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New aromatic compounds based on thiaoxazaphenanthrene. Quantum chemical investigations of structure and optoelectronic properties relationship

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Abstract

In this paper, we report theoretical study of several conjugated aromatic compounds based on thiaoxazaphenanthrene using Density functional theory method. Theoretical calculations have been carried out in order to characterize their stability, geometric and electronic properties. In fact, substituent nature, number and position are crucial parameters to define structural and electronic molecule proprieties. Besides, assessing HOMO and LUMO energy levels of components is essential in investigating suitable materials for optoelectronic applications. Thus, in this paper, we computed HOMO and LUMO energy levels of molecules based on thiaoxazaphenanthrene core. Our data have shown that these materials are well suited for optoelectronic applications.

Keywords: π-conjugated molecules; Thiaoxazaphenanthrene; DFT; Band-gap; Electronic properties, HOMO, LUMO.

1. Introduction

Organic molecules containing aromatic thiaoxazaphenanthrene and derivatives are used in various fields of science and technology and have multiple applications in biology and medicine [1, 2]. Despite the significant and wide number of applications that offer this type of compounds, complete analysis of electronic proprieties of these compounds, has not been yet carried out. These compounds have been recently synthesized and characterized by B. Bennani and al. [3]. These studies have shown that the aromatic molecules contain π-conjugation systems that can trap electrons easily. By substituting different functional groups on an aromatic system it is possible to increase or decrease the π-electron density and thereby create acceptor (p-type) and donor (n-type) molecular sub-units. Fundamental understanding of structural and energetic properties of this kind of materials could be useful so as to design new molecules. While experimental studies have shown many drawbacks as high level of disorder, difficulties to determine band gaps and geometries.

Modeling studies can provide insight into finding relationships between the structure and the electronic properties of these compounds. DFT is very attractive calculation method for finite systems because even the lowest level of DFT, the local spin density approximation (LSDA) includes some electron correlation. This is extremely important in the design of conjugated molecules [4, 5]. Computer simulation is useful in this field of research, for example, the determination of the stable and the electronic structures. This research approach has been further examined in a number of theoretical analyses that have also been published [6]. To increase our understanding of this important class of material, we report in this work, theoretical investigation of the structural, electronic, and optical properties of aromatic thiaoxazaphenanthrene and its derivatives (fig.1). The geometries structures are obtained by the DFT method using B3LYP hybrid functional density to obtain full geometries optimization. Particular attention is paid to electronic structure and absorption properties determined by ZINDO approximation.

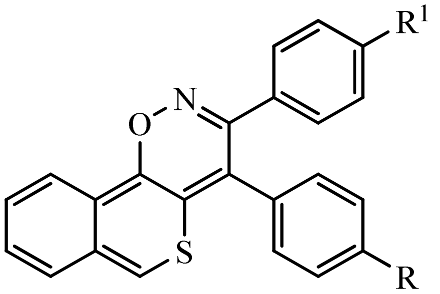


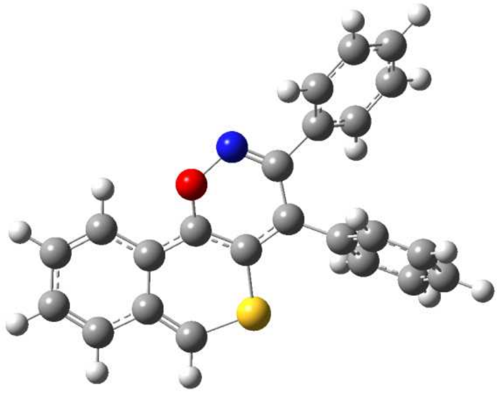
Fig.1 : Molecular structure of studied compounds (for R^1 and R see Table 1)

2. Methodologies and computation

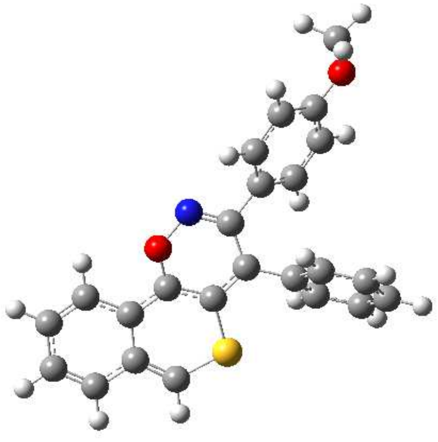
The geometries of the studied compounds were investigated by DFT. The level of three functional parameter of Becke (B3LYP) [7] and the 6-31G* basis [8] was used for all structures. All calculations were performed by the Gaussian03 package [9] and their geometries were performed without constraint on the dihedral angles. We used the optimized structures to examine the electronic density of HOMO and LUMO levels. The HOMO, LUMO and ΔE_g (LUMO-HOMO) were also calculated for the stable structure of the neutral forms. The excitation energies, wavelengths and oscillator strengths were investigated using the ZINDO calculations [10] on the fully optimized structures in the neutral forms.

3. Results and discussion

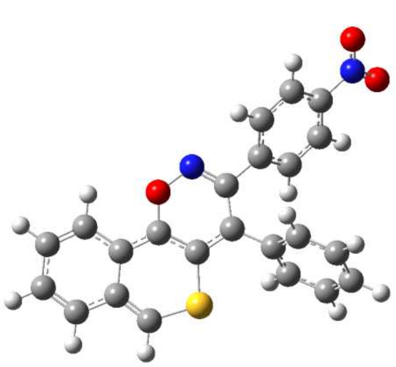
Optimized structures of all studied compounds are illustrated in Figure 2. These structures show clearly the pi-electron delocalization between the different aromatic.



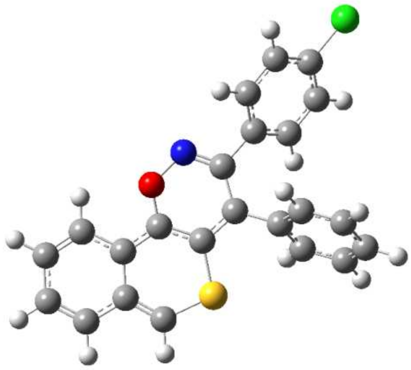
21au



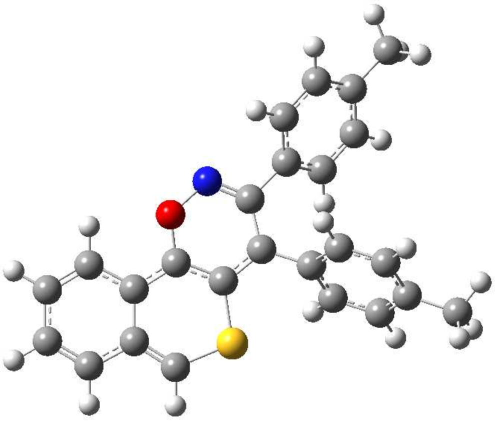
21aw



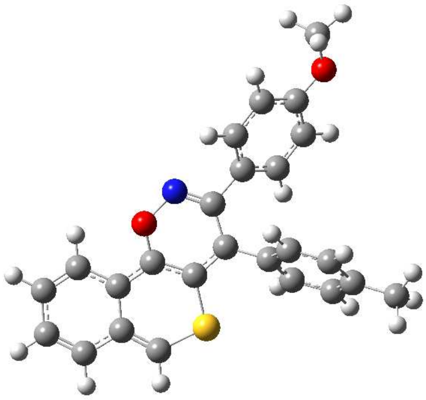
21ax



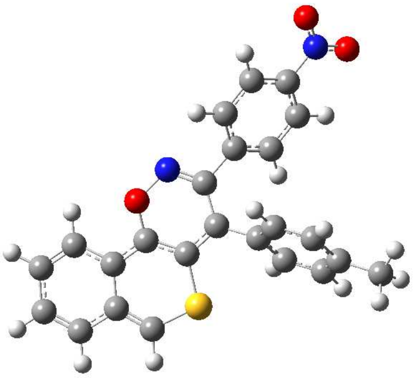
21ay



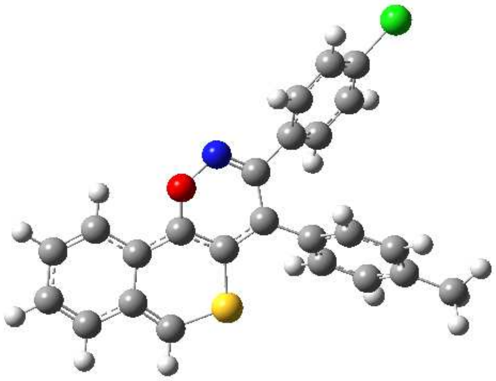
21bv



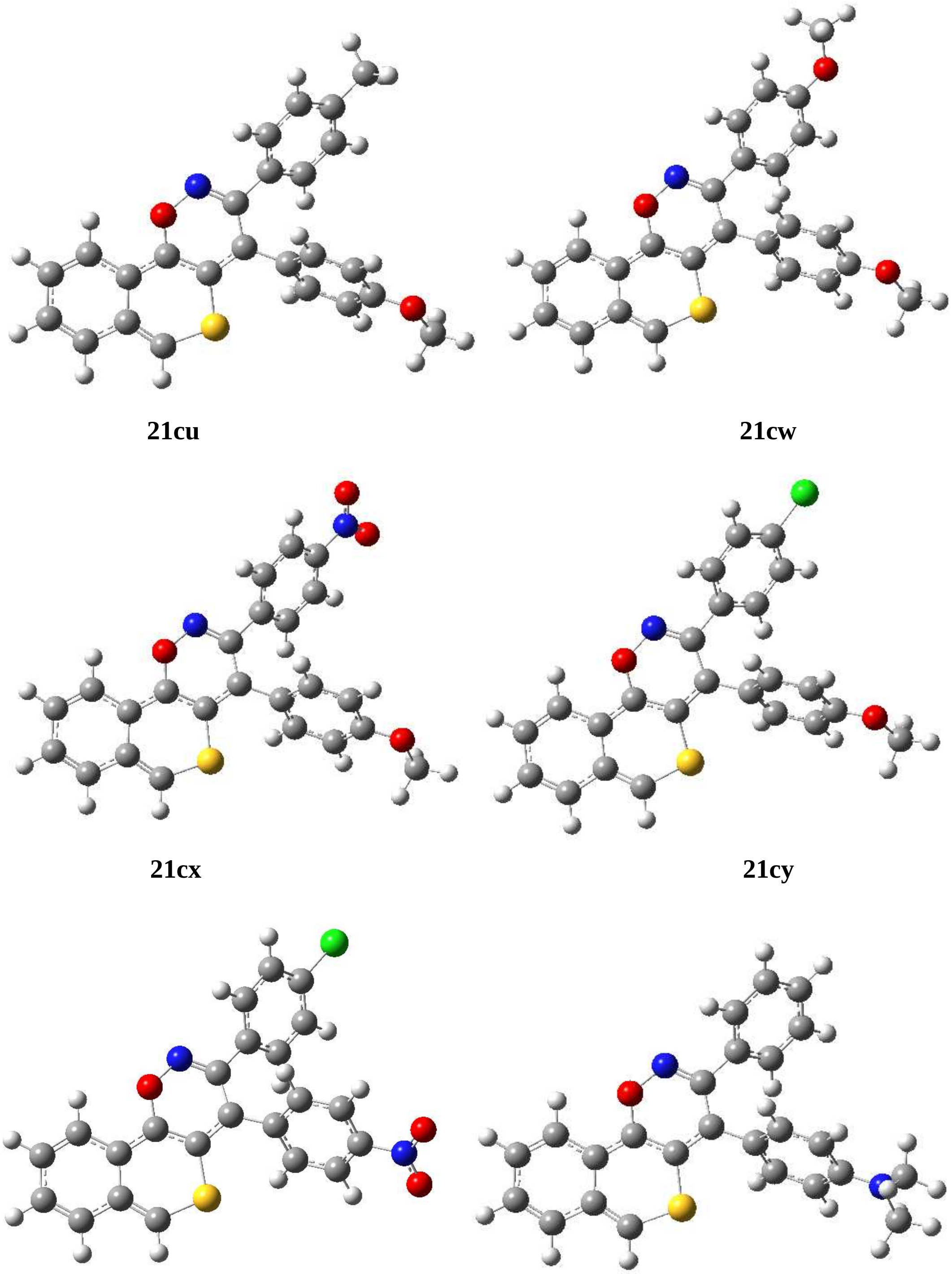
21bw



21bx



21by



21cu **21cw**

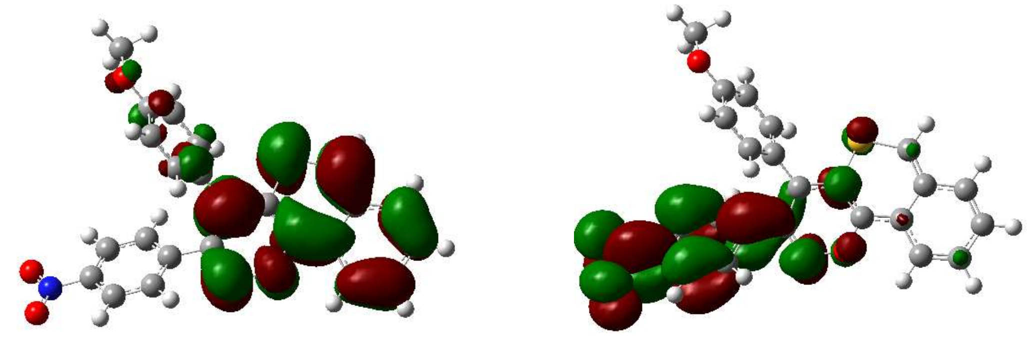
21cx **21cy**

21dy **21eu**

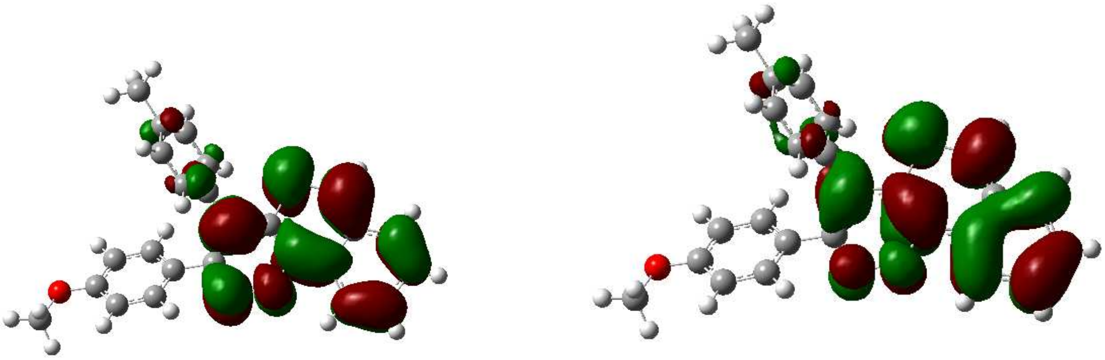
Fig. 2 : Optimized structure of the studied molecules obtained by B3LYP/6-31G* level

Bond lengths and dihedral angles (corresponding to the global minimum optimized structure in the neutral form) using B3LYP/6-31G* level were obtained. Results show, for all studied molecules, that there are no significant differences among the bond lengths and angles obtained within the aromatic rings. Otherwise, it's important to examine characters of the frontier orbitals because the relative ordering of the occupied and virtual orbitals provides a reasonable qualitative indication of the excitation properties and of the ability of electron or hole transport [11]. The HOMOs and LUMOs of all studied molecules are shown in Figure 3, the

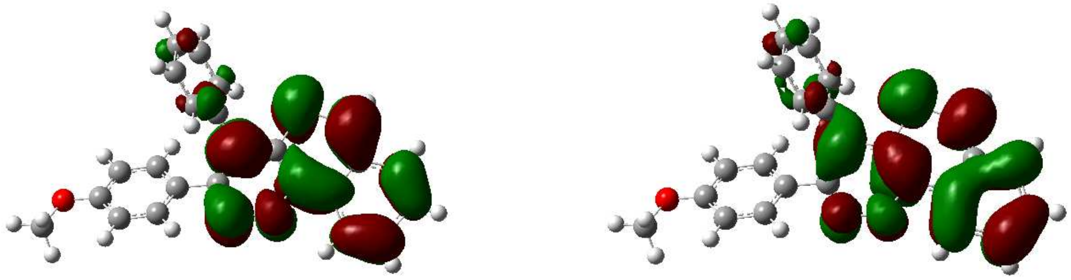
HOMO possesses an antibonding character between the consecutive subunits. This may explain the non planarity observed for these π-conjugated molecules in their ground states. On the other hand, the LUMO of all studied compounds generally shows a bonding character between the subunits. It demonstrates that in their ground states, the compounds investigated in this paper will have aromatic character.


HOMO LUMO

21cx


HOMO LUMO

21dy


HOMO LUMO

21aw

Fig.3 : B3LYP/3-21G* electronic density contours of the frontiers orbitals for some studied molecules

Experimental studies showed that the HOMO and LUMO energies were obtained from an empirical formula based on the onset of the oxidation and reduction peaks measured by cyclic voltametry. Whereas theoretical data show that HOMO and LUMO energies can be calculated by DFT calculation [12]. It's noticeable, however, that solid-state packing effects are not included in the DFT calculations, which tend to affect the HOMO and LUMO energy levels in a thin film compared to an isolated molecule as considered in the calculations.

Table 2 lists theoretical electronic parameters of the studied compounds. The calculated electronic Gap of the studied compounds 21au, 21aw, 21ax, 21ay, 21bv, 21bw, 21bx, 21by, 21cu, 21cw, 21cx, 21cy, 21eu are respectively 1.8725, 1.8704, 1.8318, 1.8749, 1.8697, 1.8695, 1.8151, 1.8719, 1.8644, 1.8644, 1.7982, 1.8660. In the case of compounds substituted with (OMe) or (Me) (21aw, 21bv, 21bw, 21cu, 21cw), one remark that they exhibit destabilization of the HOMO and LUMO levels in comparison with those of unsubstitued one (21au). This is due to electron-donating substitution of methoxy and methyl groups; while in the case of the compounds substituted by Cl (21ay, 21by, 21cy) there is a net stabilization of the HOMO and LUMO levels. Moreover, these compounds have a smaller energy gap ΔEg than the unsubstituted one, which is due to the presence of different substituents as described previously. The band gap of 21cx (OMe, NO_2), is much smaller than that of the other substituted compounds. This may be attributed to the combination of electron-donating methoxy and electron accepting $N0_2$ side groups and also to creation of the dipole Donor -acceptor around the aromatic rings.

Table 1 : Calculated values of HOMO (eV), LUMO (eV) and ΔEg (eV) energies for the studied molecules

N°	**R**	**R^1**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔEg (eV) (LUMO – HOMO)**
21au	**H**	**H**	-3.7355	-1.8630	1.8725
21aw	**H**	**OMe**	-3.6787	-1.8083	1.8704
21ax	**H**	**NO_2**	-3.9780	-2.1462	1.8318
21ay	**H**	**Cl**	-3.8293	-1.9544	1.8749
21bv	**Me**	**Me**	-3.6783	-1.8085	1.8697
21bw	**Me**	**OMe**	-3.6525	-1.7829	1.8695
21bx	**Me**	**NO_2**	-3.9447	-2.1297	1.8151
21by	**Me**	**Cl**	-3.7998	-1.9279	1.8719
21cu	**OMe**	**Me**	-3.6438	-1.7794	1.8644
21cw	**OMe**	**OMe**	-3.6189	-1.7545	1.8644
21cx	**OMe**	**NO_2**	-3.9119	-2.1136	1.7982
21cy	**OMe**	**Cl**	-3.7634	-1.8974	1.8660
21eu	**$N(Me)_2$**	**H**	-3.6468	-1.7794	1.8649

Thus, in order to investigate the substitution effect on the absorption properties of these compounds, the values of λ_{max} were calculated in Table 2. These values were determined by ZINDO methods starting with optimized geometry obtained at B3LYP/6-31G(d) level. Upon a first glance over the numbers, we notice that the calculated values of λ_{max} shifted in the same direction upon substitution whatever the substituent's nature. All the substituted molecules exhibit a red shift relative to the unsubstituted one. This is in good agreement with the observations cited in the first part. We note that calculations were performed in isolated state, while the properties were measured in liquid state. The theoretical wavelengths (λ_{max}) calculated for isolated chains are expected to be about 25 nm smaller than the experimental values obtained from condensed phase's approach [13].

Table 2 : Calculated absorption λ_{max}(nm) and Oscillator Strength (O.S) for studied molecules

N°	**R**	**R^1**	**Ea (eV)**	**λ_{max} (nm)**	**f (O.S.)**
21au	**H**	**H**	2.1659	572.43	0.5526
21aw	**H**	**OMe**	2.1648	572.73	0.5639
21ax	**H**	**NO_2**	2.1210	584.56	0.5542
21bv	**Me**	**Me**	2.1667	572.21	0.5609
21bw	**Me**	**OMe**	-	-	-
21bx	**Me**	**NO_2**	-	-	-
21cu	**OMe**	**Me**	2.1646	572.78	0.5606
21cw	**OMe**	**OMe**	2.1627	573.28	0.5658

21cx	**OMe**	**NO_2**	2.1211	584.53	0.5575
21cy	**OMe**	**Cl**	-	-	-
21eu	**$N(Me)_2$**	**H**	2.1646	572.78	0.5605

Conclusion

In this study, theoretical analysis of the geometries and electronic properties of three various compounds based on aromatic thiaoxazaphenanthrene were performed in order to display the effect of substituted groups on the structural and opto-electronic properties of these materials. We can conclude the following points. First, in the case of compounds substituted with (OMe) or (Me) (21aw, 21bv, 21bw, 21cu, 21cw), one remark that they exhibit destabilization of the HOMO and LUMO levels in comparison with those of unsubstitued one (21au) due to electron-donating substitution of methoxy and methyl groups. While compounds substituted by Cl (21ay, 21by, 21cy) showed clear stabilisation of the HOMO and LUMO levels.

In the other hand, the substituted compounds have a smaller energy gap ΔEg than the unsubstituted one, which is due to the presence of different substituents in several positions of phenyl ring. However, the band gap of 21cx (OMe, NO_2), is much smaller than that of the other substituted compounds. This may be attributed to the combination of electron-donating methoxy and electron accepting NO_2 side groups and to the creation of the dipole Donor -acceptor around the aromatic rings.

Finally, values of λ_{max} are calculated by ZINDO methods showed that values optimized geometry obtained at B3LYP/6-31G(d) level. Upon a first glance over the numbers, we notice that the calculated values of λ_{max} shifted in the same direction upon substitution whatever the nature of the substituent groups. All the substituted molecules exhibit a red shift relative to the unsubstituted one.Thus, obtained properties (small gap and high λ_{max}) suggest these materials are good candidates for optoelectronic applications. This paper underline the advantage of DFT Theoretical calculations, which can be employed to predict and assume the electronic properties and efficiency of yet prepared materials. And may be a good tool to further design novel materials for optoelectronic applications.

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