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Theoretical and experimental investigations of structural and electronic properties of 1-Benzyl-3-methyl-quinoxalin-2(1H)-one molecule

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- ✓ DFT,
- ✓ TD-DFT.

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Abstract

In this work, the molecular properties of 1-Benzyl-3-methyl-quinoxalin-2(1H)-one molecule have been investigated by DFT at B3LYP/ 6-31G (d,p). Optimized geometry, HOMO-LUMO analysis, molecular electrostatic potential (MEP), dipole moment and atomic charges of this molecule have been calculated. The theoretical geometric parameters values are in agreement with experimental values. UV absorption spectra (in the gas phase and in solution) of this molecule have been investigated by TD-DFT approach. The study shows high charge transfer within the molecule and high reactivity which permits to this molecule to be used as bioactive compound.

1. Introduction

Quinoxaline and its derivatives have received a great deal of interest from researchers owing to their biological properties [1-2] such as antimicrobial, antitumor [3], and anti-tuberculous [4]. They also present antifungal, herbicidal, anti-dyslipidemic and anti-oxidative activities [5-7]. Quinoxaline nucleus forms the building block of some well known components of therapeutic products.

Literature survey reveals the absence theoretical study for 1-Benzyl-3-methylquinoxalin-2(1H)-one (BMQ=O) (see figure1). In this work, we mainly focus on the detailed geometric properties based on the DFT calculations. The study of HOMO and LUMO analysis has been used to explain the information regarding the charge transfer within the molecule. The corresponding UV absorption spectrum and the electronic properties were illustrated and connected to the frontier molecular orbitals.

The theoretical molecular geometry results have been compared to X-ray experiment data [8]. The TD-DFT calculations were carried out using the CAM-B3LYP functional to determine the maximum wavelengths of the UV absorption spectra for the title compound. Besides, DFT calculations of the molecular electrostatic potential and natural bond orbital analyses were performed at B3LYP/6-31G(d,p) level of theory.

2. Computational methods

Density Functional Theory (DFT) [9-12] has proven to be a very useful implement in investigating the electronic and geometric structure of the molecules. The calculation of BMQ=O has been done to analyze its optimized ground state geometry using B3LYP level of theory with the 6-31G (d,p) basis set [13]. The absorption spectra of BMQ=O were carried out using time dependent density functional theory (TD-DFT) method based on the optimized ground state structures and the lowest singlet excited state structures, respectively.

Solvent effects were also taken into account by using the Conductor Polarizable Continuum Model (CPCM) [14-16]. Electronic spectrum along with HOMO-LUMO energies [17-19], of the title compound has been investigated using TD-DFT approach with CAM-B3LYP level of theory. All calculations are provided by Gaussian 03 program [20]. Density of states (DOS) [21] which provide the molecular orbital contribution of different constituting elements to the total system is calculated by using the output of Gaussian package in the free Gauss-Sum 3.0 python program [22].

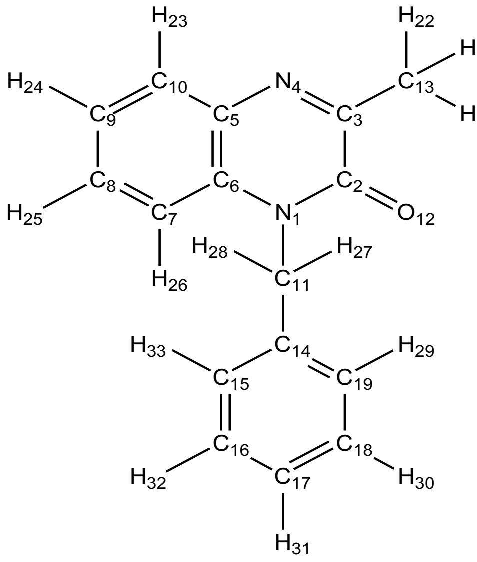

Figure 1: Numbering of the atoms for BMQ=O.

3. Results and discussion

In Table 1 we report our results concerning the optimized structural parameters (bond distances and angles) obtained by DFT (B3LYP) for BMQ=O molecule and crystal structure data from reference [8]. The global minimum energy is calculated to be -21848. 80 eV.

Table 1: Optimized geometrical parameters of BMQ=O molecule obtained by B3LYP/6-31G (d, p), X-ray data analysis [8].

Lengths(Å)	DFT	X-Ray	**Angles (°)**	DFT	X-Ray
N1-C2	1.393	1.375 (2)	C2-N1-C6	121.53	121.79 (13)
N1-C6	1.395	1.3996 (19)	C2-N1-C11	116.87	117.13 (14)
N1-C11	1.476	1.462 (2)	C6-N1-C11	121.58	121.08 (14)
C2-C3	1.486	1.472 (2)	N1-C2-C3	115.61	115.74 (13)
C2-O12	1.231	1.2251 (18)	N1-C2-O12	122.11	122.09 (16)
C3-N4	1.295	1.288 (2)	C3-C2-O12	122.28	122.16 (17)
C3-C13	1.499	1.495 (2)	C2-C3-N4	123.65	123.73 (14)
N4-C5	1.385	1.3891 (19)	C2-C3-C13	116.03	116.91 (16)
C5-C6	1.418	1.398 (2)	N4-C3-C13	120.37	119.35 (16)
C5-C10	1.405	1.393 (2)	C3-N4-C5	118.95	118.81 (13)
C6-C7	1.406	1.397 (2)	N4-C5-C6	122.29	122.21 (13)
C7-C8	1.389	1.374 (2)	N4-C5-C10	118.18	118.22 (14)
C8-C9	1.402	1.381 (3)	C6-C5-C10	119.53	119.57 (14)
C9-C10	1.385	1.369 (2)	N1-C6-C5	117.90	117.70 (13)
C11-C14	1.517	1.512 (2)	N1-C6-C7	122.85	122.91 (14)
C14-C15	1.402	1.374 (2)	C5-C6-C7	119.25	119.38 (15)
C14-C19	1.399	1.382 (2)	C6-C7-C8	119.95	119.25 (17)
C15-C16	1.393	1.385 (3)	C7-C8-C9	121.09	121.61 (17)
C16-C17	1.397	1.355 (3)	C8-C9-C10	119.32	119.15 (17)
C17-C18	1.394	1.357 (4)	C5-C10-C9	120.84	121.00 (17)
C18-C19	1.396	1.388 (3)	N1-C11-C14	114.53	113.91 (14)
			C11-C14-C15	120.46	122.77 (14)
			C11-C14-C19	120.54	118.90 (16)
			C15-C14-C19	118.96	118.34 (17)
			C14-C15-C16	120.35	120.60 (19)
			C15-C16-C17	120.33	120.7 (2)
			C16-C17-C18	119.67	119.4 (2)
			C17-C18-C19	119.96	120.9 (2)
			C14-C19-C18	120.73	120.0 (2)

The dipolar moment of this molecule is evaluated to be 2.9139 Debye, close to those found for similar molecules such as Quinoxalin-2[1H]-one and it's very greater compared to Quinoxaline dipolar moment [1-3].

The calculated bond lengths and angles values of BMQ=O are in agreement with previously reported values determined by X-ray diffraction measurements [8].

The biggest difference between calculation and experience is observed for C14-C15 bonds lengths and C11-C14-C15 bonds angles. These disparities can be linked to the fact that calculations relate to the isolated molecule, conversely experimental results which correspond to interacting molecules in the crystal lattice where intra and intermolecular interactions with the neighboring molecules are present [23].

The calculations indicate that Quinoxaline and Phenyl nucleus are not located in the same plane. The dihedral angles C2-N1-C11-C14, C6-N1-C11-C14, N1-C11-C14-C15 and N1-C11-C14-C19 are equals to -100.65°, 80.77°, 55.82° and -126.44° respectively.

Mulliken population analysis

Mulliken population analysis [24] is carried out for BMQ=O with B3LYP level using 6-31G (d, p) basis set. The Mulliken atomic charge calculation is one of the most important properties of molecular systems [25-26]. For their determination the B3LYP method in combination with the 6-31G (d,p) basis sets is used. The results represented in Table 2 and in figure 2.

It is important to mention that C2, C3, C5, C6 and C14 atoms of BQM=O present positive charge, while N1, N4, C7, C8, C9, C10,C11, C12, C13, C15, C16, C17, C18 and C19 atoms exhibit negative charges. However, nitrogen atom N1 carries the largest negative charge in studied molecule. It shows a higher negative charge than that on N4.

Table 2: *Mulliken atomic charges of BQM=O determined by DFT using B3LYP theory level at 6-31G (d, p) basis set.*

Mulliken atomic charges			
Atoms	Charges	Atoms	Charges
N1	-0.578266	C10	-0.099152
C2	0.585690	C11	-0.149498
C3	0.226090	O12	-0.541492
N4	-0.512433	C13	-0.352306
C5	0.215352	C14	0.126821
C6	0.354580	C15	-0.114537
C7	-0.110291	C16	-0.084995
C8	-0.095516	C17	-0.083633
C9	-0.092411	C18	-0.085315
		C19	-0.127866

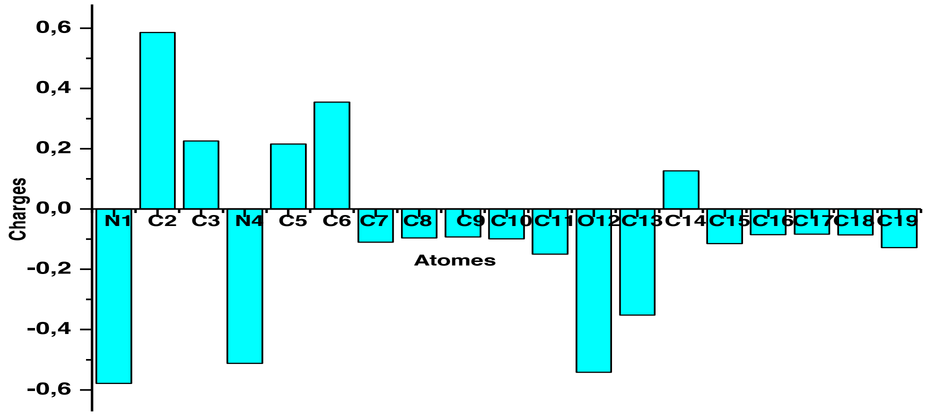

Figure 2: *Mulliken population analysis of BMQ=O.*

Molecular electrostatic potentials (MEP)

Molecular electrostatic used broadly for interpreting potentials have been provided the reactive behavior of a wide variety of chemical system in both electrophilic and nucleophilic reactions, the study of biological reconnaissance processes and hydrogen bonding interactions [27-28]. The different values of the electrostatic potential at the surface correspond to different colors; red designated regions of most electro negative electrostatic potential, blue represents regions of the most positive electrostatic potential and green represents region of zero potential. Potential decreases in the order red<orange<yellow<green<blue [29]. To predict reactive sites for electrophilic and nucleophilic attack for the studied compound, molecular electrostatic potential (MEP) surfaces were carried out by B3LYP/6-31G (d, p) optimized geometries using the computer software Gauss view. The MEP surface gives necessary information about the reactive sites. The electron total density onto which the electrostatic potential surface has been mapped is shown in figure 3. This figure envisages a visual representation of the chemically active sites and comparative reactivity of atoms [30-31]. So, figure 3 favors the existence of the intra and intermolecular C–H...O and C-H…N hydrogen-bonding [8].

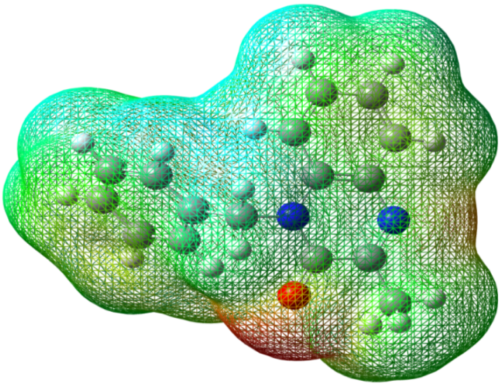

Figure 3: *Molecular electrostatic potential (MEPs) map of BQM=O calculated at B3LYP/6-31 G (d, p) method and basis set*

Frontier molecular orbitals (FMOs)

The HOMO and LUMO energies are predicted at B3LYP method with 6-31G (d, p) basis sets (see table 3). Accordingly, the BQM=O molecule contains 66 occupied molecular orbitals and 289 unoccupied virtual molecular orbital.The positive phase is represented in red color and the negative phase is represented in green color. The HOMO-LUMO energy gap was calculated to be 4.39 eV, greater than that obtained for 5-ethoxymethyl-8-hydroxyquinoline [23]. Besides, Gauss-Sum 3.0 Program [19, 31, 33] was used to calculate group contributions to prepare, the density of the state (DOS) as shown with the frontier molecular orbitals illustrated in figure 4.

Table 3: *The calculated frontier orbital energies, global energy and dipolar moment of compound using B3LYP/6-31G (d, p) level.*

B3LYP/6-31G (d,p)	
E_{HOMO} (eV)	-6.09
E_{LUMO} (eV)	-1.70
Energy gap (eV)	4.39
Global energy (eV)	-21848.80
Dipolar moment (Debye)	2.9139

UV-spectral analysis

The UV spectral analysis of BMQ=O has been carried out by TD-DFT/CAM B3LYP/6-31G (d, p) method (see table 4). The UV absorption spectra of BMQ=O is reported in figure 5 in gas phase and in four solvents: water, acetonitrile, ethanol and DMSO. The calculated results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out. Typically, according to Frank-Condon principle, the maximum absorption (λ_{max}) correspond in UV spectrum to vertical excitation TD-DFT/CAM B3LYP/6-31G (d,p) predict intense electronic transition at 291.15, 295.27, 295.33, 295.44 and 295.86 nm with oscillator strengths f = 0.1712, 0.2326, 0.2345, 0.2372 and 0.2444 for gas phase, water, acetonitrile, ethanol and DMSO respectively. The most intense contribution to the main band is an excitation from the HOMO to LUMO orbital in solvent as the second singlet excitation. Moreover, theoretical gas phase wavelength is found to be lower than theoretical wavelength in different solvent. In ethanol, the excitations are at 295.44 nm and 252.02 nm show an agreement with the experimental spectrum obtained by Anothane [34].

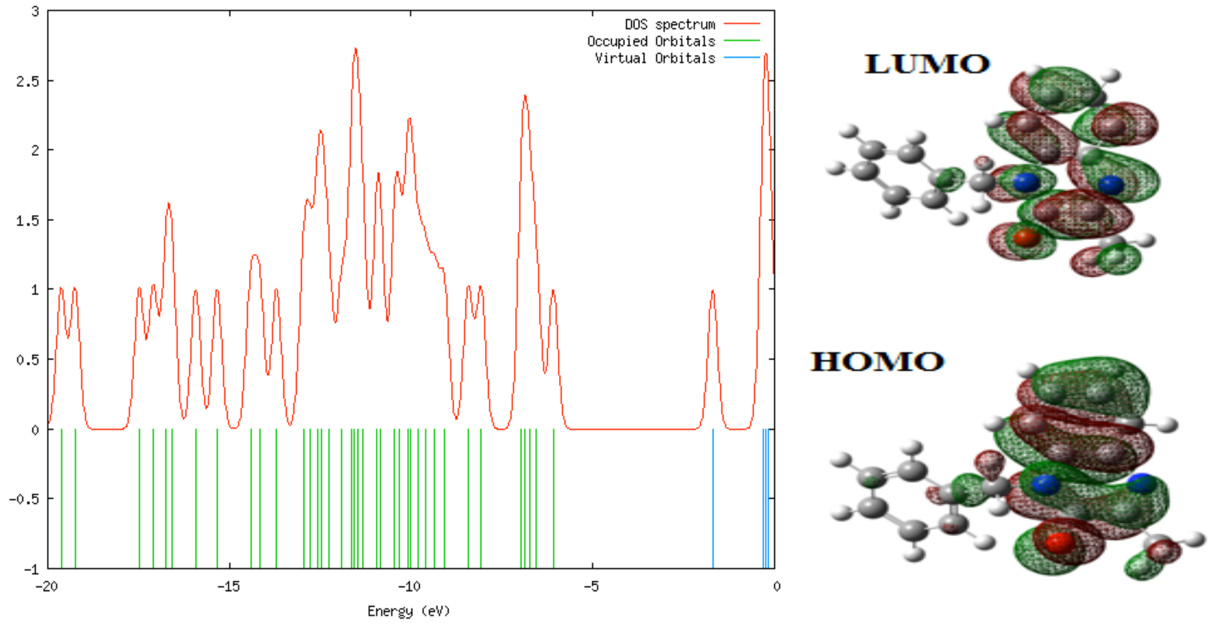

Figure 4: *Calculated total electronic density of states diagram and orbital frontiers of the title compound.*

Table 4: *Electronic Energy, wavelengths and oscillator strengths calculated by TD-DFT/CAMB3LYP/6-31G (d,p) for BMQ=O.*

Solvent	Energy (cm^{-1})	Wavelength λ (nm)	Osc. Strength	Symmetry	Major contribs
Gas phase	34345.74	291.15	0.1712	Singlet-A	HOMO->LUMO (92%)
	40241.69	248.49	0.0961	Singlet-A	H-2->LUMO (53%), H-1->LUMO (25%)
DMSO	33798.89	295.86	0.2444	Singlet-A	HOMO->LUMO (91%)
	39638.39	252.28	0.1504	Singlet-A	H-2->LUMO (44%), H-1->LUMO (40%)
Water	33866.64	295.27	0.2326	Singlet-A	HOMO->LUMO (91%)
	39678.71	252.02	0.1429	Singlet-A	H-2->LUMO (44%), H-1->LUMO (40%)
Acetonitrile	33859.38	295.33	0.2345	Singlet-A	HOMO->LUMO (91%)
	39681.13	252	0.1437	Singlet-A	H-2->LUMO (44%), H-1->LUMO (40%)
Ethanol	33847.29	295.44	0.2372	Singlet-A	HOMO->LUMO (91%)
	39678.71	252.02	0.1451	Singlet-A	H-2->LUMO (44%), H-1->LUMO (39%)

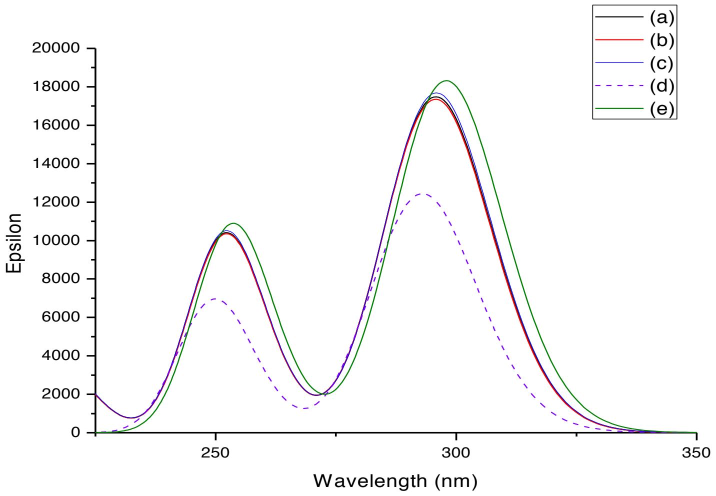

Figure 5: *Theoretical electronic absorption spectra of BMQ=O: (a) in acetonitrile, (b) in water, (c) in ethanol, (d) in gas phase, (e) in DMSO.*

The absorption spectra show similar profile for all solvents and gas phase. But in solvent, the spectra exhibit a bathochromic shift in comparison with the spectrum in gas phase. The two observed bands are assigned to (π-π*) transitions, as indicated by their high molar extinction coefficient values (ε = 5000-25.000).

Conclusion

This work provided an original study of the structural and energetic properties of 1-Benzyl-3-methylquinoxalin-2(1H)-one using the DFT/B3LYP method with the 6-31G (d, p) basis set. The results show that the DFT geometric parameters are in agreement with experimental data.The small obtained gap and atomic charges distribution reveal the possibility of high charge transfer within the molecule and a high reactivity which permits to this molecule to be considered as bioactive compound.

References

R. Benallal, B. Azize, T. Sahdane, H. Bougharraf, A. Laghrabli, B. Kabouchi, B. Elfaydy, L. Lakhrissi, B. Lakhrissi, E. M. Essassi, *J. Mater. Environ. Sci.* 6 (2015) 682.

2. A. Zouitini, Y. Kandri Rodi, H. Elmsellem, H. Steli, F. Ouazzani Chahdi, M. Ali Shariati, A. E. Janati, Y. Ouzidan, N. K. Sebbar, E. M. Essassi, *J. Mater. Environ. Sci.* 8 (2017) 4105.
3. J. A. Pereira, A. M. Pessoa, M. Natalia, D. S. Cordeiro, R. Fernandes, C. Prudencio, J. P. Noronha, M. Vieira, *Eur. J. Med. Chem.* 97 (2015) 664.
4. G. A. Rodrigo, A. E. Robinshon, M. E. Hedrera, M. Kogan, S. M. Sicardi, B. M. Fernaandez, *Trends Heterocycl. Chem.* 8 (2002) 137.
5. J. Jampilek, M. Dolezal, J. Kunes, V. Buchta, K. Kralova, Med. Chem. 1 (2005) 591.
6. K. V. Sashidhara, A. Kumar, G. Bhatia, M. M. Khan, A. K. Khanna, J. K. Saxena, *Eur. J. Med. Chem.* 44 (2009) 1813.
7. Watkins A. J., Nicol G. W., Shawa L. J., *Soil Biol. Biochem.* 41 (2009) 580.
8. Y. Ramli, A. Moussaif, H. Zouihri, S. Lazar, E. M. Essassi, *Acta Cryst. Section E,* 66 (2010) 1922.
9. M. Toy, H. Tanak, *J. Theo. Comput. Chem.* 11 (2012) 745.
10. E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* 52 (1984) 997.
11. R. Bauernschmitt, R. Ahlrichs, *Chem. Phys. Lett.* 256 (1996) 454.
12. M. E. Casdia, C. Jamorski, K. C. Casida, D. R. Salahub, *J. Chem. Phys.* 108 (1998) 4439.
13. Z. Rouifi, M. El Faydy , H. About, F. Benhiba, H. Ramsis, M. Boudalia, H. Zarrok, R. Touir, M. El M'Rabet, H. Oudda, A. Guenbour, B. Lakhrissi, *J. Mater. Environ. Sci.* 9 (2018) 453.
14. Y. Takano, K. N. Houk, *JCTC.* 1 (2005) 70.
15. J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 105 (2005) 2999.
16. M. Cossi, N. Rega, G. Scalmani, V. Baone, *J. Comput. Chem.* 24 (2003) 669.
17. M. Ramegowda, *Spectrochim. Acta Part A.* 137 (2015) 99.
18. V. Balachandran, V. Karpagam, G. Santhi, M. Kavimani, *Spectrochim. Acta Part A.* 137 (2015) 165.
19. J. B. Bhagyashree, H. T. Varghese, C. Y. Panicker, C. V. Alsenoy, J. Samuel,*Spectrochim. Acta Part A.* 137 (2015) 193.
20. M. J. Frisch et al., Gaussian 03, Revision. D.01 and D.02, Gaussian, Inc., Walling-ford, CT, 2005.
21. L. Salassa, C. Garino, G. Salassa, R. Gobetto, C. Nervi, *J. Am. Chem. Soc.* 29 (2008) 9590.
22. N. M. O'Boyle, A. L. Tenderholt, K. M. Langner, *J. Comp. Chem.* 29 (2008) 839.
23. H. Bougharraf, R. Benallal, M. El faydy, D. Mondieig, Ph. Negrier, T. Sahdane, B. Kabouchi, B. Lakhrissi, A. Zawadzka, *Opt Quant Electron.* 48 (2016) 141.
24. R. S. Mulliken, *J. Chem. Phys.* 23 (1995) 1833.
25. V. Balachandran, V. Karpagam, G. Santhi, B. Revathi, G. Ilango, M. Kavimani, *Spectrochim. Acta, Part A: Mol. Biomol.Spectrosc.* 137 (2015) 165.
26. M. Prabhaharan, A. R. Prabakaran, S. Gunasekaran, S. Srinivasan, *Spectrochim.Acta, Part A: Mol. Biomol. Spectrosc.* 136 (2015) 494.
27. J. S. Murray, J. M. Seminario, M. C. Concha, P. Politzer, *Int. J. Quant. Chem.* 44 (1992) 113.
28. P. Politzer, M. C. Concha, J. S. Murray, *Int. J. Quant. Chem.* 80 (2000) 184.
29. V. Balachandran, G. Santhi, V. Karpagam, A. Lakshmi, *Spectrochim. Acta Part A : Mol. Biomol.Spectrosc.* 110 (2013) 130.
30. V. P. Gupta, A. Sharma, V. Virdi, V. J. Ram, *Spectrochim Acta. Part A.* 64 (2006) 57.
31. S. Demir, F. Tinmaz, N. Dege, I. O. Ilhan, *J. Mol.Struct.* 1108 (2016) 637.
32. B. Kosar, C. Albayrak, *Spectrochim. Acta A.* 78 (2011) 160.
33. C. Ravi kumar, I. Hubert Joe, V. S. Jayakumar, *Chem. Phys. Lett.* 460 (2008) 552.
34. C. A. Anothane, thesis, Faculty of Science, Mohammed V University, Rabat, (2010).

(2017) ; http://www.jmaterenvironsci.com