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Experimental and theoretical study of the structural and spectroscopic properties of Quinoxalin-2[1H]-one molecule at room temperature in its ground state

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Abstract

In this work, we present an experimental study of quinoxalin-2-[1H]-one molecule by UV-visible absorption and emission spectroscopy at room temperature in polar solvents. This study is complemented by calculations of conformational, charge distribution, energy properties and electronic transitions positions of the molecule in the ground state using AM1 and ZINDO semi- empirical methods.

Keywords: Quinoxalin-2-[1H]-one, Absorption, Emission, Conformation, Charges distribution, Solute-solvent interactions.

1. Introduction

Quinoxaline and its derivatives have attracted significant interest in the biological and pharmaceutical fields [1-6]. The synthesis of this molecule and some derivatives has attracted the attention of chemists over the past decade [7]. Quinoxalin-2-[1H]-one (Figure 1) is an example of these molecules. It is composed of two rings: one is aromatic and the other containing two nitrogen atoms and C=O bond. In the literature, to our knowledge, no specific study has been made on structural and spectroscopic properties of this molecule. In this work, we present an experimental study on the UV-visible absorption and emission of quinoxalin-2-[1H]-one molecule in different solvents (acetonitrile, ethanol and water). We also present theoretical results concerning the geometry, the charge distribution in this molecule at the ground state and the electronic transitions positions.

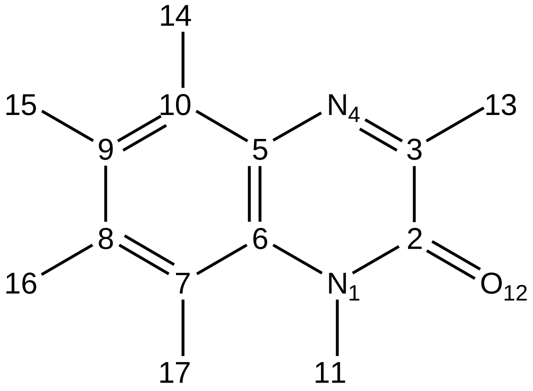

Figure 1: Structure of quinoxalin-2-[1H]-one molecule.

2. Materials and Methods

2[1H]-quinoxalinones was prepared by adopting Hong's method [8] which consists of the reaction of 1, 2-o-phenylenediamine and glyoxilic acid in refluxing n-butanol. The structure of pure compound was characterized on the basis of ^{1}H NMR and IR spectral analysis. The absorption spectra were performed using a spectrophotometer V-570JASCO and the emission spectra are made with a spectrofluorophotometer RF-5301 PC SHIMADZU. They are recorded at room temperature for a solute concentration of 10^{-4} M. The theoretical calculations are made with Gaussian 03 [9].

3. Results and discussion

3.1. Experimental part

Absorption spectra of quinoxalin-2-[1H]-one molecule in different solvents at room temperature are shown in Figure 2. The absorption spectrum in acetonitrile (very polar solvent) shows three absorption bands located at almost 230nm, 280nm and 340nm. It is shifted towards low energies passing to ethanol and water (protic solvents) especially for the band located around 280nm. An absorption appears at 251nm in water. This is in agreement with the indication given in the reference [10].

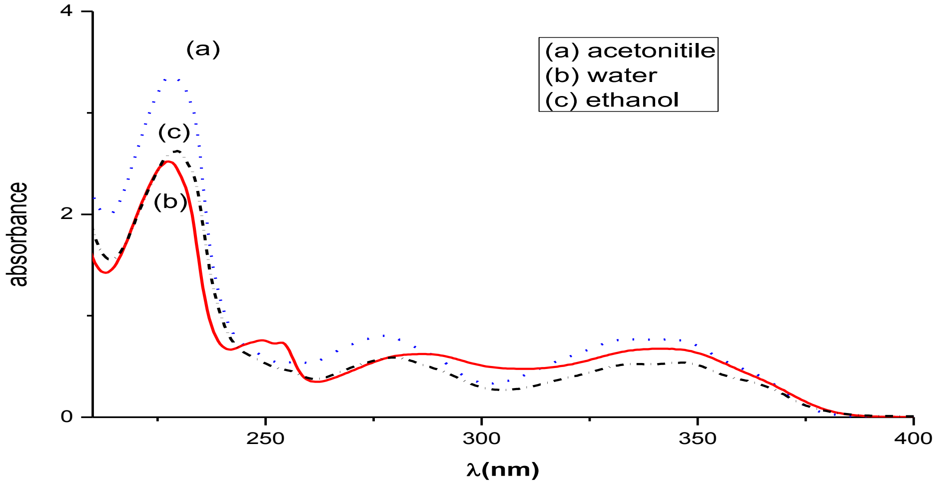

Figure 2: Absorption spectra of quinoxalin-2[1H]-one in various solvents at room temperature.

Figure 3 represents the emission spectra in various solvents at room temperature. This figure shows an emission between 360nm and 540nm.The maximum of emission in acetonitrile is located at 409nm. Bathochromic shifts of 354cm $^{-1}$ and 920cm $^{-1}$ are evaluated respectively for ethanol and water. The emission spectrum in water is less structured than those in the acetonitrile and ethanol solvents.

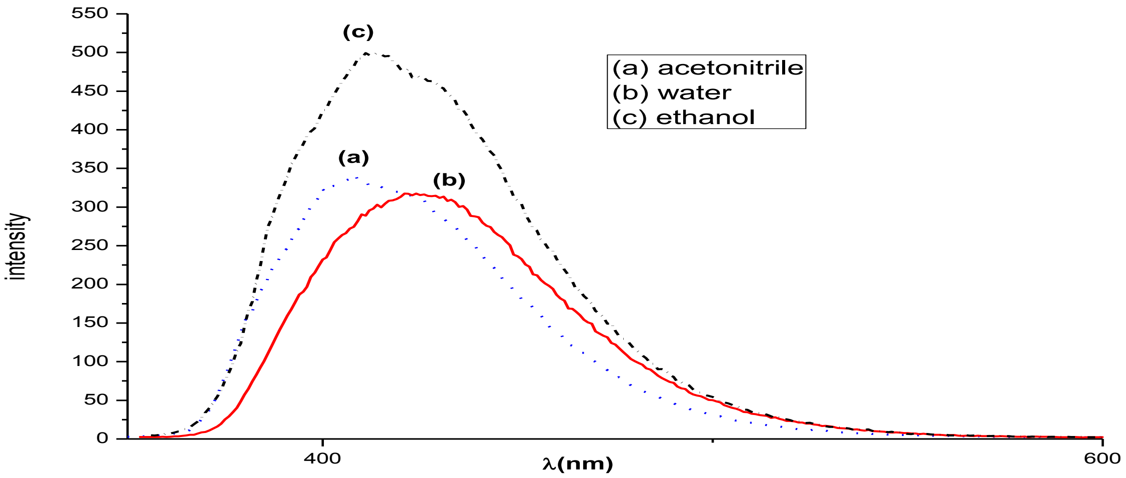

Figure 3: Emission spectra of quinoxalin-2-[1H]-one in various solvents at room temperature.

The displacements of the emission spectra in ethanol and in water can be attributed to tautomeric form and the formation of complexes by hydrogen bonding between solute and solvent molecules. The types of these complexes can be OH… π or NH… O. It was shown in former works [11-13] that these bonds are responsible of bathochromic shifts and stabilization of molecular systems.

3.2. Theoretical part

The optimization of quinoxalin-2-[1H]-one molecule geometry in its ground state is carried out using the AM1 method. This method gave good results in similar works [14-15]. The geometric parameters (bond lengths and valence angles) of the quinoxalin-2-[1H]-one molecule in ground state are reported in Table 1.

The aromatic ring presents an hexagonal regular geometry with bond lengths C-C around 1,4 Å except the C7-C8 and C9-C10 bonds (1.383Å). The valence angles are close to 120° except for the C10-C5-C6 angle. In the heterocyclic, the valence angles are different, in particular on the level of the atoms located near the C=O bond. The N1-C2-C3 and C2-C3-N4 angles values are 115.546° and 124.881° respectively.

Table 1: Bond lengths (Å) and valence angles (degree) values of the quinoxalin-2(1H)-one molecule in ground state.

Bond lengths (Å)		Valence angles (°)	
N1-C2	1.397	N1-C2-C3	115.546
C6-N1	1.393	C6-N1-C2	120.928
C2-C3	1.494	C2-C3-N4	124.881
C2-O12	1.242	C3-N4-C5	118.161
C3-N4	1.294	N4-C5-C6	121.230
N4-C5	1.405	C5-C6-N1	119.251
C5-C6	1.435	C5-C6-C7	119.446
C10-C5	1.413	C6-C7-C8	119.921
C6-C7	1.415	C7-C8-C9	120.834
C7-C8	1.383	C8-C9-C10	120.513
C8-C9	1.401	C9-C10-C5	120.459
C9-C10	1.383	C10-C5-C6	118.825
		N1-C6-C7	121.302
		N4-C5-C10	119.944

We also determined by the AM1 method, the charge distribution within quinoxaline-2-[1H]-one molecule in ground state (Figure 4). The obtained value of the dipolar moment of this molecule is 3.5161 Debye. This value is close to those found for similar molecules as quinoxalinedione and 7,10-Dimethylquinoxalinedione and it's very greater compared to quinoxaline dipolar moment [3, 15].

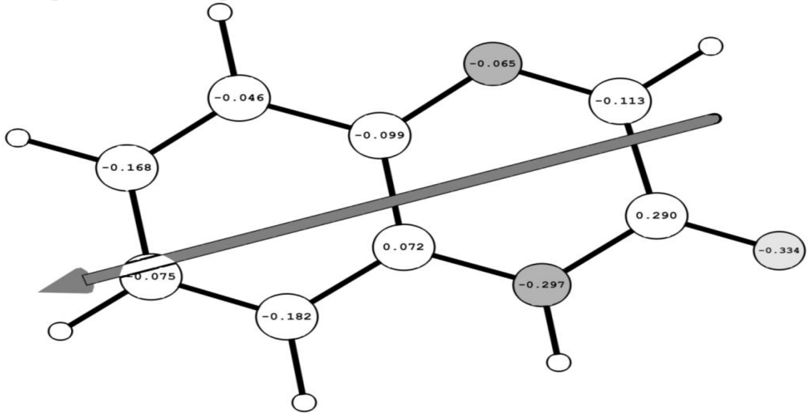

Figure 4: Charge distribution for quinoxalin-2[1H]-one molecule and representation of dipolar moment direction in the ground state.

The Figure 4 indicates that the C2 atom presents a positive value of 0,290e. This is due to its juxtaposition with O12 oxygen atom of charge with -0,33e. The C6 atom also present a positive value 0,07e due to its proximity of N1 nitrogen atom and C=O bond (electron attracting). The great value of the quinoxalin-2-[1H]-one dipolar moment and the charges on the nitrogen atoms and the carbon atom in the C=O bond can explain the strong interaction of this molecule with its environment.

In Table 2, we reported the positions of maxima absorption bands obtained experimentally by UV-visible spectroscopy and those obtained theoretically by AM1 method for quinoxalin-2-[1H]-one molecule in the considered solvents.

Table 2: Experimental (exp.) and calculated (cal.) values (eV) of the absorption bands maxima for quinoxalin-2-[1H]-one molecule in various solvents.

isolated molecule	Acetonirile		Ethanol		water	
cal.	exp.	cal.	exp.	cal.	exp.	cal.
3.62	3.71	4.13	3.58	4.12	3.65	3.62
4.28	4.48	4.66	4.43	4.64	4.48	4.26
4.94	-----	---	----	---	4.94	4.94
5.71	5.41	5.41	5.41	5.39	5.46	5.69

The obtained theoretical values for electronic transitions are qualitatively in agreement with the absorption spectra recorded in various solvents especially in the case of the quinoxalin-2-[1H]-one in water for which we find the absorption around 251nm.

Conclusion

In this work, we studied the UV-visible absorption and emission of quinoxalin-2-[1H]-one molecule. The spectra show a strong interaction between this molecule and the solvent. The modifications of the spectra are more important in the case of complex formations by hydrogen bonding. The theoretical study allowed the determination of the geometry and the charge distribution within the molecule at the ground state, as well as the positions of absorption bands maxima in the considered solvents.

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