

Photo-electronic Computational study of 2- (aryl) -2- (7 (4) - (arylsulfonyl) oxime-1-ethyl-1H-indazol-4-ylidene acetonitrile molecules: DFT and TD-DFT study

*Siham Lakrikh *, Hajar Atmani , Bouchra Mekkaoui , Latifa Laallam, Ahmed Jouaiti*

Laboratory of Sustainable Development, Faculty of Sciences and Technologies, Sultan Moulay Slimane University, Beni Mellal, Morocco.

Abstract

In this paper, we used theoretical methods density functional theory to determine the properties of the seven organic molecules based on 2-(aryl)-2-(7(4) -(arylsulfonyl) oxime-1-éthyl-1H-indazol-4-ylidene) acetonitrile. These photo-electronic parameters are very interesting in the photovoltaic field. Such as, energies of High Occupied Molecular Orbitals, Energies of Low Occupied Molecular Orbitals and energy of gap. We explored our results in the determination of electronic and photo-electronic properties of these studies molecules using Time-Dependent Density Functional Theory, indeed the object was to determine the molecules wavelengths, as far as trace the visible ultra-violet spectrum and determine the transition states in the last step. The established results and the elaborated properties shown throughout the document the importance of these molecules especially in photovoltaic fields.

* Corresponding author:

Siham.lakrikh2013@gmail.com

Received 31 July 2020,

Revised 02 Dec 2020,

Accepted 01 May 2020

Keywords: DFT; TD-DFT; E_{LUMO} ; E_{HOMO} ; $\Delta E_{(\text{HOMO-LUMO})}$; UV-Vis.

1. Introduction

As mentioned in previous works [1-2], chemical, spectroscopic absorption and emission characteristics make them suitable for use in optoelectronics and solar cell applications because of their high absorption in the excited state in the long term [3-4]. We used the theoretical method DFT in this work and on the seven molecules of 2- (aryl) -2- (7 (4) - (arylsulfonyl) oxime-1-ethyl-1H-indazol-4-ylidene acetonitrile molecules named M1, M2, M3, M4, M5, M6 and P7 [7-6-5]. Then, we determined the electronic and photo electronic properties of these studied molecules shown in Fig. 1, in order to demonstrate the utility of these compounds in the photovoltaic field [8]. Generally, to calculate electronic and photo electronic characteristics of molecules, we use the DFT with base set 3-61(d) G, in order to obtain good and significant results of our work. In this work, the values of the electronic and photo electronic properties have been calculated by using the DFT and TD-DFT: B3LYP method and 6-31G (d) base set. Firstly, we use DFT method to compute the electronic values and optimize the geometry of the molecular structure. Then, TD-DFT method is used to examine all transitions states, the UV spectrum in addition of photo electronic characteristics. The wavelength and excitation energy as a common example.

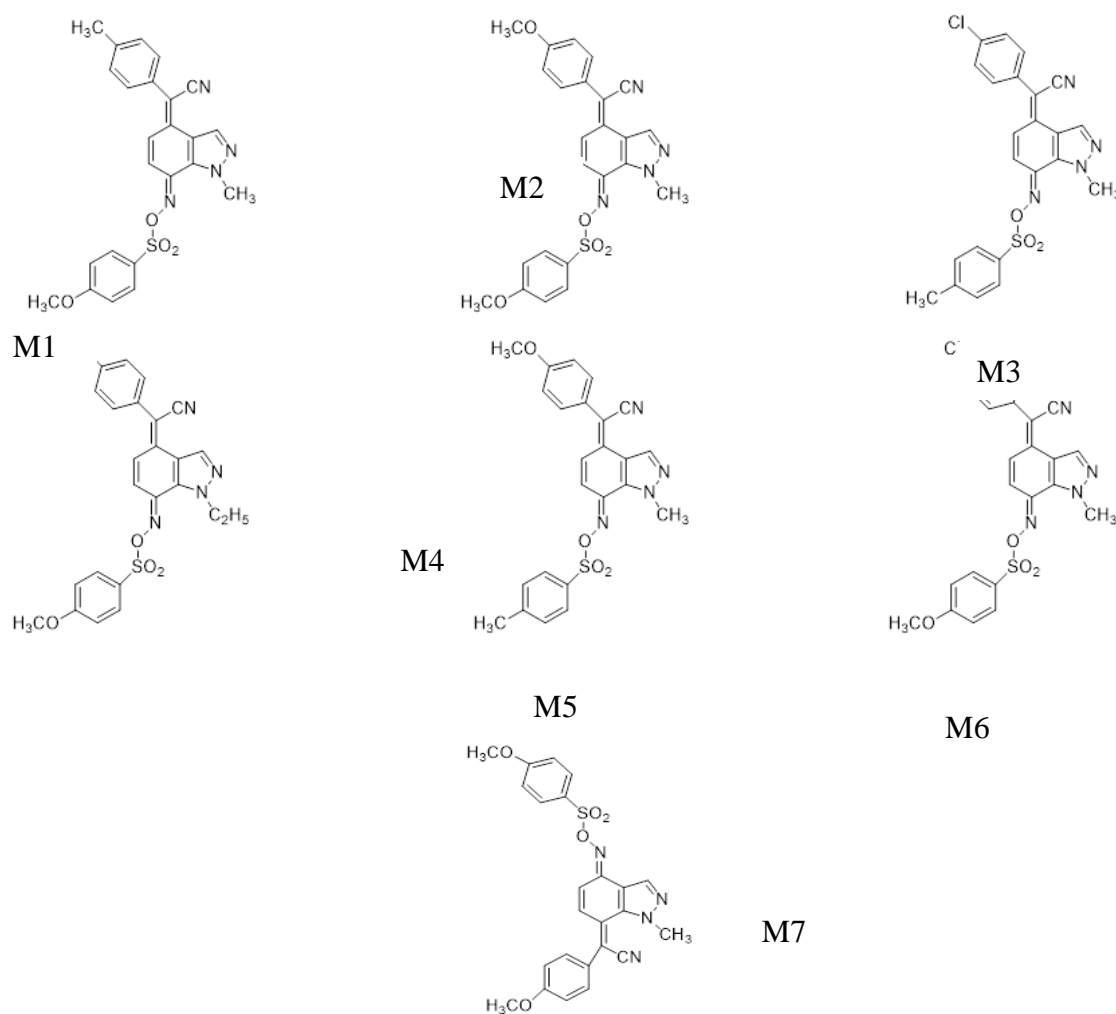


Figure 1: Studied compounds M1; M2; M3; M4; M5; M6 and M7

1. Materials and methods

The characteristics and structural descriptors of these seven organic compounds have been found by applying Gaussian software [9], using density theory (DFT) [10] with the function of the three Becke parameters and the Lee Yang-Parr function (B3LYP) [11- 12] related to 6-31G(d). During our work, we followed this approach to optimize the geometry of the molecules in the fundamental state, it used also to find the lowest energies, the HOMO energies, the LUMO energies and the difference energies for the molecules [13]. Electronic and photoelectronic factors like oscillator forces (OS) or optical transitions are found using Density-Time Functional Theory (TD-DFT) [14] coupled to the B3LYP/6-31 G (d). We are also able to construct and plot the ultra-violet absorber spectra of the compounds studied applied on the GaussView software [15]. Similar previous works [16] used the same approach that give us significant and relevant results.

3. Resultants and discussion

3.1. Organic compounds optimization

To fully understand our test molecule's electronic behavior, we use the DFT method to determine the charge distribution on the boundary orbit of the organic molecules M1 to M7. We can remark that the separate charge between spent and virtual orbits provide a reasonably qualitative indication during the excitation process [17]. We represent below an optimal geometry structure of studied compounds shown in Fig. 2, as far as a spatial tracing of the HOMO and LUMO distributions of the eight organic molecules that are analyzed theoretically by DFT method. Fig. 3. The distribution of these seven compounds is identical for all candidates for both HOMO and LUMO, we can clearly observe a localized destruction on all 2-(aryl)-2-(7(4)-(arylsulfonyl)oxime-1-ethyl-1H-indazol-4-ylidene)acetonitrilesunit molecules, which means that all molecules represent a high electronic coupling ...

Band gap energies calculated by B3LYP/6-31(d)G are represented in Table 1. The gap energy (E_{gap}) is evaluated theoretically as a difference between the HOMO and LUMO levels, with the following equation (1): $E_{gap} = (E_{HOMO} - E_{LUMO})$. Equation (1)

The energies of all derivatives range from 2.774 eV to 3.291 eV in the order of: $M2 < M1 < M3 < M4 < M6 < M7 < M5$. In comparison to the M5 molecule, there is a destabilization of the HOMO energy and a stabilization of the LUMO energy levels. Table 2 illustrated the Voc values of the studied dyes calculated by equation (2):

$$V_{OC} = |E_{HOMO}^{Donor}| - |E_{LUMO}^{acceptor}| - 0,3 \quad \text{Equation (2)}$$

With an energy range from 2.201 eV to 2.608 eV for PCBM and from 1.501 eV to 1.908 eV for TiO₂. This suggests that the electron transfer will be easy from the studied compounds Mi to PCBM or TiO₂. Further, these values are sufficient to obtain the high efficient electron injection, then then we calculate parameter α_1 for all the compounds Mi=1-7 by following equation (3) [18]:

$$\alpha_1 = ELUMO_{Mi=1-7} - ELUMO_{PCBM} \quad \text{Equation (3)}$$

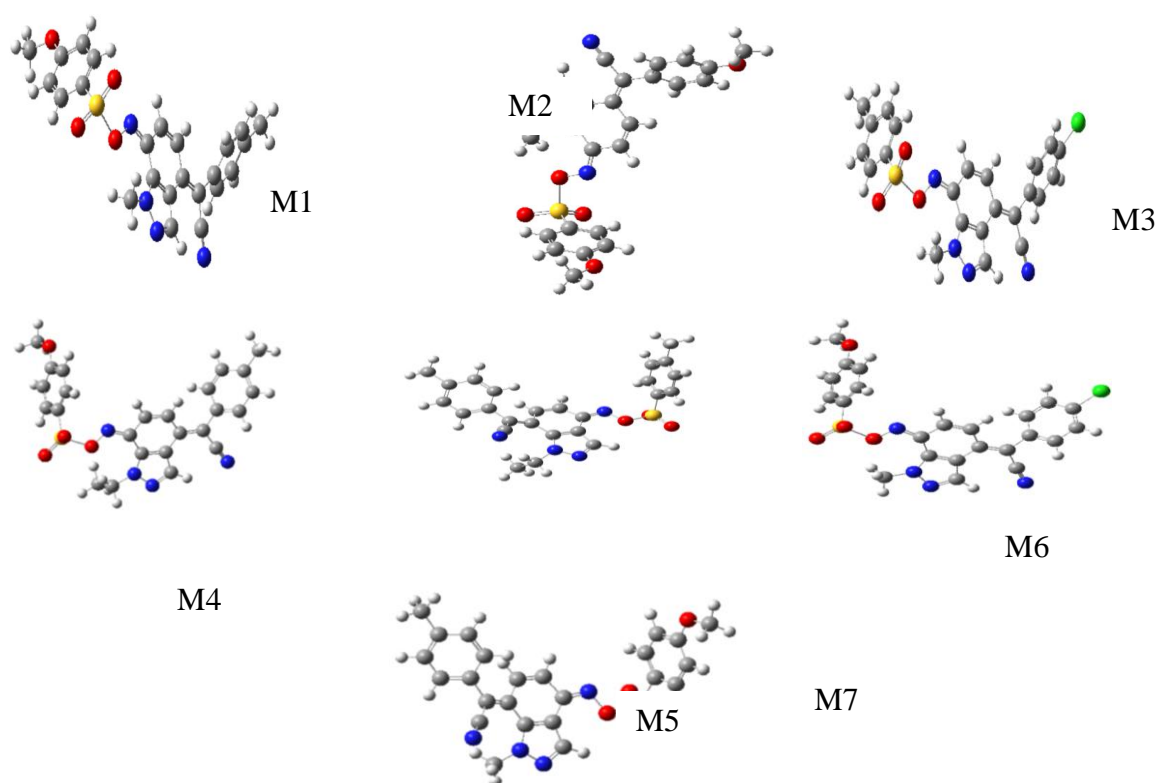
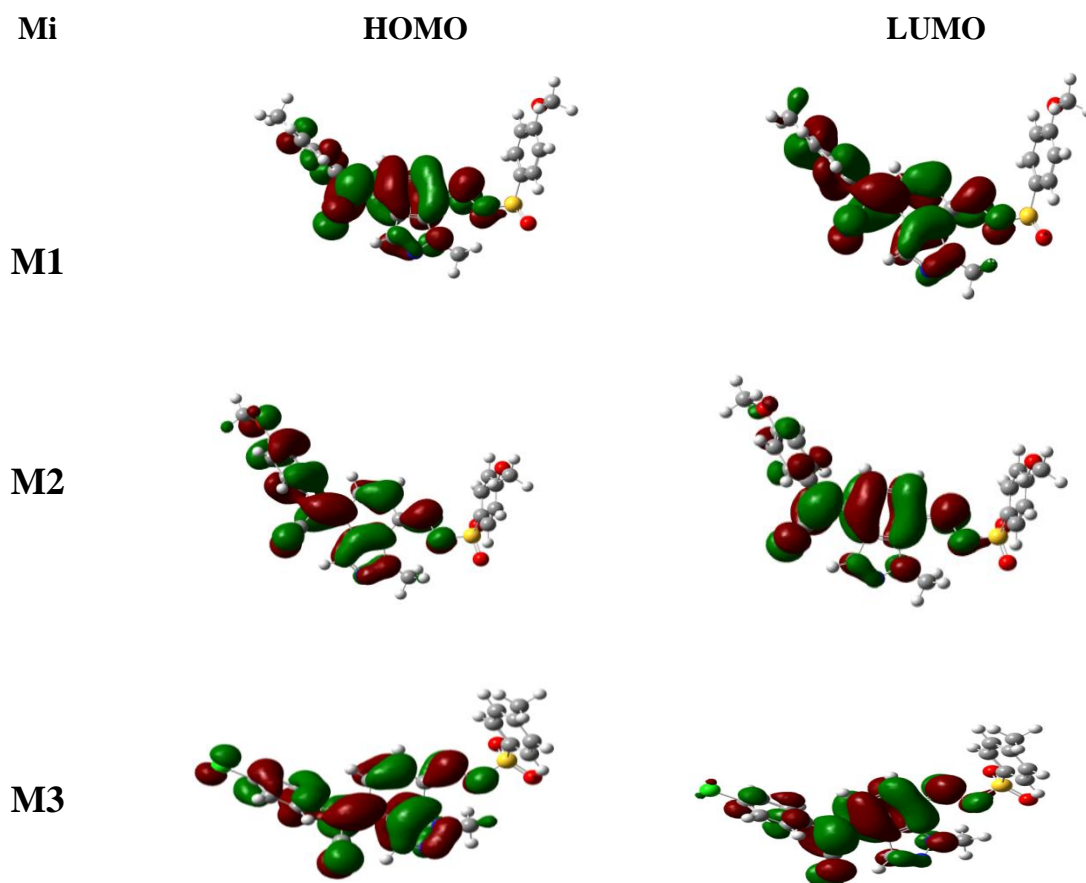


Figure 2: The optimized geometrical structures of the studied molecules.



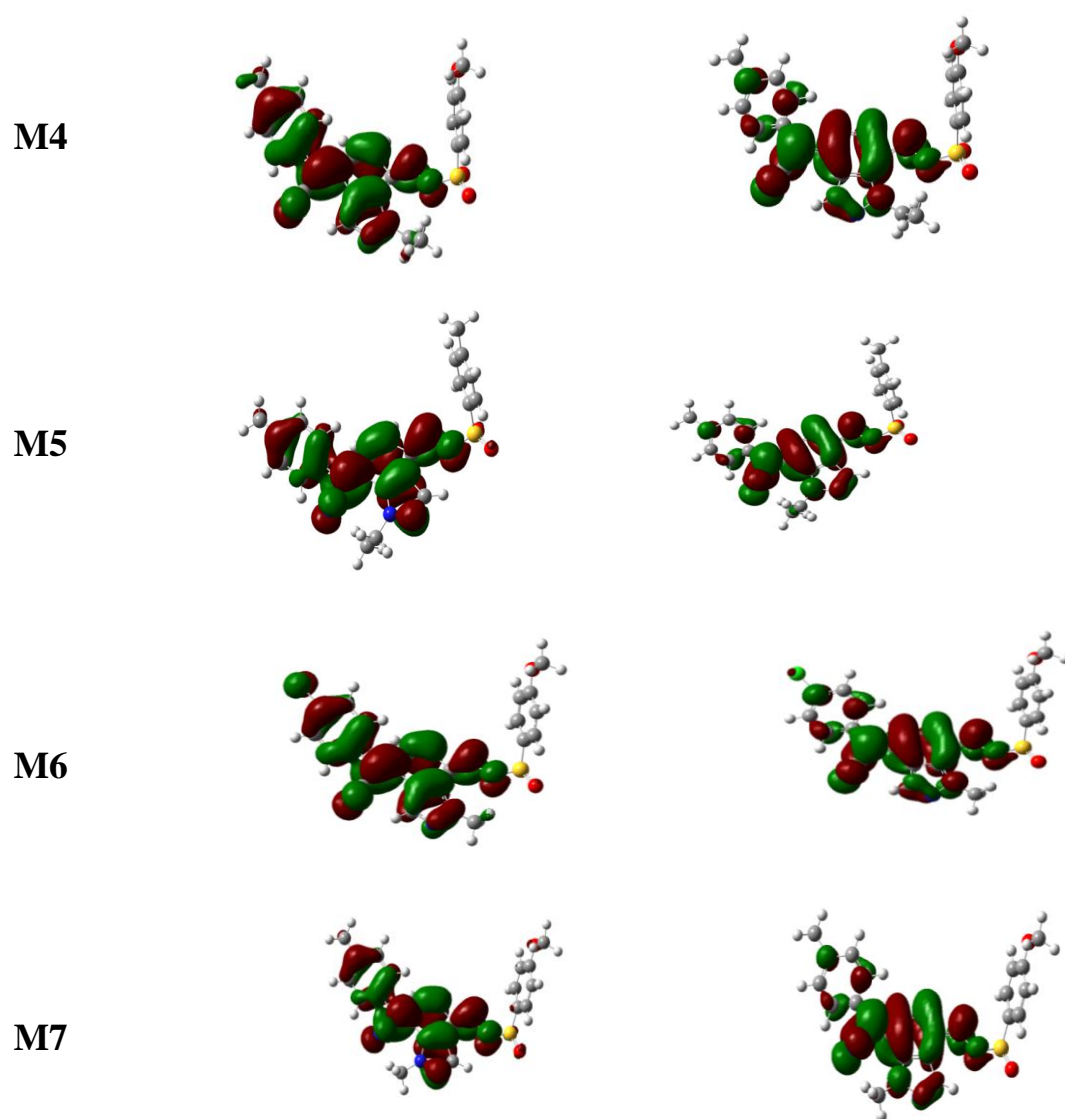


Figure 3: The contour plots of HOMO and LUMO orbitals of the studied compounds

Table 1: The E_{HOMO} , E_{LUMO} and E_{gap} obtained by B3LYP/6-31(d)G of the studied molecules .

Mi	E_{HOMO} (ev)	E_{LUMO} (ev)	E_{gap} (ev)
M1	-5.879	-2.819	3.06
M2	-5.701	-2.927	2.774
M3	-6.099	-3.024	3.075
M4	-5.879	-2.779	3.1
M5	-6.143	-2.852	3.291
M6	-6.087	-2.979	3.108
M7	-6.108	-2.823	3.285

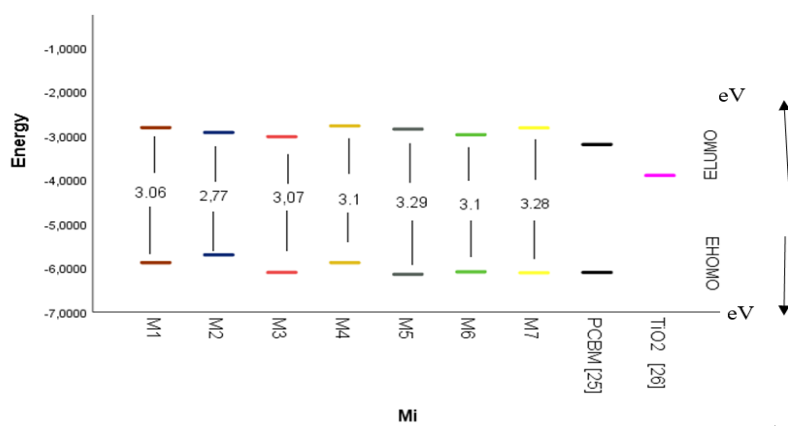


Figure 4: E_{HOMO} and E_{LUMO} of the studied compounds.

Table 2: Energy values of EHOMO, ELUMO and the open circuit voltage Voc

Mi	HOMO(eV)	LUMO(eV)	VOC (eV)		α_i/PCBM (eV)
			PCBM	TiO2	
M1	-5.879	-2.819	2.379	1.679	0.381
M2	-5.701	-2.927	2.201	1.501	0.273
M3	-6.099	-3.024	2.599	1.899	0.176
M4	-5.879	-2.779	2.379	1.679	0.421
M5	-6.143	-2.852	2.643	1.943	0.348
M6	-6.087	-2.979	2.587	1.887	0.221
M7	-6.108	-2.823	2.608	1.908	-0.023
PCBM [19]	-6.1	-3.2			
TiO2 [20]		-3.9			

* α_i = ELUMO (Donor) - ELUMO (PCBM); (The donor compounds are Mi).

3.2 Absorption proprieties

In this study, we used DFT to measure the electronic and spectroscopic performance properties based on TD-DFT for all organic compounds, to understand the influence of the properties on the photovoltaic application for a better control of the structure-property correlations. Based on our theoretical analysis results, we can validate the suitability of these compounds for photovoltaic applied applications as a function of their geometric, electronic and optical properties. E_{HOMO} and E_{LUMO} , mentioned in Table 1, are important factors in determining charge transfer that exist between donors and acceptors as the Egap. Table 3 shows that E_{HOMO} for molecules M7 and M5 is higher than PCBM Energies of HOMO. The value of the open voltage of the studied molecules is between 2.201eV and 2.643eV, in the case of PCBM (Table 2), these values are sufficient for possible efficient electron injection. The contribution of the molecular boundary orbital (MO) is mandatory in the determination of the separate charge states of the studied molecules, since the relative order of the occupied and virtual orbitals that provides a reasonable qualitative indication of the excitation properties as well as the capacitance. The absorption value of a photovoltaic material from the optimized structure of the B3LYP / 6-31 G (d) method is crucial for the application of a photovoltaic

material; we have determined and traced the ultraviolet to visible spectra of M1 to M7 by using the TD and DFT method. The simulated ultraviolet and visible absorption spectra are the same as in the previous [fig 5](#).

Table 3: Data absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31(d)G.

	Electronic transitions	λ_{abs} (nm)	E _{ex} (eV)	O.S (eV)	Transition
M1	S ₀ → S ₁	407.13	3.0454	0.7519	HOMO -5 → LUMO
	S ₀ → S ₂	352.34	3.5189	0.0576	HOMO-1 → LUMO
	S ₀ → S ₃	435.62	3.5873	0.0082	HOMO-5 → LUMO
M2	S ₀ → S ₁	435.06	2.8498	0.6781	HOMO-1 → LUMO
	S ₀ → S ₂	352.42	3.5281	0.1057	HOMO-1 → LUMO
	S ₀ → S ₃	348.63	3.5563	0.0010	HOMO-6 → LUMO
M3	S ₀ → S ₁	404.88	3.0622	0.7595	HOMO -3 → LUMO
	S ₀ → S ₂	348.89	3.5536	0.0287	HOMO-3 → LUMO
	S ₀ → S ₃	344 .03	3.6036	0.1710	HOMO-3 → LUMO
M4	S ₀ → S ₁	404.95	3.0617	0.7265	HOMO -5 → LUMO
	S ₀ → S ₂	347.83	3.564	0.0414	HOMO-5 → LUMO
	S ₀ → S ₃	347.60	3.5668	0.0416	HOMO-5 → LUMO
M5	S ₀ → S ₁	382.08	3.245	0.6742	HOMO-5 → LUMO
	S ₀ → S ₂	357.64	3.4668	0.0307	HOMO -5 → LUMO
	S ₀ → S ₃	348 .30	3.6327	0.0786	HOMO -5 → LUMO
M6	S ₀ → S ₁	401.36	3.0891	0.7633	HOMO-4 → LUMO
	S ₀ → S ₂	358.50	3.4584	0.0296	HOMO-1 → LUMO
	S ₀ → S ₃	348.31	3.5596	0.1130	HOMO-4 → LUMO
M7	S ₀ → S ₁	382.87	3.2383	0.6759	HOMO -5 → LUMO
	S ₀ → S ₂	360.90	3.4355	0.0326	HOMO-2 → LUMO
	S ₀ → S ₃	355.07	3.4919	0.134	HOMO-5 → LUMO

The absorption values measured by nm the values λ_{max} in the ultraviolet domain between 380 nm and 780 nm, for the molecules being studied we found by using our method these values 407.13 nm; 435.06 nm; 404.88 nm; 404.95 nm; 382.08 nm; 401.36 nm; 382.87 nm; respectively from M1 to M7, as well as the main excitation configuration of the computed molecules. In the ordered order: M2> M1> M4> M3> M6>M5>M7.

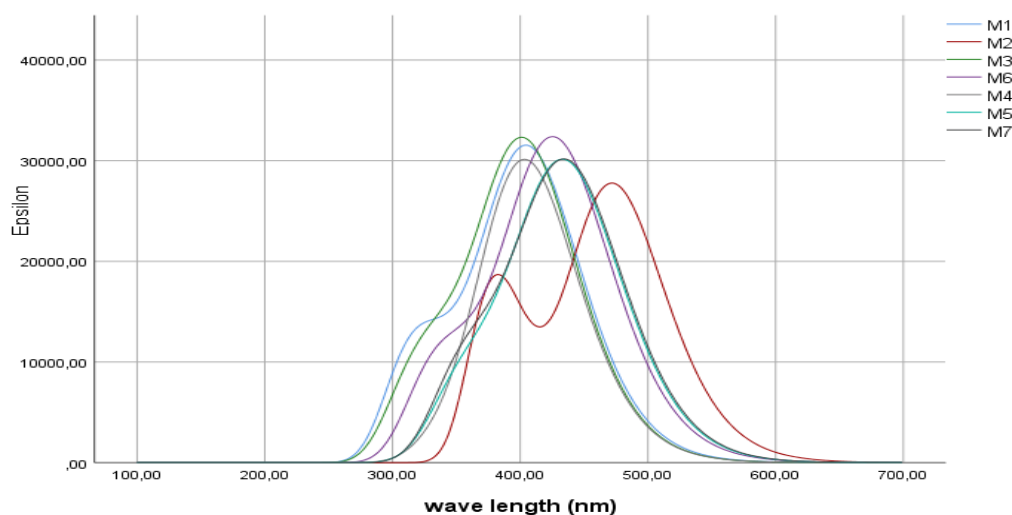


Figure 5: The absorption spectra λ_{max} of the studied compounds

5. Conclusion

In this work, we were interested in using the TD-DFT/B3LYP method and 6-31 (d)G base set to study the theoretical analysis of the eight synthesized organic molecules of 2-(aryl)-2-(7(4)-(arylsulfonyl)oxime-1-ethyl-1H-indazol-4-ylidene)acetonitriles :M1;M2;M3;M4;M5;M6; M7. It is clear that the Ultraviolet-visible properties were obtained by using the TD/DFT method. The absorption maxima obtained are very significant in the range of 435.06 – 382.08 nm. As illustrated previously in document, Egap of the studied molecules was in the range of 2.774 - 3.291 eV. We observe the same remark for the Homo and LUMO energies. On the other hand, the calculated Voc values of the studied molecules are between 2.643 eV and 2.201 eV in the case of PCBMs. But in the case of TiO₂, we found values between 1.501 eV and 1.943 eV.

Reference

- [1] L. Siham, M. Bouchra, L. Latfa, and J. Ahmed, "Electronic and photoelectronic properties of N-(5-indazolyl)-arylsulfonamides molecules: DFT / TD-DFT study," in *2020 IEEE 6th International Conference on Optimization and Applications (ICOA)*, (2020): 1–6, doi: 10.1109/ICOA49421.2020.9094521.
- [2] A. A. Taherpour, A. Yari, F. Ghasemhezaveh, and M. A. Zolfigol, "The first principle computational study for the competitive mechanisms of oxidative aromatization of 2-substituted imidazolines using KMnO₄/SiO₂," *Journal of the Iranian Chemical Society*, 14:(2017) 2485–2493, doi: 10.1007/s13738-017-1183-0.
- [3] F. Garnier, G. Horowitz, X. Peng, and D. Fichou, "The oligothiophene-based field-effect transistor," *Adv. Mater.*, 2(1990): 562–568.
- [4] F. Huang, "Development of new conjugated polymers with donor– π -bridge– acceptor side chains for high performance solar cells," *Journal of the American Chemical Society*, 131(2009):13886–13887.
- [5] R. H. Friend, "Electroluminescence in conjugated polymers," *Nature*, vol. 397(1999): 121–128.
- [6] H. R. Memarian, F. Rezaie, H. Sabzyan, and M. Ranjbar, "Substituent effect on the tautomerism of 5-acetyl-2-methoxydihydropyrimidines: experimental NMR and computational DFT studies," *Journal of the Iranian Chemical Society*, 11(2014): 1265–1274, doi: 10.1007/s13738-013-0395-1.
- [7] Y. Achour, M. Khouili, H. Abderrafia, S. Melliani, M. R. Laamari, M. El Haddad, "DFT Investigations

and Experimental Studies for Competitive and Adsorptive Removal of Two Cationic Dyes onto an Eco-friendly Material from Aqueous Media,” *Int. J. Environ. Res.* 12 (2018): 789-802, <https://doi.org/10.1007/s41742-018-0131-x>.

[8] M. J. Frisch *et al.*, “Gaussian 09, Revision A. 02, 2009, Gaussian,” *Inc., Wallingford CT*, 2009.

[9] E. Opoku, G. Arhin, G. B. Pipim, A. H. Adams, R. Tia, and E. Adei, “Site-, enantio- and stereo-selectivities of the 1, 3-dipolar cycloaddition reactions of oxanorbornadiene with C, N-disubstituted nitrones and dimethyl nitrilimines: a DFT mechanistic study,” *Theoretical Chemistry Accounts*, 139 (2020): 1–15.

[10] A. D. Becke, “A half-half theory of density functionals,” *J. Chem. Phys.* 98 (1993):1372.

[11] A. D. Becke, “P hys. Rev. A 1988, 38, 3098. b) C. Lee, W. Yan, RG Parr,” *Phys. Rev. B*, 37(1988): 785.

[12] T. G. Díaz-Rodríguez, M. Pacio, R. Agustín-Serrano, H. Juárez-Santiesteban, and J. Muñiz, “Understanding structure of small TiO_2 nanoparticles and adsorption mechanisms of PbS quantum dots for solid-state applications: a combined theoretical and experimental study,” *Theoretical Chemistry Accounts*, 138 (2019) :92.

[13] P. W. Ayers, M. Levy, and Á. Nagy, “Time-independent density functional theory for degenerate excited states of Coulomb systems,” *Theoretical Chemistry Accounts*, 137 (2018):152.

[14] Y. Lin, H. Fan, Y. Li, and X. Zhan, “Thiazole-based organic semiconductors for organic electronics,” *Advanced Materials*, 24 (2012):3087–3106.

[15] S. Lakrikh, M. El Idrissi, L. Laallam, A. Zeroual, E. M. Rakib, and A. Jouaiti, “Quantitative Analysis Of The Structure-Activity Relationship Of 1, 2-Benzodiazole Derivatives: DFT Study,” *RESEARCH JOURNAL OF PHARMACEUTICAL BIOLOGICAL AND CHEMICAL SCIENCES*, 9 (2018): 874–889.

[16] Z. Guo, W. Liang, Y. Zhao, and G. Chen, “Real-Time Propagation of the Reduced One-Electron Density Matrix in Atom-Centered Orbitals: Application to Electron Injection Dynamics in Dye-Sensitized TiO_2 Clusters,” *The Journal of Physical Chemistry C*, 112 (2008):16655–16662, doi: 10.1021/jp802007h.

[17] A. P. Bella, R. V. Solomon, S. A. Vedha, and J. P. Merlin, “Enhanced luminescence efficiency of structurally tailored new coumarin-based heterocyclic organic materials: a DFT/TD-DFT study,” *Theoretical Chemistry Accounts*, 138 (2019): 53.

[18] M. Bourass *et al.*, “DFT theoretical investigations of π -conjugated molecules based on thienopyrazine and different acceptor moieties for organic photovoltaic cells,” *Journal of Saudi Chemical Society*, 20 (2016): S415–S425.

[19] Z. Wu, B. Fan, F. Xue, C. Adachi, and J. Ouyang, “Organic molecules based on dithienyl-2, 1, 3-benzothiadiazole as new donor materials for solution-processed organic photovoltaic cells,” *Solar energy materials and solar cells*, 94 (2010), pp. 2230–2237.

[20] H. Tian *et al.*, “Effect of different electron donating groups on the performance of dye-sensitized solar cells,” *Dyes and Pigments*, 84 (2010), pp. 62–68.