DFT and TD-DFT study of the Organic Light Emitting Diode (OLED)

Souhila Bekhbekh[1,2] and Nadia Ouddai[2]

[1]Departement de Chimie, Faculté de Sciences Exactes, Univ-Constantine 1, Algeria

[2]Laboratoire de Chimie des materiaux et des vivants, Activite, Reactivite Univ- Hadj Lakhdar - Batna, Algeria

***Corresponding author: E.Mail: ouddai_nadia@yahoo.fr**

ABSTRACT

Density functional theory has been used to know the electronic structure and optical properties of organic light-emitting diode (OLED) 1,4-Difluro-2,5 dibutoxy benzene BBF_2 compound, where X= Cl, At, and I. The quantum calculation has shown that the alkyloxy group hasn't effect on the HOMO/LUMO energy. The topological analysis revealed a ionic bond in benzene ring, located in C—H··· Cgi, (2.47 A) Cgi is the centre of the benzene. TD-DFT calculations found that, for BBI_2, $BBAt_2$, HOMO/LUMO transitions in the UV are strongly bathochromically shifted compared of these BBF_2, and $BBCl_2$.

KEY WORDS: DFT, TD-DFT, OLED, emitting.

1. INTRODUCTION

Since to rapid development of organic light-emitting diode (OLED); thus have been studied on the small molecule, on the small polymers and organometallic compounds (Tang and vanslyke, 1987; Burrounghs, 1990; Bakova, 2011; Heydova, 2012). Organic light-emitting diodes has a large quantity of research on the meta effect (Gan and Song, 2004; Kiran Sankar, 2014), organic small molecules are endowed with high molar absorption coefficient and large luminescence yield (Zhaoyang and Min, 2015; Adam, 2009; Roy, 2011)[7-9]. For instance thiophene has received much attention due of the potential applications (Leriche, 2007; Lin, 2012; Forrest and Thompson, 2007; Facchetti, 2007; Mariano, 2009; Gigli, 1999; Takatoshi and Minori, 2014)[10-16].

Our research project consists of a theoretical analysis of compound 1,4-Difluro-2,5 dibutoxy benzene, (BBF_2), the schematic structure of the studied compound is presented in Figure 1.

In this work we carried out a quantum calculation based on the density functional theory (DFT) and time dependent (TD-DFT) to study a model molecules, the electronic structure and optical properties from the compound BBF_2, (see Figure 1) we will analyze the change of the electron absorption spectra furthermore, we replace compound BBF_2, where F=, Cl, I and At and we used the QTAIM to understand the nature and properties of the bond.

X= F (I, Cl and At), Figure 1. The schematic structures

2. Computational details: DFT and TD-DFT were carried out using the Amsterdam density functional (ADF) program (Velde, 2001). The generalized-gradient approximation (GGA) was employed in the geometry optimization by using the Perdew-Burke-Ernzerhof (PBE, 1996; 1997) with TZP basis set. Associated with conductor-like screening model (COSMO) (Pye and Ziegler, 1999) in dichloromethane solution, utilizing the TD-PBE/SAOP functional the approximation (ZORA) (Van Lenthe, 1999). TD-DFT calculations were using statistical average of orbital potentials (SAOP) by Schipper (2000).

3. RESULTS AND DISCUSSION

3.1. Geometry optimisation and topological study of electron density:

QTAIM analysis: The geometry optimisation has been performed using DFT methods. All the structures has been computed with the generalized-gradient approximation (GGA) by using the Perdew–Burke–Ernzerhof (PBE, 1996; 1997) with TZP standard basis set and topological analysis of electron density at DFT optimised structures was performed via the QTAIM of Bader (1999). The dihedral angles O1-C4-C3-C2 and C3-O1-C1A-F (respectively 2.3 ° and 0.0 °) for BBF2, where X = Cl, At and I, show that the alkyl chains are coplanar with the benzene ring, these results are confirmed by the value of the dipole moment 0.00 Debye. According value of electron density and its Laplacian at CP are indicative of closed-shell interactions; we found ionic bond, critical point is located in benzene ring Cgi (see Figure 2); this halogen bond linear located in C—H··· Cgi, (2.46 Å), C— Cgi, (1.38 Å) , and C—H··· Cgi, (178°), bond length, bond angle and dihedral angle computed for compounds are given in Table 1.
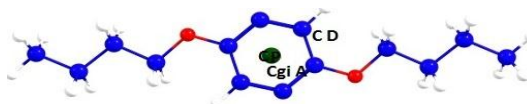

Figure.2.Representative critical point

Table 1: Optimized bond length (Å) and bond angles (°) for compounds with [a:] X=F, [b:] X=Cl, [c:] X=At and [d:]X=I

BBX$_2$					
Bond length (Å)		**Bond angle(°)**		**Dihedral angle(°)**	
F$_1$-C$_1$	1.94[a]	C2-C1-Br1	119[a]	C4-O1-C3-C2	2.3[a]
Cl-C$_1$	1.75[b]	C2-C1-Cl	119[b]		2.3[b]
At-C$_1$	1.90[c]	C2-C1-AT	119[c]		2.3[C]
I-C$_1$	2.16[d]	C2-C1-I	119[d]		2.7[d]
O1-C$_3$	1.36[a]	O1-C3-C1A	118[a]		
	1.36[b]		118[b]		
	1.36[c]		117[C]		
	1.36[d]		118[d]		
O1-C4	1.45[a]	O1-C3-C2	124[a]		
	1.45[b]		124[b]		
	1.45[c]		124[c]		
	1.43[d]		124[d]		

3.2. Electronic absorption spectra from TD-DFT calculations: Solvent effects are significant in TD-DFT calculations, due the charge transfer absorption more sensitive form solvent polarity (Jian, 2014). It is important to understand the influence of solvent on the spectral properties of the compounds. Since (COSMO) is known as the most successful model to find for the solvent effects, TD-DFT calculations have been carried out in one solvent dichloromethane (CH$_2$Cl$_2$) and the results are shown in Figure 3.   The absorption spectra are dominated in the UV regions which are given in Table 2. The electronic excitation to the lowest singlet π-π* excited state is dominated by the HOMO → LUMO transition. The Frontier molecular orbitals calculated by TD-DFT PBE/SAOP/TZP in solution phase are given in Figure 4. The main difference in the absorption spectra of these compounds is that HOMO→ LUMO transition of BBI$_2$ and BBAt$_2$ are strongly bathochromically shifted compared with these of BBF$_2$ and BBCl$_2$ this is related to the lower HOMO-LUMO gap value of BBI$_2$ and BBAt$_2$, in compounds BBF$_2$ and BBCl$_2$ respectively, therefore, absorption UV reveal two maximum peaks at 278 nm and 299 nm with lowest intensive of absorption , also, 235nm , 240 nm agree well transition H-1→L, other we have found two peaks have located in 220nm and 185nm with highest intensive of absorption. Two compounds BBI$_2$ and BBAt$_2$ are shown absorption maxima at 351nm and 372nm, respectively in solution phase with oscillator strength set as zero of absorption transition H→L. The low lying excited state $\lambda_{H \to L}$ (nm) of compounds, transition energies ΔE (eV) and oscillator strength (f) are given in Table 2.

Table.2.$\lambda_{H \to L}$ (nm) of compounds, transition energies ΔE (eV) and oscillator strength (f) calculated by TD-DFT PBE/SAOP/TZP in solution phase

	ΔE (eV)	**$\lambda_{H \to L}$ (nm)**	**f**
BBF$_2$	4.46	278	0.13
BBCl$_2$	4.15	299	0.22
BBI$_2$	3.53	351	0.00
BBAT$_2$	3.33	372	0.00
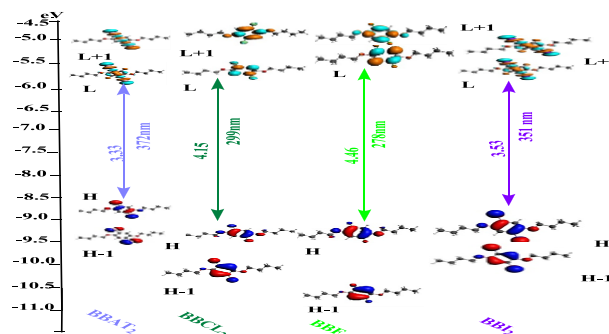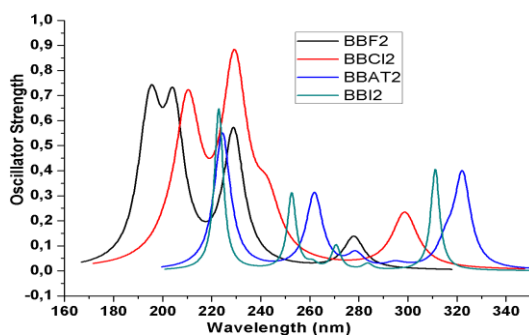
Figure.3.Theoretical UV-vis absorption spectra of compounds BBX$_2$ (X= F, Cl , I, At)

Fig.4. Frontier molecular orbitals calculated by TD-DFT PBE/SAOP/TZP in solution phase

4. CONCLUSION

In this work; we presented the results of DFT and TD-DFT calculations on a series of organic light-emitting diode 1,4-Difluro-2,5 dibutoxy benzene BBF_2 compound where X= Cl, At and I. The quantum calculation DFT appeared that the alkyloxy groups hasn't effect on the HOMO- LUMO energy gap, it is clear in the frontier molecular orbital and these results confirmed by dipole moment where it equal 0.00 Debye so that the absence effect of alkyloxy on the planarity of these molecules. The topological analysis reveals ionic bond located in benzene ring; halogen bond linear located in C—H··· Cgi, (2.47 Å) Cgi is the centre of the benzene. TD-DFT calculations shows that in compounds BBI_2, $BBAt_2$, HOMO-LUMO transitions are strongly bathochromically shifted compared of these BBF_2, and $BBCl_2$, also, it is clear the influence for halogen I, and At in the frontier molecular orbital, allows these compounds good candidates to give emitter in visible.

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