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**EXPERIMENTAL AND THEORETICAL INVESTIGATION OF MOLECULAR
STRUCTURE AND CHARGE TRANSFER WITHIN SOME 8-HYDROXYQUINOLINE
DERIVATIVES**

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ABSTRACT

A series of novel 8-hydroxyquinoline derivatives: 5-HHQ, 5-MHQ, 5-EHQ and 5-PHQ were synthesized and characterized by means of IR, ¹H and ¹³C NMR spectroscopic analysis. The crystal structures of 5-EHQ and 5-PHQ were solved by X-ray diffraction measurements on single crystal, the two others on powder samples. The UV–Visible spectra of molecules were performed in acetonitrile and ethanol. Density Functional Theory (DFT) and Hartree Fock (HF) methods have been used to determine its optimized geometrical parameters. Theoretical calculations such as HOMO-LUMO energies in fundamental state, in acetonitrile and ethanol, electronic dipole moments and atomic charges distribution were carried out for the title molecules using DFT (B3LYP) method at 6-311G (d, p) set. The results give us some explanation on the molecular structures, the intra charge transfer, relationships between the number of carbons connected to 5-hydroxymethyl-8-hydroxyquinoline and the bioactivity of selected derivatives.

KEYWORDS: 8-hydroxyquinoline, X-ray, UV–Visible, DFT-HF, charge transfer, bioactivity.

INTRODUCTION

The 8-hydroxyquinoline derivatives continue to request the interest of researchers for the potential applications in the pharmaceutical, biological and electroluminescent field. The study of their activity with respect to the bacteria in various solvents at different temperatures had a great success during the last decade [1, 2]. Some derivatives considered as a large number of metal chelator [3, 4] to combat many diseases like Alzheimer's and Wilson's diseases. Others derivatives such as zinc (II) bis (8-hydroxyquinoline) complex have been investigated as electroluminescent (EL) materials [5-11] including electro-transporting and emitting materials, which are applied in molecular-based OLEDs [12-16]. In an aim of contributing to understand the structure-physical properties relationship of these molecules, we studied the effect of the carbons chain attached to position 13 of 5-hydroxymethyl-8-hydroxyquinoline grouping, on some structural and energy property of 8 hydroxyquinoline derivatives. For this, a series of four 8-hydroxyquinoline derivatives was synthesized and characterized by the spectroscopic methods such as IR, ¹H and ¹³C NMR. The crystallographic analysis for 5-hydroxymethyl-8-hydroxyquinoline (5-HHQ) and 5-methoxymethyl-8-hydroxyquinoline (5-MHQ) were carried out by high quality powder X-Ray diffraction whereas the molecule 5-ethoxymethyl-8-hydroxyquinoline (5-EHQ) and 5-propoxymethyl-8-hydroxyquinoline (5-PHQ) were characterized by both powder sample and single crystal X-Ray diffraction. Based on the calculation results by DFT approach, we also compared the geometrical parameters between calculation and experience of these molecules. An evaluation of HOMO-LUMO gap and charge distribution in a ground state and in

two polar solvents permitted us to understand the impact of the structural properties on the reactivity of these molecules.

MATERIALS AND METHODS

Synthesis

A mixture of 10g of hydroxy-8-hydroxyquinoline recrystallized in hexane and 11ml of methanol at 37% is treated by a gas hydrochloric acid current during 2 hours; the reaction mixture is abandoned 24 h. The reaction leads to the formation of a yellow solid of (methyl-5-hydroxy 5-hydrochlorate 8-hydroxyquinoline). This latter is isolated by filtration on sintered glass, and then washed three times with acetone to eliminate the traces of start product (8-hydroxyquinoline). Finally, the solid yellow product is oven dried and stored in a desiccators containing NaCl under vacuum. The product is then treated by a mixture of R-OH, NaHCO₃. R changes depending on the desired final product (Fig. 1)

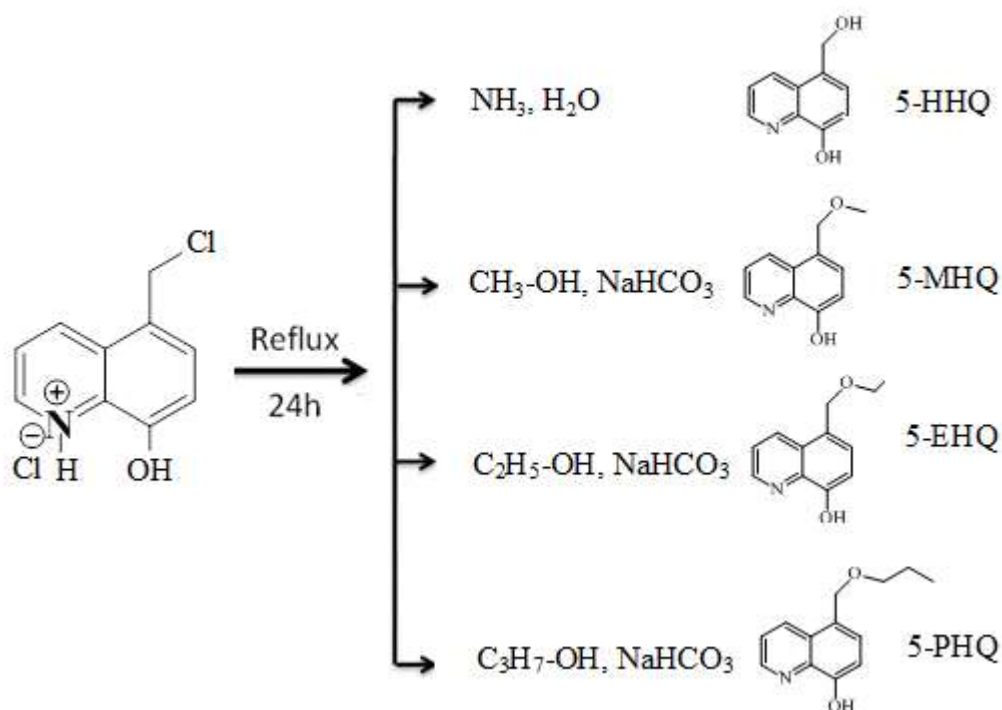


Fig. 1: synthesis of 8-hydroxyquinoline derivatives

X-ray measurements

Powder X-ray diffraction measurements were performed using Inel CPS120 powder diffractometer (Debye–Scherrer geometry, transmission mode). Data sets were collected at room temperature (293 K) and Monochromatic Cu-Kα₁ radiation ($\lambda = 1.54056\text{\AA}$) was selected with asymmetric focusing incident-beam curved quartz monochromator. The diffracted lines were collected on a 4096 channel detector over an arc of 120 and centered on the sample. External calibration using the Na₂Ca₂Al₂F₁₄ (NAC) cubic phase mixed with silver behenate was performed using cubic spline fittings. Single-crystal diffraction experiment was carried out using the diffractometer Rigaku Ultrahigh microfocus X-ray rotating anode equipped with Dectris Pilatus 200K detector. The Cu-Kα wavelength was $\lambda = 1.54187\text{\AA}$. Results were obtained at 260K. The structure was solved by direct methods using SHELXS-97 [17] program and the software Crystal Clear-SM Expert 2.1.

Fig. 2 represents the diagrams of diffraction recorded for these molecules. We represented here only the peaks obtained for 0 to 60° for 2θ. Obtained results show a good agreement between the calculated profile and the

Crystallographic data are presented in Table 1. Additional information concerning the parameters of molecules is available on line via Internet site Cambridge Crystallographic Database Center. The CCDC are 1403302, 1403720, 1480549 and 1401718 respectively for the molecules 5-HHQ, 5-MHQ, 5-EHQ and 5-PHQ.

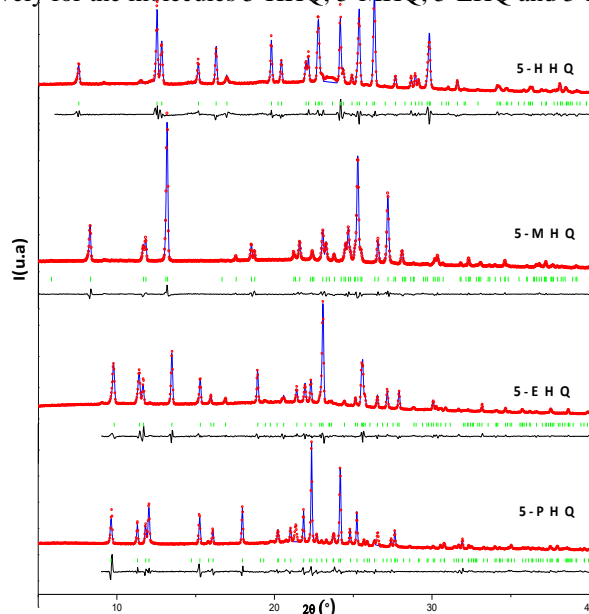


Fig. 2: Experimental (red) and calculated (blue) diffraction patterns along with the difference profile (black) and calculated Bragg reflections (green) of derivatives at 295 K.

Parameters	5-HHQ	5-MHQ	5-EHQ	5-PHQ
Empirical formula	C10 H9 N O2	C11 H11 N O2	C12 H13 N O2	C13 H15 N O2
Formula weight	175.18	189.21	203.23	217.26
Temperature (K)	294(1)	294	295	293(2)
λ (Å)	1.540562	1.54056	1.54187	1.54187
Space group	P2 ₁ /c	P2 ₁	Pbca	P2 ₁ /c
Structure	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
a (Å)	12.383(2)	4.1161(4)	7.9551(12)	9.2816(6)
b (Å)	4.7356(8)	14.962(2)	17.981(3)	14.9966(12)
c (Å)	14.616(3)	15.164(3)	15.125(2)	8.4884(7)
β °	109.482(11)	91.137(9)	90	95.716(3)
Volume (Å ³)	808.0(3)	933.7(2)	2163.5(6)	1175.65(15)
Z (Z')	4(1)	4(2)	8(1)	4(1)
D (g/cm ³)	1.440	1.346	1.248	1.227

Table 1: Crystallographic data and structure refinement for 8-hydroxyquinoline derivatives.

The two molecules 5-HHQ and 5-PHQ crystallize in a monoclinic system with space group P2₁/c and four molecules per unit cell, whereas 5-MHQ has the same number of molecules per unit cell but crystallizes in a P2₁ monoclinic system. 5-EHQ has a Pbca orthorhombic structure and eight molecules per unit cell. The molecules of the solved structures for the derivatives are presented in Fig. 3. An ortep drawing is presented in Fig.4 as example of numbering of the atoms, which is identical for the four molecules except for one hydrogen of the methyl group for the smaller molecule.

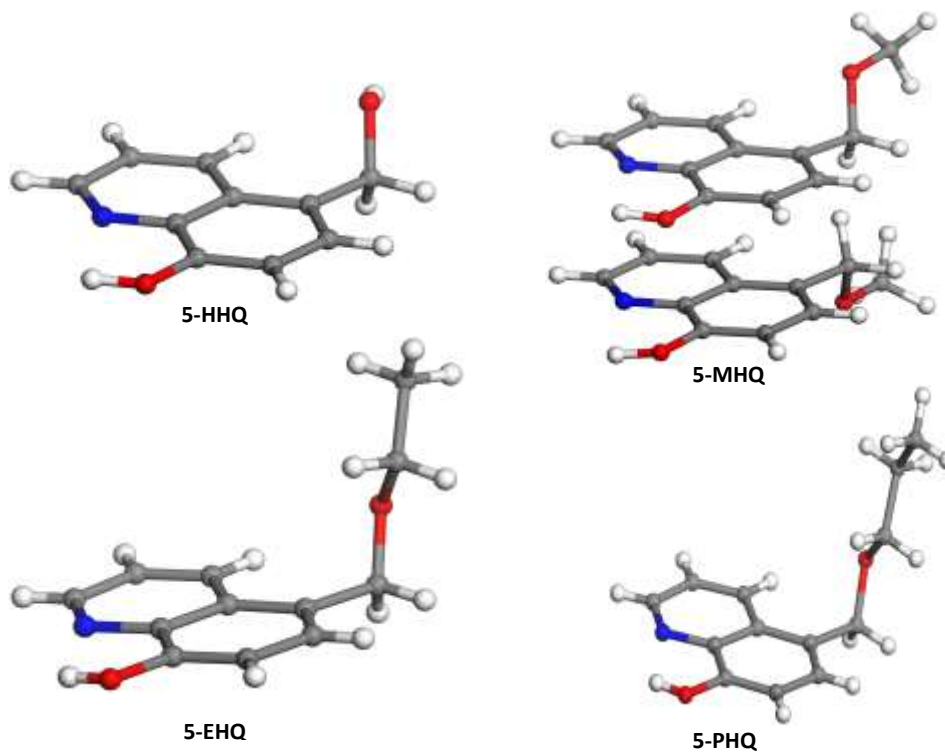


Fig. 3: Structures display of 5-HHQ, 5-MHQ, 5-EHQ and 5-PHQ molecules obtained by X-ray diffraction.

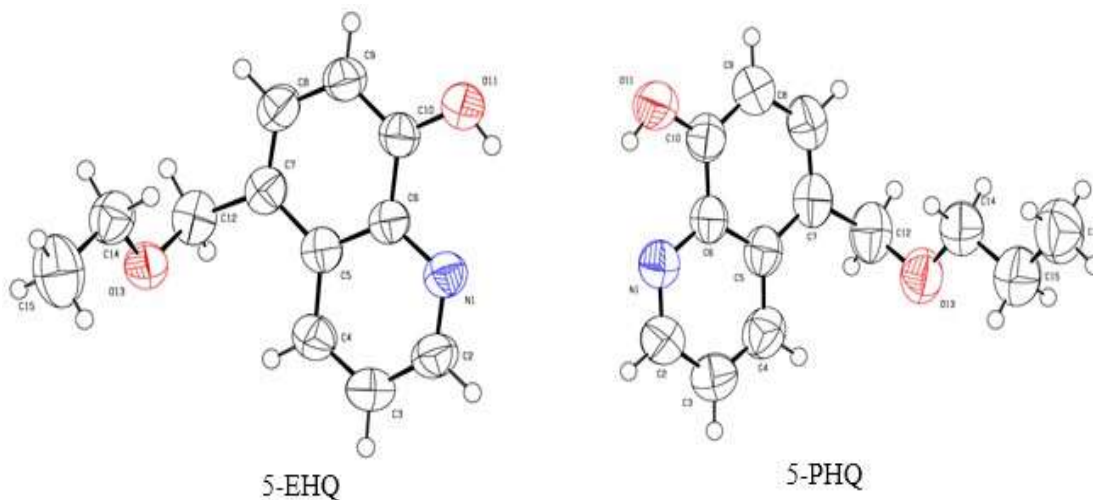


Fig. 4: ORTEP diagram of 5-EHQ and 5-PHQ molecules with numbering of the atoms.

Computational studies

The geometrical parameters, energy, dipole moment (μ), atomic charges distribution and HOMO-LUMO energy for title derivatives in ground state were performed at DFT and HF level of theory with 6-311G(d,p) basic set, using the program Gaussian 03 at room temperature [18]. The two theoretical methods are the most used to study the chemical and biochemical phenomena within a large variety of molecules [19-21]. Those methods lead to results similar to those obtained by ab-initio calculation, for example.

RESULTS AND DISCUSSION
Effect of the interactions on the geometrical conformation of the studied derivatives

The analysis by X-ray diffraction shows that all the studied derivatives are non-planar. The values of torsion angle (C5-C7-C12-O13) observed are: 64.9°, 66.8°, 62.7° and - 68.9° for 5-HHQ, 5-MHQ, 5-EHQ and 5-PHQ respectively. We note that the variation of that torsion angle for all the molecules is weak and seems independent of the number of carbon atoms substituted to oxygen at position 13. This independence may be due to the fact that the number of carbon added in position 13 does not significantly affect the electronegativity of oxygen. So only the influence of moderate intermolecular hydrogen bonds at the oxygen acceptor in position 13 can impose a certain geometric conformations in molecules. While the torsion angle appears to be very important in the 5-PHQ molecule, were the hydrogen bonds involving oxygen at position 13 is absent.

The cohesion and the stability of derivative structures are insured by a network of three different kinds of hydrogen bonding interactions O-H...N, C-H...O and O-H ... O. We notice, from the fig. 5 and the geometric values listed in the table 2 that all molecules possess a weak intramolecular hydrogen bond O-H ... N type, involving the functional OH group, which allows these molecules to have a good reactivity with different solvents even at room temperature. In addition, 5-HHQ, 5-MHQ and 5-EHQ molecules have moderate intermolecular bonding of O-H ... N type who is responsible of geometrical conformation in the molecular packing, while 5-PHQ molecule has only weak intermolecular bonds. Other hydrogen bonds between these molecules are intermolecular C-H ... O type, where the C-H is the donor of hydrogen bond. However, hydrogen bonds involving these atoms are often very low. The molecule 5-HHQ has an additional type of moderate intermolecular hydrogen bond, O-H ... O. All hydrogen bond parameters are summarized in table 2. Moderate intermolecular bonds type OH ... N involving the OH group as a donor and nitrogen atom as an acceptor, shifted both adjacent molecules plans with a gap from approximately 0.6 Å to 0.9 Å for the 5-HHQ, 5-MHQ and 5-HQP, or in 5-PHQ, where this type of bonds is low, the same plans are confused (Fig. 6).

Molecules	D	H	A	D - H(Å)	H...A(Å)	D...A(Å)	D - H...A(°)
5-HHQ	O11	H1	N1	0.980	2.506	2.819	98.1
	O11	H1	N1	0.980	2.160	3.031	148.0
	O13	H13	O13	0.990	1.800	2.761	166.0
	C2	H2	O11	1.020	2.550	3.124	116.0
	C3	H3	O11	1.020	2.440	3.170	128.0
5-MHQ	O11	H11	N1	0.980	2.538	2.852	98.6
	O11	H11	N1	0.980	1.910	2.726	139.0
	C2	H2	O11	1.020	2.530	2.951	104.0
	C12	H12 A	O13	1.090	2.370	3.426	164.0
5-EHQ	O11	H11	N1	0.977	2.508	2.794	96.6
	O11	H11	N1	0.977	2.053	2.905	144.6
	C2	H2	O11	1.024	2.547	3.061	110.6
	C3	H3	O13	1.015	2.403	3.329	151.2
5-PHQ	O11	H11	N1	0.840	2.280	2.750	116.0
	O11	H11	N1	0.840	2.220	2.850	132.0
	C2	H2	O11	0.930	2.520	3.034	115.0

Table 2: Hydrogen bonds for 8-hydroxyquinoline derivatives [Å and deg].

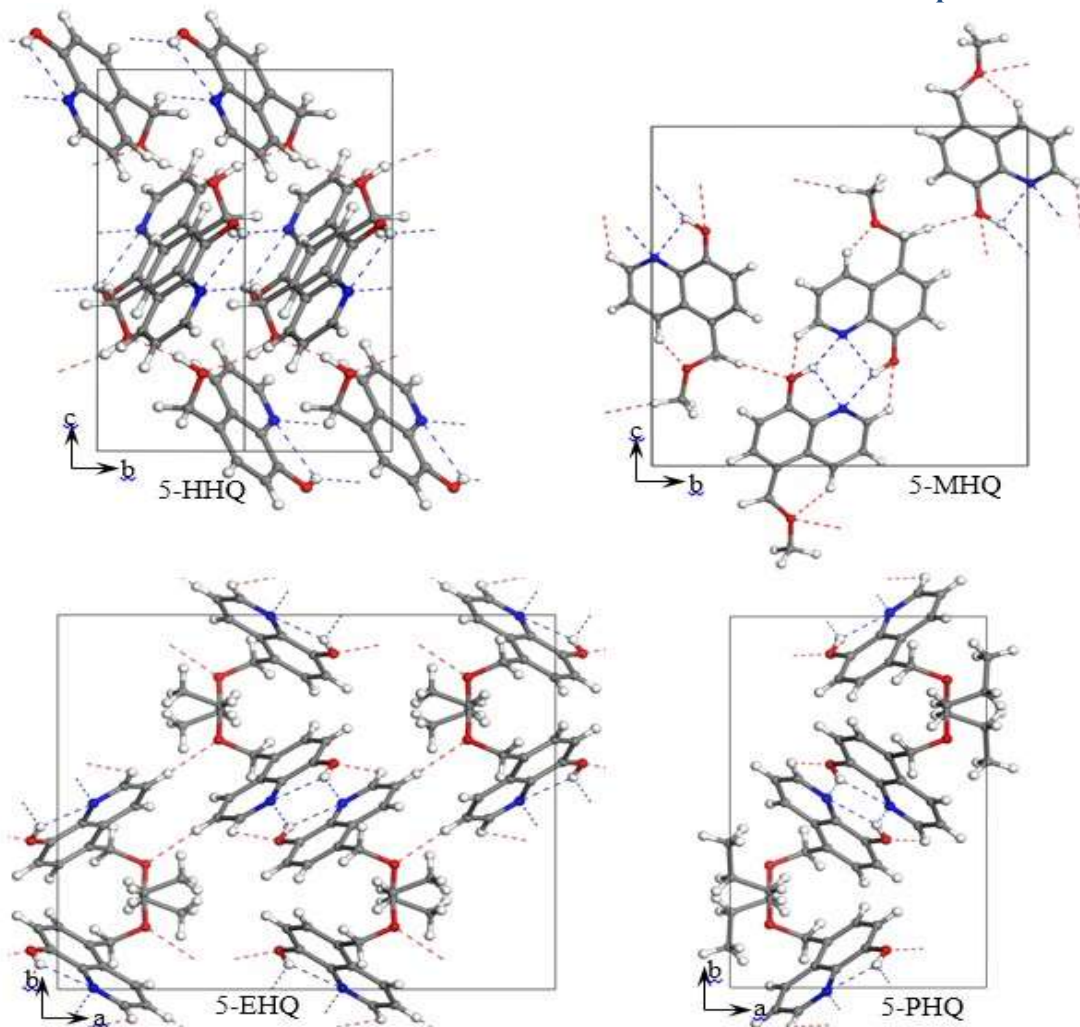


Fig. 5: Hydrogen Bonding contacts (dashed lines) in crystal lattice of selected derivatives: 5-MHQ along a, 5-MHQ along a, 5-EHQ along c and 5-PHQ along c.

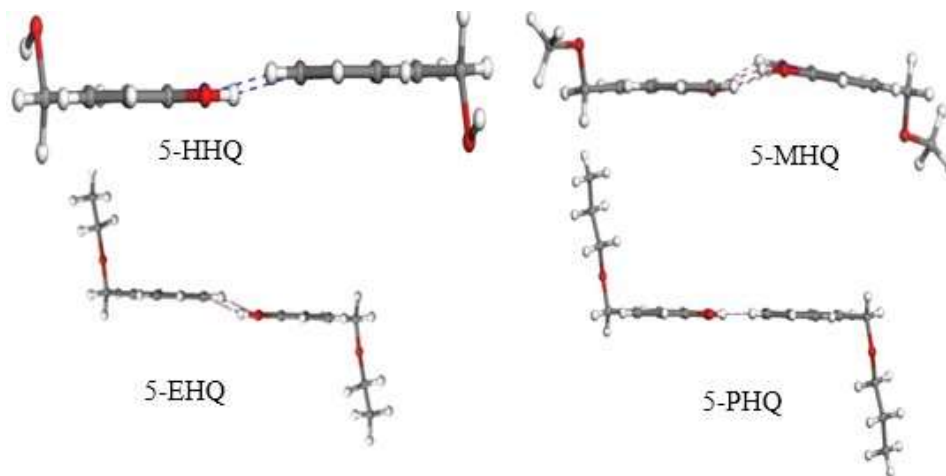


Fig. 6: Geometric display of the hydrogen bonds

The noncovalent and attractive π - π interactions play a very significant role in the orientation of the molecules. A detailed description of the factors, origins, strength and orientational dependence that contribute to π stacking interactions is not yet available. But they certainly govern molecular recognition and influence the structures. In this study, such interactions were detected between two 8-hydroxyquinoline rings within all studied derivatives. The centroid-centroid distance measured for all derivatives is similar, indicating, in this case, the independence of that interaction type of the molecule orientation and of the numbers of carbon atoms substituted to the oxygen at position 13. By increasing the number of torsions from 5-HHQ to 5-PHQ, centroid-centroid distances fluctuate between 3.4 and 3.5 Å, face-to-face, with a dihedral angle of 0° (Fig. 7). So we have C7-C10=3.558 Å and N1-C4=3.519 Å for 5-HHQ, C3-C6=3.500 Å and C4-C9=3.492 Å for 5-MHQ, C6-C7=3.478 Å and C4-C9=3.519 Å for 5-EHQ and C6-C7=3.547 Å and C4-C9=3.557 Å for 5-PHQ. Those values are similar to the values reported for other π - π interactions [22-23].

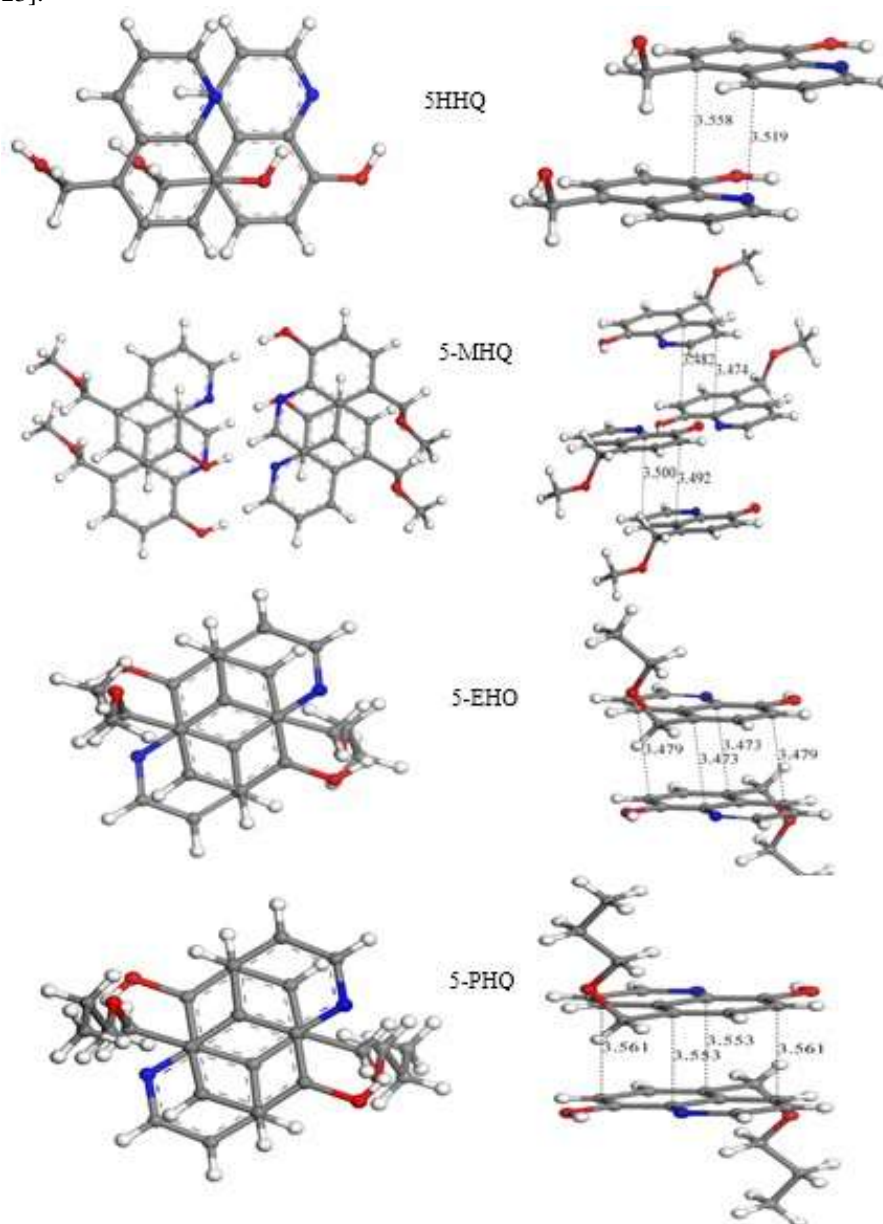


Fig. 7: Structure diagram of derivatives showing the intermolecular π - π stacking interactions between two 8-hydroxyquinolene rings.

Effect of the substituent on the absorption spectrum

The absorption spectra were performed using a spectrophotometer V-570JASCO. Fig. 8 represents UV-visible spectra of 5-EHQ and 5-PMQ molecules, dissolved in acetonitrile aprotic solvent ($\mu = 3.82$ D) and in ethanol, protic solvent ($\mu = 1.69$ D). The spectra showed an important transition for the two molecules located around 243nm, which assigned to the π - π^* transition, the maximal absorption is observed for 5-EHQ molecule who's containing only two torsions, for the same molecule, this absorption is strongly depends on the polarity of solvent. In the case of the 5-PHQ molecule, containing three torsions, this dependence is low, a slight deviation is observed around 216 nm transition. Whereas by comparing the spectra of molecules with substituents at O13, containing two different heteroatoms (O and N), such as 5-AHQ and 5-EHQ, the dependence of the solvent polarity becomes considerable (Fig. 9)

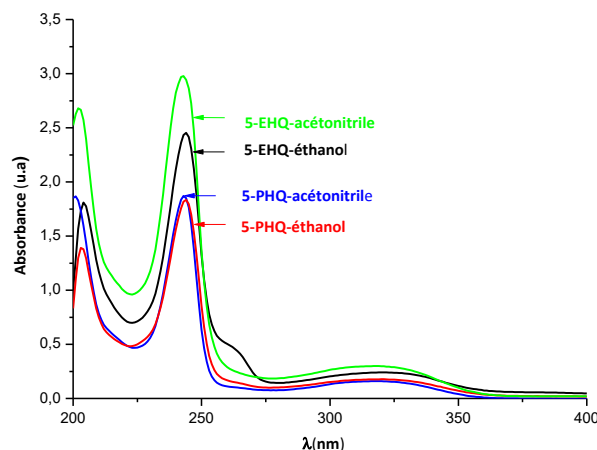


Fig. 8: The absorption spectra of 5-EHQ and 5-PHQ molecules in ethanol and acetonitrile.

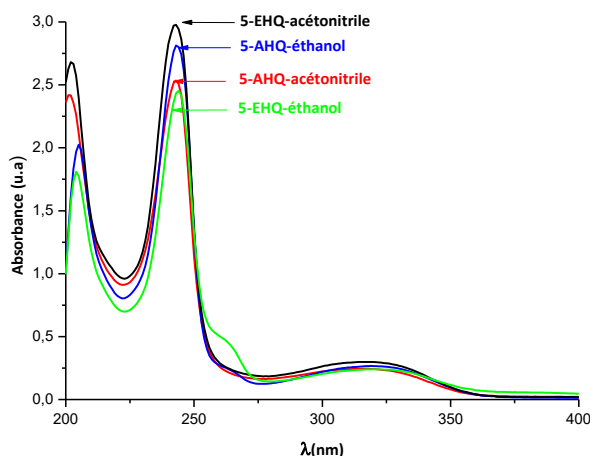


Fig. 9: The absorption spectra of 5-AHQ and 5-EMQ in ethanol and acetonitrile.

Theoretical study of the four 8-hydroxyquinoline derivatives

Geometric parameters

The calculations have been performed with Gaussian 03 program package at room temperature. Title compounds were subjected to density functional theory (DFT) and the approach of Hartree-Fock (HF) calculations in order to obtain the optimized geometrical parameters, with standard 6-311G (d,p) basis set. We reported in Table 3 only geometric values presenting some differences with experimental data. We observed that the bonds values obtained by calculations are slightly lower than those obtained by X-ray analysis. At the same time, values obtained by the HF approximation are lower than those estimated by the DFT method. As mentioned before [24-25], HF

approximation produced satisfactory results for geometric calculations but with errors due to neglect of electron correlations resulting in an underestimation depending on the size of molecule, so DFT calculations seems the most adapted calculation method for the selected derivatives.

By comparing the values obtained experimentally and that obtained by calculation, we note that the calculated values for molecules geometry (bond, angle, torsion) are slightly lower than crystallographic data. This difference is highlighted in the geometric parameters involving the atoms which acting in intra and intermolecular hydrogen bonding, such as oxygen and nitrogen (Table 2). Or these interactions are absent in optimized molecules, because the calculations refer to the isolated state, resulting in geometric conformations different from these given by X-ray analysis. Groups substituted at oxygen in position 13 for optimized derivatives are oriented in direction opposite to that obtained by X-ray diffraction. The greatest differences, between the crystallographic data and those optimized by DFT method, are noted at the C2-N1-C6 angle of 5-HHQ molecule where $\Delta\theta=4.7^\circ$, N1-C2-C3 of 5-EHQ molecule where $\Delta\theta=4.7^\circ$, N1-C6-C10 of 5-MHQ molecule where $\Delta\theta=4.1^\circ$, and O13-C12-C7 of 5-PHQ molecule where $\Delta\theta=2.6^\circ$

Geometric Parameters	X-rays				DFT			
	5-HHQ	5-MHQ	5-EHQ	5-PHQ	5-HHQ	5-MHQ	5-EHQ	5-PHQ
Bond (Å)								
C6-C10	1.411(5)	1.409(9)	1.406(5)	1.417(3)	1.434	1.430	1.433	1.4334
C7-C12	1.489(5)	1.485(9)	1.487(8)	1.510(4)	1.510	1.504	1.505	1.505
O13-C12	1.423(7)	1.434(9)	1.439(11)	1.432(3)	1.431	1.425	1.424	1.424
O13-C14	---	1.435(8)	1.434(10)	1.418(3)	--	1.414	1.421	1.421
Angle (°)								
C2-N1-C6	122.7(3)	123.0(6)	123.3(5)	117.17(18)	117.9	118.1	118.0	118.0
N1-C2-C3	119.5(3)	119.5(6)	119.0(5)	124.0(2)	123.7	122.9	123.7	123.7
N1-C6-C10	119.3(3)	119.9(5)	119.6(5)	117.6(17)	117.9	115.8	117.9	117.9
C5-C7-C12	122.4(4)	123.2(5)	122.5(6)	120.7(19)	121.5	121.9	120.3	121.4
O13-C12-C7	112.7(4)	108.6(5)	112.2(5)	113.1(2)	114.5	110.4	110.5	110.4
O13-C14-C15	---	---	108.9(8)	110.3(2)	--	---	108.5	108.8
C12-O13-C14	--	114.9(7)	116.9(7)	113.5(19)	---	112.4	112.9	113.0
Torsion(°)								
C14-O13-C12 -C7	---	-168.0(6)	77.1(13)	-68.7(3)	--	178.5	-178.6	-178.3
C5-C7-C12-O13	64.9(5)	66.1(8)	62.7(8)	-68.9(3)	-59.5	62.6	-65.2	-65.2
Geometric Parameters	HF							
	5-HHQ	5-MHQ	5-EHQ	5-PHQ				
Bond (Å)								
C6-C10	1.434	1.428	1.433	1.433				
C7-C12	1.511	1.506	1.506	1.506				
O13-C12	1.405	1.398	1.398	1.398				
O13-C14	--	1.393	1.398	1.398				
Angle (°)								
C2-N1-C6	118.5	118.6	118.6	118.6				
N1-C2-C3	123.6	123.1	123.5	123.5				
N1-C6-C10	117.8	116.3	117.8	117.8				
C5-C7-C12	121.4	121.4	121.5	121.5				
O13-C12-C7	113.8	110.6	110.6	110.5				
O13-C14-C15	--	---	108.8	109.3				
C12-O13-C14	--	113.9	114.4	114.5				
Torsion(°)								
C14-O13-C12 -C7	---	178.1	-178.4	-178.6				
C5-C7-C12-O13	-61.4	63.5	-65.3	-65.4				

Table 3: Principal geometry parameters for studied derivatives given by X-ray analysis, DFT/B3LYP/6-311G (d,p) and HF/6-311G(d,p) calculations.

Calculation of orbital molecular HOMO-LUMO energies

The molecular orbital theory is one of the best theories to explain the chemical stability of a molecule. A small HOMO-LUMO gap indicates a significant charge transfer within the molecule. In our case, the energy band gap of the derivatives studied is about 4.46 eV in the isolated state, 4.46 eV in acetonitrile and 4.39 eV in ethanol (Table 4). These values are relatively low, and imply high reactivity which is the result of a significant degree of ICT from phenol group to the pyridine group through π conjugated path. This transfer is illustrated by the HOMO-LUMO surfaces and the result is consistent with the values and orientation of the dipole moments and the appearance of a charge transfer band in the electronic absorption spectrum (Fig. 8 and 9). The theoretical study confirms that regardless of the number of added carbon in position 13 of 8-hydroxyquinoline derivatives, these latter are easily polarizable and presents a high biological activity. Optimized molecules, HOMO-LUMO surfaces and dipole moments are reported in Table 5.

Molecules	Fundamental energy and gap at isolated state (eV)	Fundamental energy and gap in acetonitrile	Fundamental energy and gap in ethanol
5-HHQ	$E_f = -16104.68$ $\Delta E_{\text{HOMO-LUMO}} = 4.465$	$E_f = -17175.018$ $\Delta E_{\text{HOMO-LUMO}} = 4.465$	$E_f = -17175.014$ $\Delta E_{\text{HOMO-LUMO}} = 4.301$
5-MHQ	$E_f = -17174.81$ $\Delta E_{\text{HOMO-LUMO}} = 4.468$	$E_f = -16105.072$ $\Delta E_{\text{HOMO-LUMO}} = 4.412$	$E_f = -16105.064$ $\Delta E_{\text{HOMO-LUMO}} = 4.414$
5-EHQ	$E_f = -18244.66$ $\Delta E_{\text{HOMO-LUMO}} = 4.463$	$E_f = -19315.119$ $\Delta E_{\text{HOMO-LUMO}} = 4.428$	$E_f = -19315.111$ $\Delta E_{\text{HOMO-LUMO}} = 4.429$
5-PHQ	$E_f = -19314.75$ $\Delta E_{\text{HOMO-LUMO}} = 4.464$	$E_f = -18245.024$ $\Delta E_{\text{HOMO-LUMO}} = 4.427$	$E_f = -18245.016$ $\Delta E_{\text{HOMO-LUMO}} = 4.428$

Table 4: Fundamental energy and HOMO-LUMO gap (eV) for the 8-hydroxyquinoline derivatives.




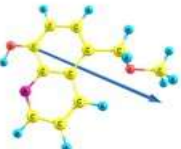


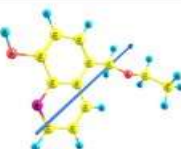


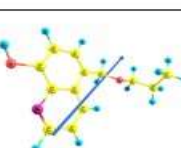


Molecules	Optimized molecules	Dipole moments (Debye)	HOMO	LUMO
5-HHQ		2.33		
5-MHQ		3.19		
5-EHQ		3.03		
5-PHQ		2.92		

Table 5: Display of optimized molecules and HOMO-LUMO surfaces, obtained by DFT (B3LYP), for the studies 8-hydroxyquinoline derivatives.

Charges distribution within 8-hydroxyquinoleine derivatives

The binding capacity and the molecular conformation are greatly depending on the electric charges of the atoms. [26-28]. Fig. 10 represents the calculated charge distribution compared to that obtained by X-ray analysis for all derivatives studied, the atoms N1, O11 and O13 presents a strong electronegativity in both cases; calculated values and those obtained by experiment.

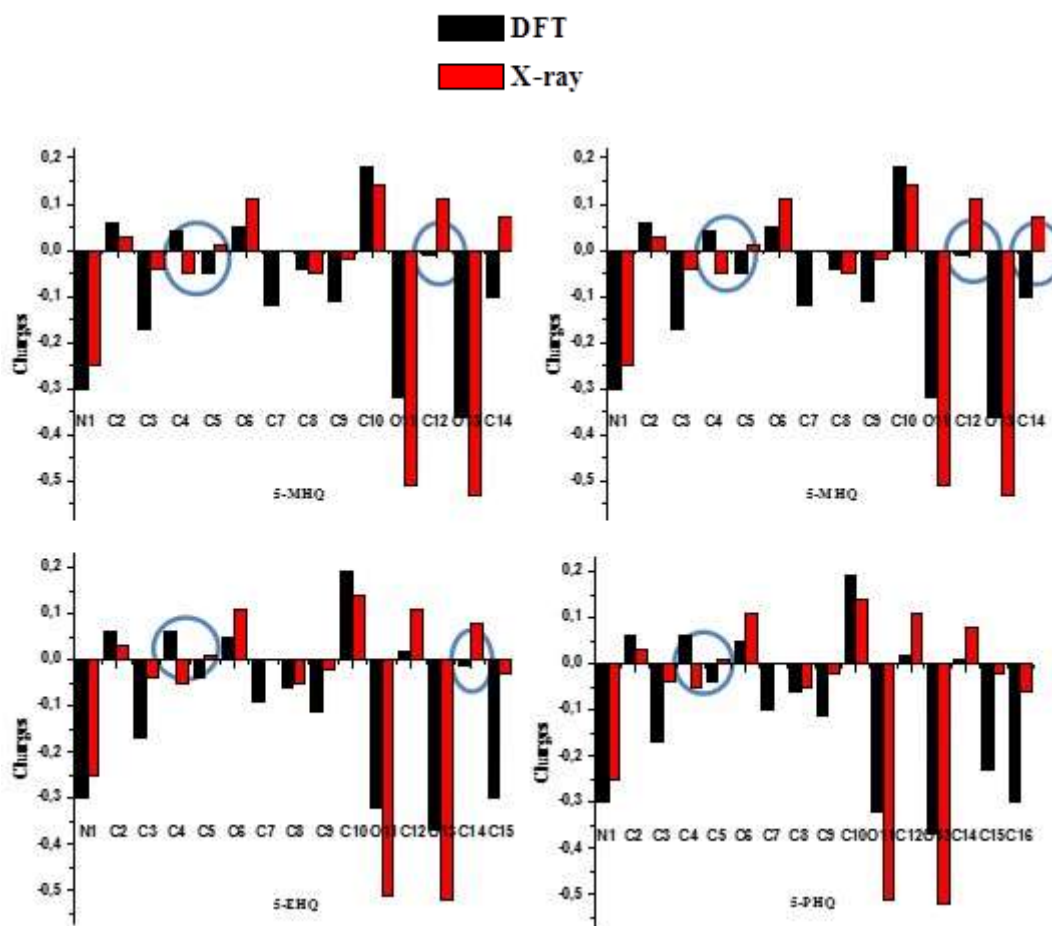


Fig. 10: The atomic charges for 5-HHQ, 5-MHQ, 5-EHQ and 5-PHQ molecules.

The Millikan charges for other atoms appear to be in good agreement. Whereas, a slight disagreements are found between the calculations and X-ray analysis for C4, C5, C12 and C14 atoms where the calculated charge values show opposite signs to those obtained by X-ray analysis. This behavior can be explained by the fact, that the neighboring atoms: C2, C3 and O13 are involved in moderate intermolecular bonding thus influencing the charge distribution at these atoms. This influence is very important in the molecules 5-PHQ, where such disagreement appears only at C4 and C5 molecules. Because the hydrogen bond that can influence the distribution at C12 and C14, are absent in this derivative (Fig. 5)

The representation of the energy to the ground state as a function of carbon number added at position 13 (Fig. 11) shows that this energy decreases gradually as the number of carbon added increases, suggesting that the stability of geometrical conformation became higher by increasing the number of twists in the molecules. Or this energy in both solvents (acetonitrile and methanol) varies randomly as we add carbon atoms. This can be attributed to the fact that the substituents containing only carbon atoms and does not influence the electronegativity of these molecules,

resulting in a weak intra and inter interaction effect this justifies the comparable values of HOMO-LUMO gap for all studied derivatives.

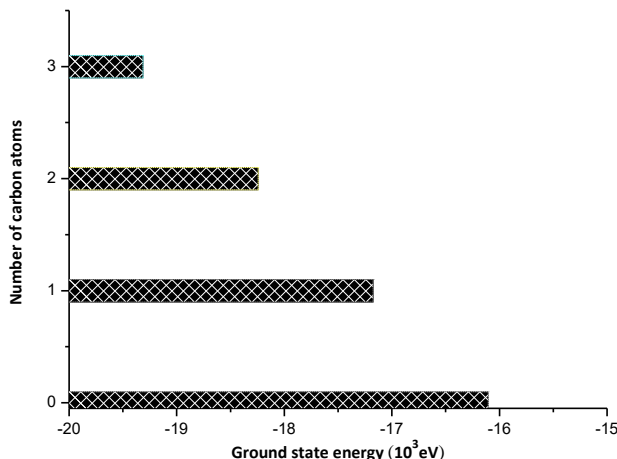


Fig.11: The ground state energy as a function of carbon number added at position 13 of 5-HHQ molecule.

CONCLUSION

This review was focused on the experimental and theoretical study of four 8-hydroxyquinoline derivatives, to conclude about the reactivity of these molecules, for biological and pharmaceutical applications. XRD investigation showed that the cohesion and the stability of the structures are insured by three different kinds of intermolecular moderate hydrogen bonding interactions OH...N, CH...O, OH...O and weak intramolecular hydrogen bonding interactions. The π - π stacking system is independent of the geometric conformations of the studied derivatives.

Based on theoretical investigation, we indicate that some differences on geometric parameters may be noticed between DFT(B3LYP) and X-rays analysis data. Those differences resulted in a slight disagreement between the absorption energy performed in ethanol and acetonitrile and HOMO-LUMO energy calculated in the same solvents. The low values of the HOMO-LUMO gap of these molecules in the ground state and the existence of weak intramolecular hydrogen bond involving the OH group revealed a high reactivity of all 8-hydroxyquinoline derivatives considered.

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