion for PM3 method. The semiempirical method does not describe the solvating processes, but it may provide some information about the interaction centers, changes in the charge distribution and in the bond distance when different solvent molecules are present in the surroundings of the main structure. The semi-empirical PM3 method provides a good description of charge distribution, and is acceptable for systems of the given size.

Table 1. The geometric parameters calculated for α -8-HQ, β -8-HQ and tautomer of 8-HQ at B3LYP/6-31+G and semiempirical PM3 level

Parameters	α -8-HQ		X-ray	β -8-HQ		tautomer
	B3LYP/ 6-31+G	PM3		B3LYP/ 6-31+G	PM3	
N–C2	1.317	1.332	1.331	1.315	1.323	1.343

C2–C3	1.415	1.419	1.338	1.415	1.423	1.424
C3–C4	1.375	1.375	1.357	1.372	1.366	1.361
C4–C10	1.417	1.422	1.402	1.417	1.425	1.439
C10–C5	1.418	1.415	1.41	1.418	1.417	1.373
C5–C6	1.378	1.382	1.365	1.373	1.37	1.419
C6–C7	1.413	1.403	1.427	1.412	1.409	1.359
C7–C8	1.377	1.395	1.371	1.38	1.384	1.451
C8–O	1.351	1.36	1.367	1.358	1.362	1.236
C8–C9	1.428	1.432	1.393	1.432	1.436	1.474
C9–N	1.358	1.388	1.374	1.358	1.391	1.368
C9–C10	1.424	1.42	1.428	1.43	1.413	1.439

In order to evidence the solvent influence, we simulated a „solvent box” with calculated number of solvent molecules and the two conformers and the tautomer were placed in its centre. After geometry optimizations the β -8-HQ conformer was modified in α -8-HQ and the result was very similarly for these two conformers. In Figure 3 is presented the „solvent box” of 17 ethanol and α -8-HQ.

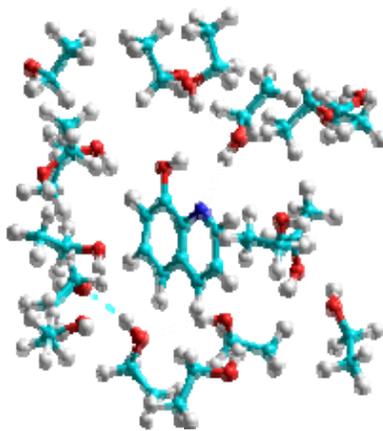


Figure 3. 8-hydroxyquinoline in ethanol “solvent box”

Because in the alkane solutions (Figure 4a) and in crystal structure (Figure 4c) the dimer of 8-HQ is the main structure, we optimized a dimer planar structure and then we placed this structure in the middle of „solvent box”. After geometry optimization, we have observed that the solvent changes the structure of 8-HQ dimer in correlation with the polarity of solvents. Thus, the hexane has not significantly changed the dimer structure, the dipole moment is zero and the dihedral angle remains zero (Figure 4a).

In chloroform, the dihedral angle becomes $\theta = 83.55$ compared with $\theta = 48.49$ in the crystal structure (Figure 4b). The deviations of dihedral angle from planarity modify the dipole moment value that becomes $\mu = 2.182$ D in chloroform and $\mu = 7.142$ D in crystal structure. In polar protic solvents like water and ethanol the intermolecular bond the dimer was broken and the two 8-HQ molecules were completely separated by solvent molecules. In order to evidence the influence of solvent on 8-HQ molecule, we isolated one molecule of 8-HQ and then we performed single point PM3 semi empirical calculations.

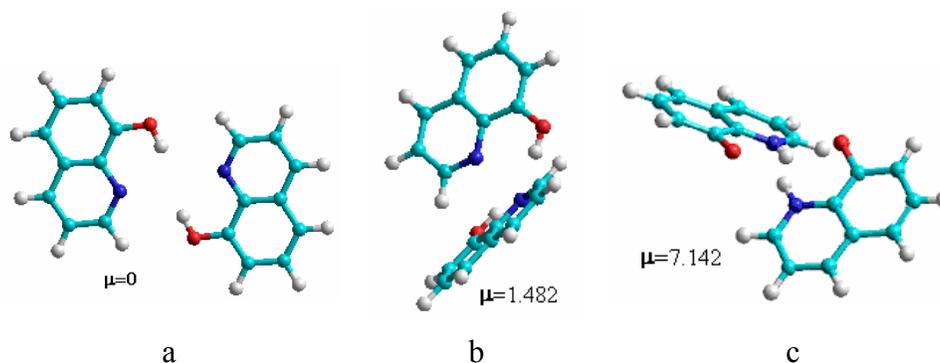


Figure 4. 8-hydroxyquinoline dimer in a) hexane; b) chloroform c) tautomer in crystal structure

Table 2. Values of the total energy, border energy levels, dipole moments and mean polarizability of the most stable clusters

Solvent	Structure	No. of molecules	Total energy (a.u.)	Dipole (D)	Polarizability (a.u.)	E HOMO (eV)	E LUMO (eV)
	α -8-HQ		-59.8796	2.192	86.00	-8.8121	-0.6774
	β -8-HQ	-	-59.8776	2.081	87.96	-8.8037	-0.5854
	tautomer	-	-59.8535	4.844	102.10	-7.6807	-1.1769
	dimer	-	-59.8829	2.187	87.70	-8.7958	-0.6939
n-hexane	α -8-HQ	12	-59.8796	2.192	86.37	-8.7900	-0.6852
	dimer	17	-59.8829	2.192	87.71	-8.7911	-0.6894
chloro-	α -8-HQ	15	-59.8793	2.203	86.01	-8.8163	-0.6794
form	dimer	19	-59.8828	2.202	87.75	-8.7709	-0.6712
ethanol	α -8-HQ	17	-59.8820	2.170	89.28	-8.7572	-0.7807
water	α -8-HQ	28	-59.8825	2.045	89.31	-8.7255	-0.7706
	dimer	35	-59.8744	2.284	86.55	-8.8958	-0.7367

The computed total energies, HOMO and LUMO energy levels, dipole moments and mean polarizability of one single molecule are given in Table 2. It is observed that these properties do not vary very much by passing from free molecule to the solutions. The tautomer has the greatest value of total energy, dipole moments and mean polarizability. In the same time, the total energy increases and dipole moments decrease with the polarity of solvents. An exception is observed in chloroform when the dipole moment is increased.

Conclusions

The spectrum of 8-hydroxyquinolines in different solvents evidences that the ability of solvent molecule to form hydrogen bonding plays an important role in stabilization of specific 8-HQ conformers. Our theoretical

investigations, with semi - empirical PM3 method, to the 8-HQ dimer in centre of the “solvent box”, evidence that the most stable structure in hexane is the plane dimer with $\mu=0$ D and the dimer with $\mu=2.182$ D in chloroform. In polar protic solvent, like water and ethanol the 8-HQ molecules are completely separated by solvent molecules.

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