Role of aromatic π-bridge acceptor on optical and electronic properties in D-A-D molecule based on thienylevinylenefor photovoltaic devices: DFT study

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ABSTRACT: In this work, we report theoretical analysis on the geometries and optoelectronic properties of eight new small conjugated compounds based on thienylevinylenein a donor–bridge–donor (D-A-D) system with different heterocyclic bridges as acceptor moieties (A) inserted in the middle of the molecule, these compounds were designed and characterized by using density functional theory (DFT) and time-dependent (TD) calculations. The study of the structural and optoelectronic properties (HOMO, LUMO, Gap energy, Voc) is realized by using DFT method at Becke's three-parameter functional and Lee–Yang–Parr functional (B3LYP) level with 6-31G(d) basis set.The calculations were performed by Gaussian 09 program supported by Gauss View 5.0. While the absorption properties are obtained by TD-DFT/B3LYP/6-31G(d) method.The effects of the heterocyclic acceptor bridges on the geometries and optoelectronic properties of these molecules are discussed to investigate the relationship between structure and optoelectronic properties. These properties suggest these materials as good candidates for organic solar cells.

KEYWORDS: Conjugated molecules, thienylevinylene, optoelectronic properties, DFT calculations, HOMO-LUMO gap, organic solar cell.

1   INTRODUCTION

Since the discovery of conducting polymers in 1977 [1] and when the three scientists founders of the conjugated conducting polymer chemistry; Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa, they won the Nobel Prize in chemistry for their discovery in 2000, after that, conjugated polymers and oligomers have attracted an increasing amount of attention for various organic optoelectronic devices because of their low cost production, lighter and mechanical flexibility of the device and large area usage. In particular, their applications inorganic light emitting diodes (OLEDs) [2], organic solar cells (OSCs) [3], [4], [5], sensors [6] and organic field effect transistors (OFETs) [7]. Among all the conjugated polymers, poly (phenylenevinylene) (PPV) and poly (thienylenevinylene) (PTV), but PTV has attracted much attention because it has the ability to replace the phenyl ring in PPV by the thiophene ring rich in electron and has a positive effect on conductivity and stability of the doped polymers [8]. Therefore, thevinylene bridges between thiophene moieties in these polymers improve the electronic properties of thienylenevinylene polymers [9], [10], [11], [12], [13], [14] by enhancing the planarity [15] and the effective conjugation length [16], [17], [18]. Moreover, poly (thienylenevinylene)s(PTVs) are an interesting class of materials for organic solar cell applications as active layer because of their natural small bandgapEg~1.7eV, they have high planarity and conductivity [19],therefore having a high absorption in the visible range of the solar spectrum. Furthermore, PTVs have high charge carrier (hole) mobility [20]. In addition these materials were easily synthesized [21].

In this paper, a series of eight conjugated compounds as D-A-D model(P1, P2, P3, P4, P5, P6, P7 and P8) based on thienylenevinylene containing the electron acceptor moieties in their middles as bridge(fig.1).The eight electron acceptors can be grouped from P1 to P8 respectively in the following structures: Benzo[1,2-c;4,5-c] bis[1,2,5] thiadiazole, [1,2,5] Thiadiazolo [3,4-g] quinoxaline, Pyrido [3,4-b] pyrazine, Thieno [1,2,5] thiadiazole, [1,2,5] Oxadiazolo [3,4-c] pyridine, Naphtho [2,3-c][1,2,5] thiadiazole, [1,2,5] thiadiazolo [3,4-c] pyridine and Thieno [3,4-b] pyrazine. The geometries, optoelectronic properties and absorption spectra of these dyes are studied by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP level with 6-31G(d,p) basis set. Our major goal is to understand and to investigate the effects of the acceptor strength on the geometric and optoelectronic properties to predict and to drive next syntheses towards compounds more useful as active layer in photovoltaic devices such organic solar cell.
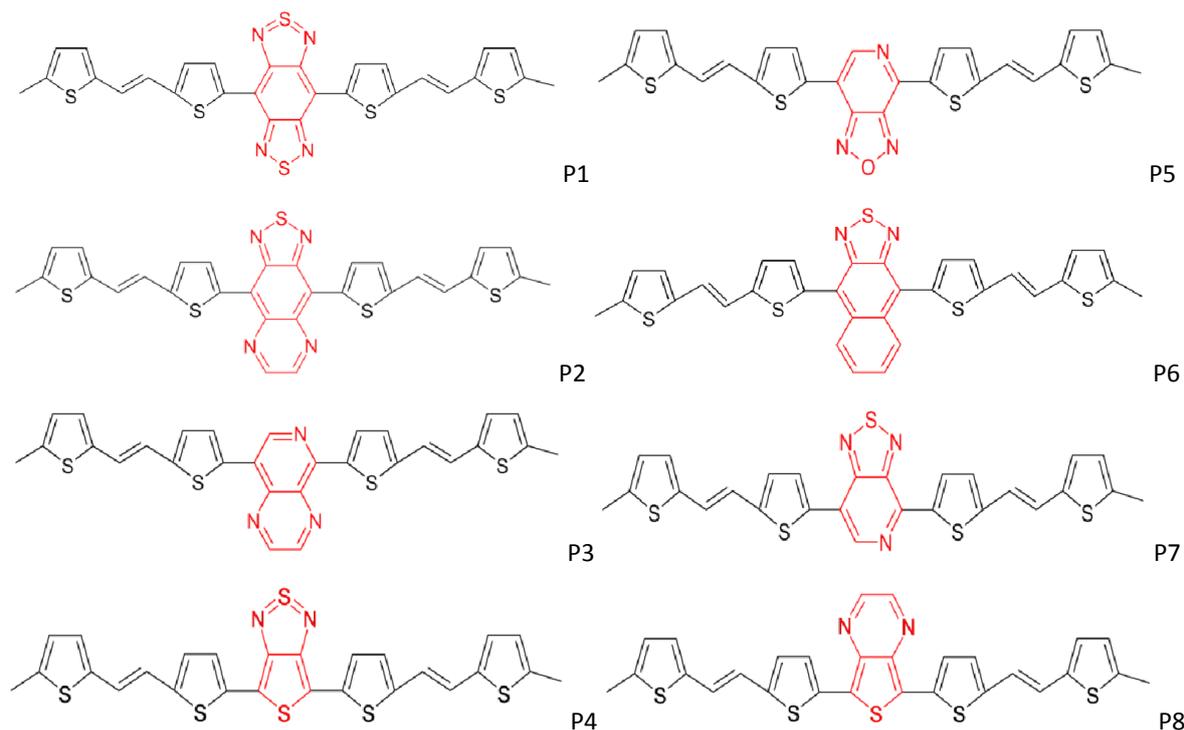

*Fig. 1.Studied compounds P1, P2, P3, P4, P5, P6, P7 and P8.*

2 COMPUTATIONAL METHODOLOGY

The calculations were carried out using the GAUSSIAN 09 package [22].Density functional theory (DFT)with the three-parameter compound of Becke (B3LYP) [23] and the 6-31G(d) basis set [24] was used to optimize the geometries of the studied molecules and to determine theHOMO/LUMO energies and the band gap energy (is evaluated as the difference between the HOMO and LUMO energies).Vertical electronic excitation spectra, including maximalwavelengths(λ_{max}), oscillators strengths(O.S) and excitation energy(Ex) were systematically investigated using TD-DFT/B3LYP/6-31G(d) method, on the basis of the optimized ground state structures. All calculations were carried out in the gas phase.In fact, these calculation methods have been successfully applied to other conjugated polymers [25].

3 RESULTS AND DISCUSSION

3.1 STRUCTURE AND GEOMETRIC PROPERTIES

All the molecular geometries have been calculated with the DFT/B3LYP/6-31G (d)method using *Gaussian 09* program. The optimized structures of the studied molecules are depicted in fig. 2. In the one hand, the dihedral angles results of these optimized structures summarized in Table 2, weshow that they have similar conformations (quasi planar conformation) except for P6 structure there is a slight twist in θ_2 (~41°) and θ_3(~11.44°).

P1

P2

P3

P4
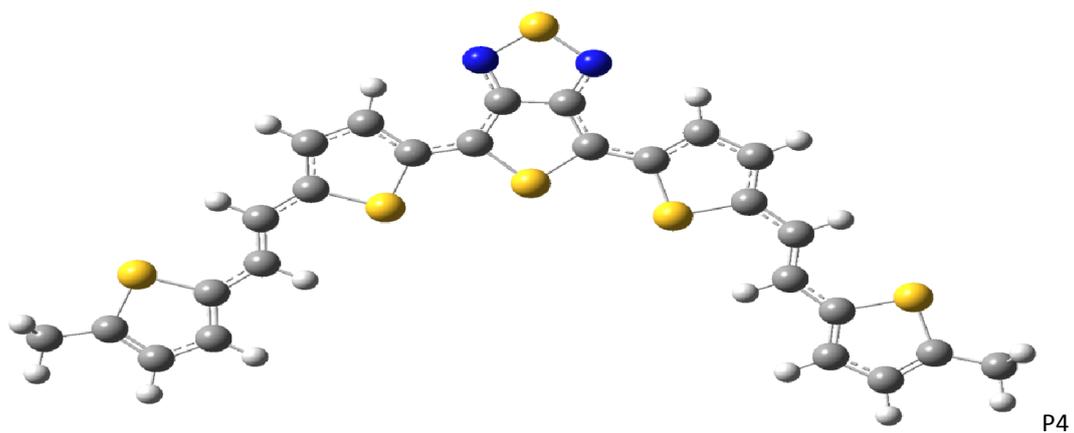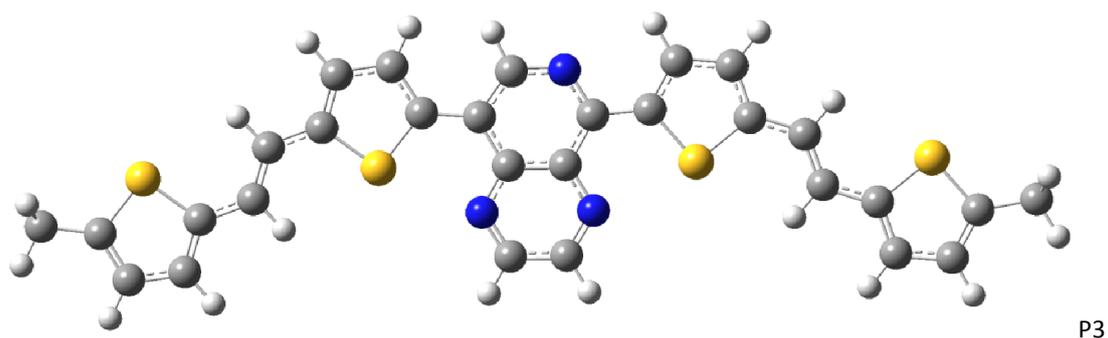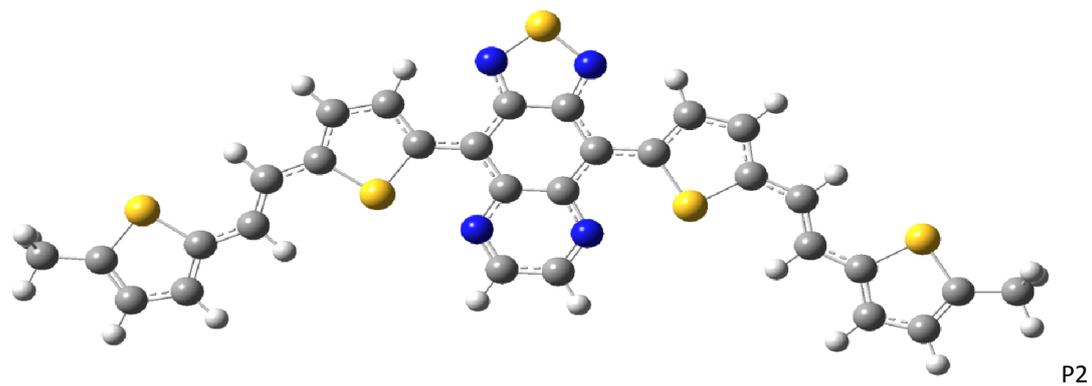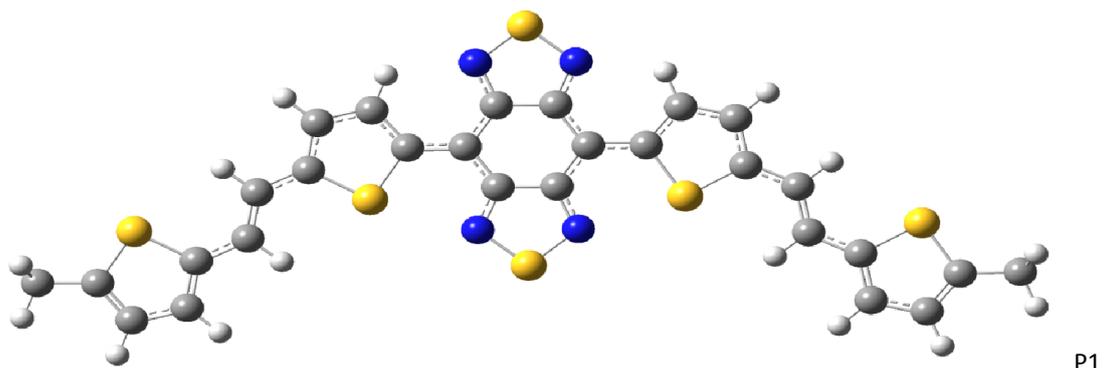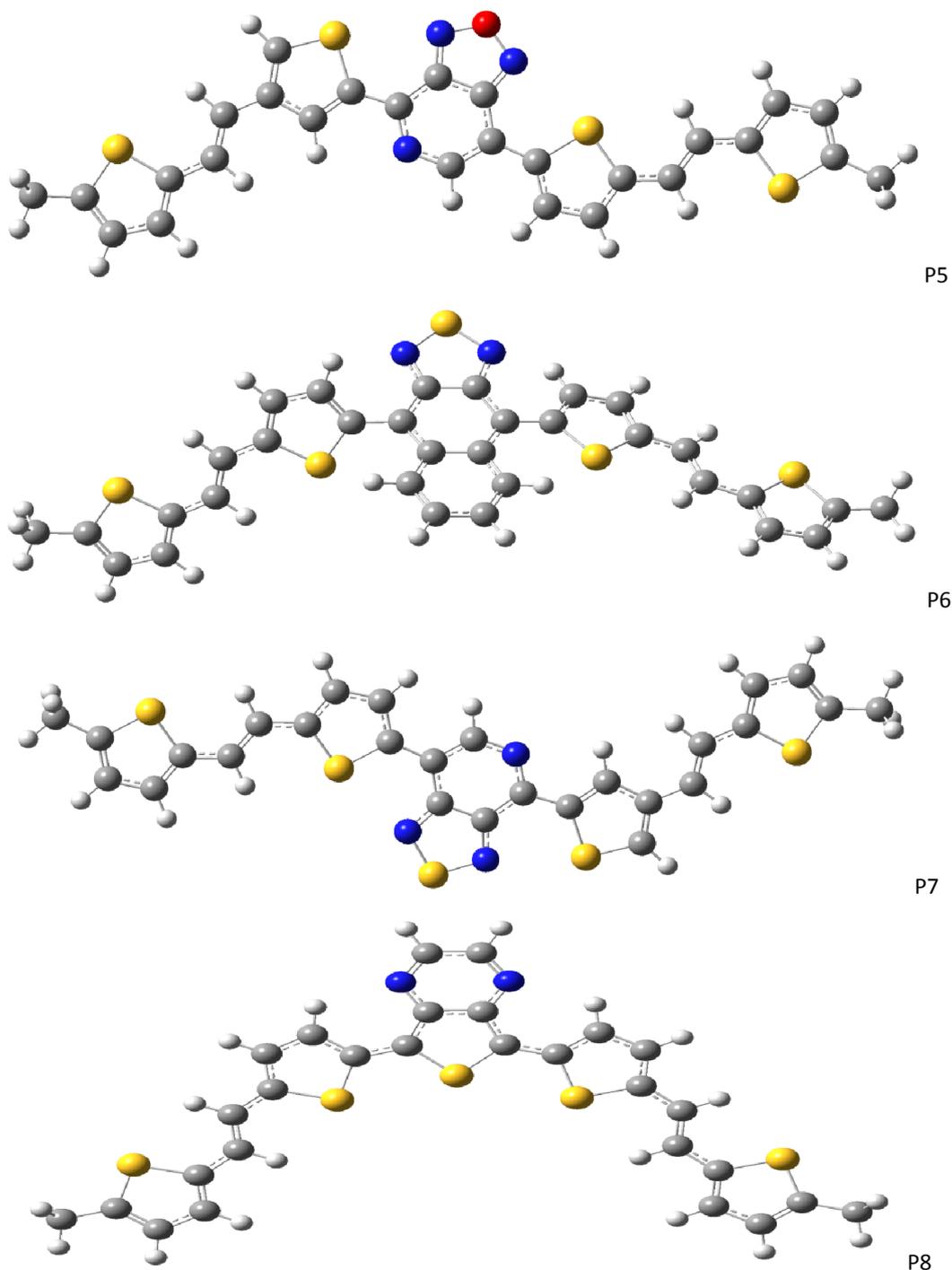
Fig. 2.optimized geometries obtained by B3LYP/6-31G(d) of the studied molecules

On the other hand, the bond lengths di(Å); (i=1-8)across the optimized molecules chain are summarized in Table 1 and Fig. 3. From the results of the table 2, we found a slight effect of the acceptor group on the bond lengths, and we noted that with the Benzo[1,2-c;4,5-c] bis[1,2,5] thiadiazole acceptor group in P1 a much decrease of the simple bond lengths(d1, d3, d4, d5, d5, d6 and d8) and the double bond lengths (d2 and d7) are shorter than that of the other molecules.
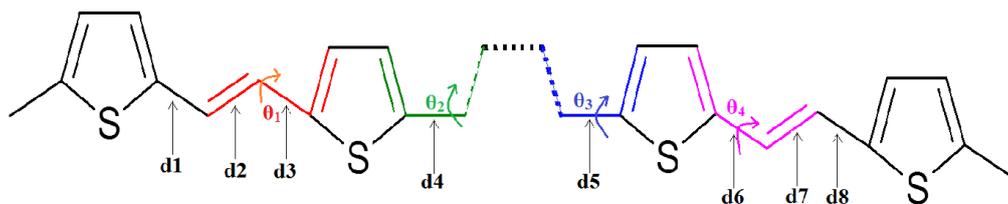
Fig. 3.The scheme of the bond lengths and dihedral angles

Table 1. Bond-length (Å) values obtained by B3YP/6-31G(d).

Molecule	di (Å)							
	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
P0 (without acceptor) [27]	1.4403	1.3565	1.4383	-	-	1.4383	1.3565	1.4403
P1	1.4368	1.3601	1.4340	1.4376	1.4376	1.4340	1.3601	1.4368
P2	1.4379	1.3590	1.4362	1.4466	1.4467	1.4362	1.3590	1.4379
P3	1.4401	1.3567	1.4396	1.4559	1.4539	1.4391	1.3571	1.4396
P4	1.4379	1.3590	1.4335	1.4229	1.4229	1.4335	1.3591	1.4379
P5	1.4443	1.3514	1.4566	1.4523	1.4486	1.4387	1.3571	1.4390
P6	1.4406	1.3559	1.4404	1.4622	1.4631	1.4370	1.3577	1.4390
P7	1.4397	1.3568	1.4392	1.4517	1.4557	1.4564	1.3514	1.4446
P8	1.4389	1.3579	1.4358	1.4321	1.4321	1.4358	1.3579	1.4389

Table 2.Dihedral angles (°) values obtained by B3YP/6-31G(d)

Molecules	θ(°)			
	θ_1	θ_2	θ_3	θ_4
P0[27]	180.00	-	-	179.99
P1	179.99	0.00	0.00	179.99
P2	179.99	0.00	0.00	179.99
P3	179.99	0.00	0.00	179.99
P4	179.99	0.01	0.00	179.99
P5	179.99	0.00	0.00	179.99
P6	178.99	41.06	11.44	179.05
P7	179.99	0.00	0.01	179.99
P8	179.97	0.00	0.00	179.99

3.2 ELECTRONIC AND OPTICAL PROPERTIES

The HOMO(highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are useful for understanding more details on excited-state propertiesand of the ability of electron or hole transport [26].

The contour plots of HOMO and LUMO orbitals of studied molecules by B3LYP/6-31G(d) are shown in Fig. 2. The general HOMO shows antibonding character between the bridges C–C atoms ofthe subunits. In contrary, the LUMOs of all compounds generally show a bonding character between the subunits.Moreover, it can be clearly seen that for all the molecules the HOMOs covered the entire molecule, while, the LUMOs are distributed mainly on the acceptor unit.

HOMO LUMO
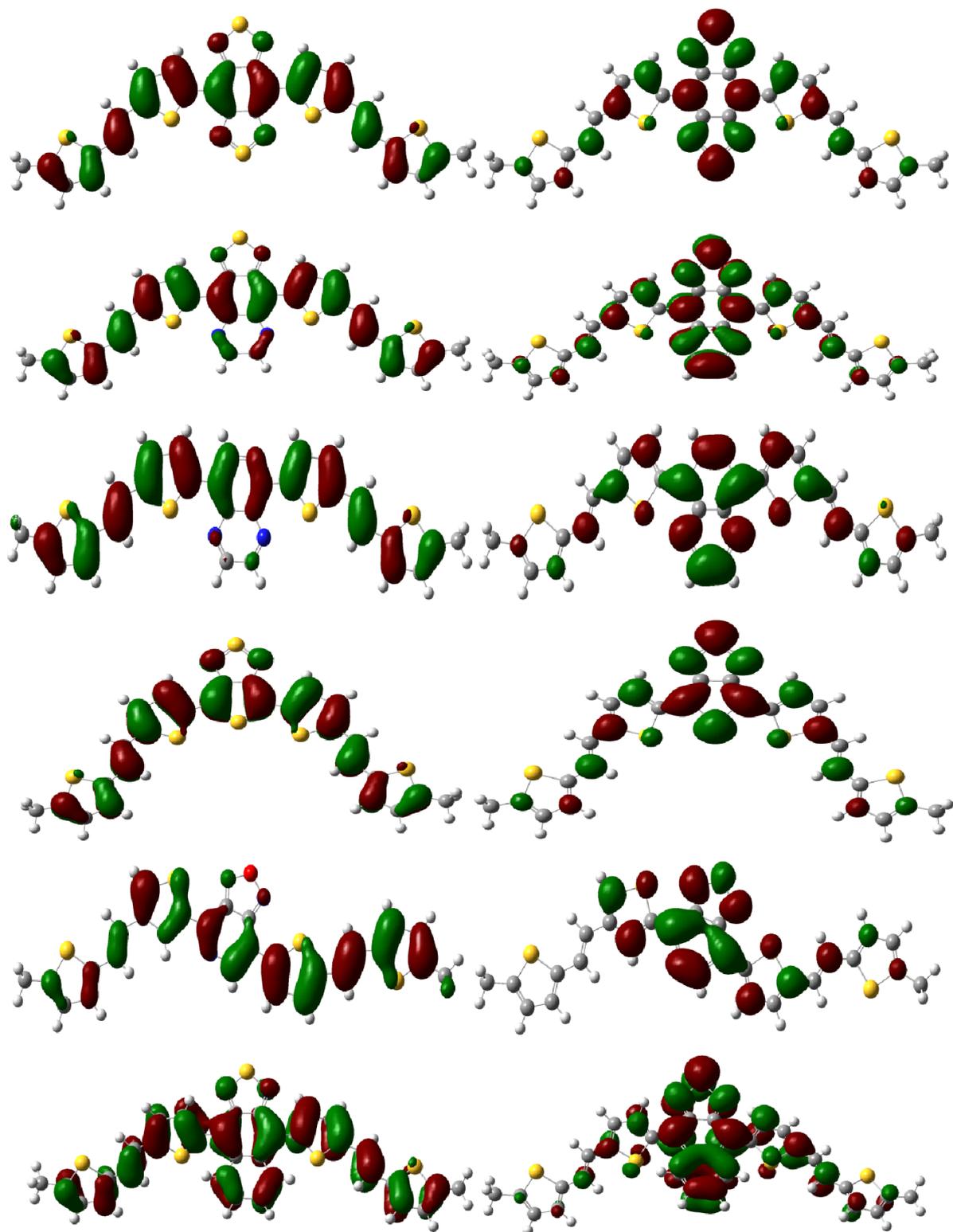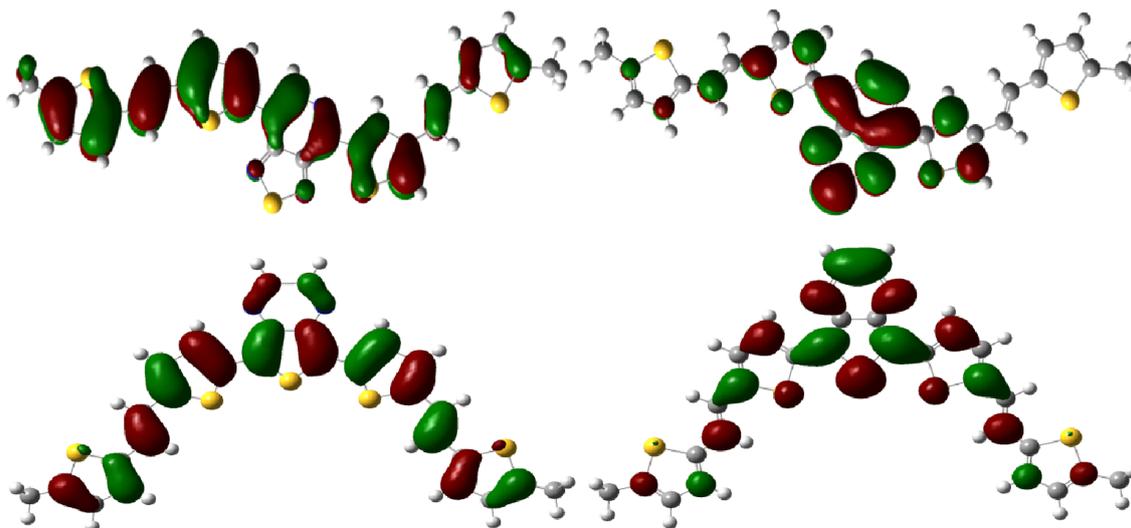
Fig. 4. The contour plots of HOMO and LUMO orbital's of the studied compounds

To gain insight into the effect of the acceptor groups on electronic properties, the E_{HOMO} and E_{LUMO} energies of the studied molecules were examined. The results of the E_{HOMO}, E_{LUMO} and band gap energy values are depicted in table 3 and fig. 5.On the one hand, comparing these values with theirs of the molecule without acceptor group (E_{HOMO}= - 4.6764 eV, E_{LUMO}=-2.0754 eV and Eg= 2.6009 eV)[27], we noticed clearly a decrease in the E_{LUMO}(stabilization of the LUMOs levels) and Eg energies of the studied compounds, while the HOMO energies of different compounds are nearly the same. On the other hand, we showed that the E_{LUMO} and Egare in the order ofP3 > P8>P6 > P7>P5 > P4 > P2 > P1 and P5 > P3> P7> P8>P6 > P4 > P2 > P1, respectively. This decrease in the gap energy is attributed to the electron accepting strength of several acceptor groups. We noted that P1 has the law gap energy among the studied compounds (Eg(P1) = 1.1eV), this can be explain by the stronger electron-withdrawing of Benzo[1,2-c;4,5-c] bis[1,2,5] thiadiazole.

Table3. Theoretical electronic properties parameters (HOMO, LUMO, Gap) obtained by B3LYP/6-31G(d) of the studied molecules

| Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E gap (eV)
P0[27]	- 4.6764	- 2.0754	2.6009
P1	-4.5196	-3.4103	1.1093
P2	-4.5654	-3.2221	1.3432
P3	-4.7197	-2.6693	2.0504
P4	-4.4540	-3.0288	1.4252
P5	-5.0372	-2.9762	2.0610
P6	-4.6582	-2.8853	1.7729
P7	-4.9290	-2.9177	2.0112
P8	-4.5253	-2.7183	1.8070
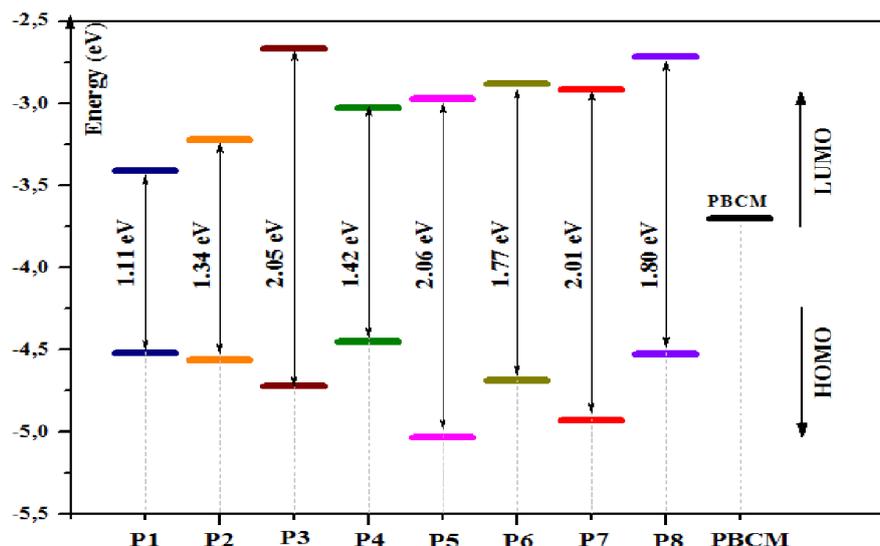
Fig. 5. Schematic energy levels of the studied compounds and the LUMO energy of PBCM.

Generally, the most of the active layer in bulk heterojunction structure using a blend of p-conjugated molecular donors and fullerene derivative acceptors [28], [29], [30], [31]. Herein, we have the compounds Pi as donors, blended with [6.6]-phenyl-C61-butyric acid methyl ester (PCBM), which is the mostly used as acceptor in solar cell devices. So, to evaluate the possibilities of electron transfer from the excited studied molecules to the conductive band of the acceptor, the HOMO and LUMO energy levels of the donor and acceptor were compared. As shown in fig.5, the LUMO energy levels of all compounds are higher than that of the acceptor PBCM(E_{LUMO} (PBCM) = -3.7eV). Moreover, molecules in excited states have a strong ability to inject electrons into the PCBM acceptor. In addition, the maximum open circuit voltage (Voc) is the very important photovoltaic parameter which related to the difference between the highest occupied molecular orbital (HOMO) of the donor (molecules Pi) and the LUMO of the electron acceptor (PCBM), taking into account the energy lost during the photo charge generation [32]. The theoretical values of open-circuit voltage Voc have been calculated from the following expression:

$$V_{oc} = \left| E_{HOMO} (Donnor) \right| - \left| E_{LUMO} (Acceptor) \right| - 0.3$$

The Voc calculated values of our studied molecules range from 0.45 to 1.03 eV (see table 4).These values are sufficient for a possible efficient electron injection. These values are sufficient for a possible efficient electron injection. Further, all the studied compounds can be used as sensitizers because the electron injection process from the exited molecule to the condition band of PCBM and subsequent regeneration is possible in sensitized solar cells (see fig.5).

Another parameter denoted $α_I$ is the difference between the LUMO energy levels of the studied compounds Pi and the HOMO energy level of PCBM [$α_i$ = E_{LUMO} (Acceptor) - E_{LUMO} (Donor)].As shown in table 4, the values of $α_I$ are in the range of 0.28-1.03 eV, suggesting that the photo excited electron transfer from Pi to PCBM may be sufficiently efficient to be useful in photovoltaic devices[33].

Table 4.Energy Values of E_{HOMO}, E_{LUMO} and the Open Circuit Voltage Voc by eV.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	Voc (eV)	*α_i(eV)
P1	-4.5196	-3.4103	0.5196	0.2897
P2	-4.5654	-3.2221	0.5654	0.4729
P3	-4.7197	-2.6693	0.7197	1.0307
P4	-4.4540	-3.0288	0.4540	0.6712
P5	-5.0372	-2.9762	1.0372	0.7238
P6	-4.6582	-2.8853	0.6582	0.8147
P7	-4.9290	-2.9177	0.9290	0.7823
P8	-4.5253	-2.7183	0.5253	0.9817
PCBM	-6.1000	-3.7000	-	-

*α_i = ELUMO (Pi) - ELUMO (PCBM);   (Pi, i=1…8).

Table 5. Data absorption spectra obtained by TD/DFT method for the compounds studied in the optimized geometries at B3LYP/6-31G(d).

Compounds	λmax (nm)	*E_{ex} (eV)	**O.S (eV)	MO/character (%)
P1	494.35	2.5080	1.4377	HOMO ⟶ LUMO+1 (85%)
P2	477.02	2.5991	1.1383	HOMO ⟶ LUMO+1 (80%)
P3	445.13	2.7853	1.1743	HOMO ⟶ LUMO+1 (96%)
P4	522.60	2.3724	0.9709	HOMO ⟶ LUMO+1 (94%)
P5	398.79	3.1090	0.6679	HOMO ⟶ LUMO+1 (80%)
P6	464.77	2.6676	0.9199	HOMO ⟶ LUMO+1 (80%)
P7	415.34	2.9851	1.0623	HOMO ⟶ LUMO+1 (89%)
P8	449.96	2.5457	0.7687	HOMO ⟶ LUMO+1 (96%)

The vertical electronic transition energies andoptical absorption spectra of P1-P8 were calculatedby TD-B3LYP/6-31G(d). Figure 5 shows the calculated opticalabsorption spectra.

The detailed computational absorption maximal wavelength (λ_{max}), oscillator strength (O.S), transition energy (E_{ex}) and the major molecular orbital (MO) involved in the transition are listed in Table 5. We noted that all optical absorption corresponds to transitions from HOMO to LUMO+1.Additionally, compared with P5, the maximum absorption peaks shows a bathochromic shift from 398 to 522 nm.
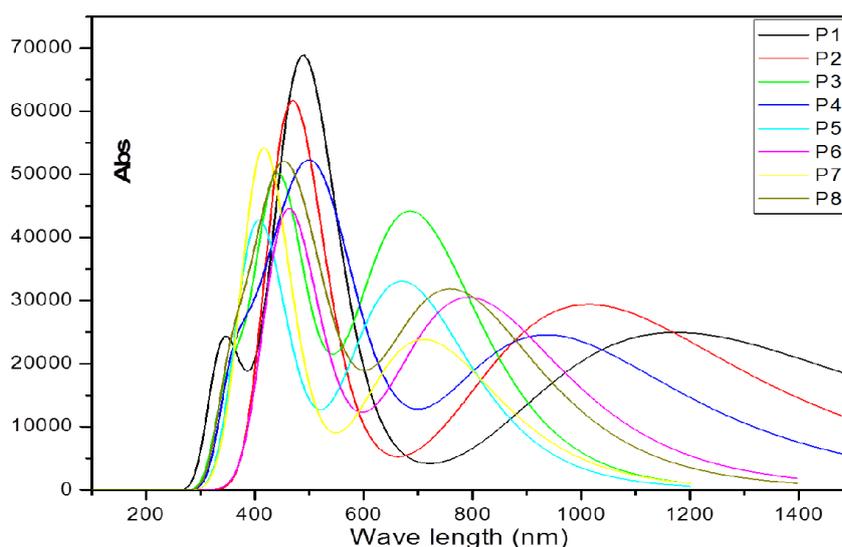

Fig. 5Simulated UV–visible optical absorption spectra of studied compounds with the calculated data at the TDDFT/B3LYP/ 6-31G (d) level
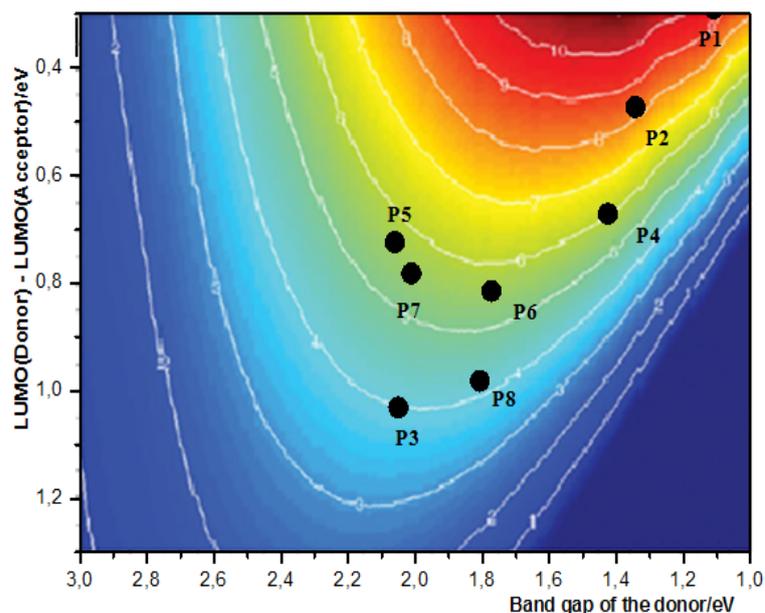
Fig. 6.Contour plot showing the power conversion efficiency with PCBM as acceptor material (LUMO level 3.7 eV).

In order to estimate the properties of the designed molecules, we used the Scharber diagrams [34] to predict PCEs (%) of the solar cells combining P1–P8 and PCBM. We can predict the overall PCEs from the band gaps and the LUMO (donor)-LUMO (PCBM) energy of the donors (see fig.6). The predictions by the diagram show that the PCEs of P1 and P2 (with the smallest band gap and lowest LUMO energy level among the studied molecules) are 9% and8%respectively when used in combination with PCBM.

4   CONCLUSION

In this letter, the quantum chemical investigation using DFT/B3LYP/6-31G(d) method on the geometries and opto-electronic properties of eight conjugated compounds(P1-P8) based on thienylenevinylene and various acceptor units A (as D-A-D structure) is performed in order to display the effect of molecular structure on the opto-electronic properties of these materials. The concluding remarks are:

- Generally, the optimized structures for all studied compounds have similar conformations (quasi planar conformation).
- The modification of chemical structures by the introduction of acceptor units Ain the molecule backbone (as D-A-D structure) can modulate and improve the electronic and optical properties of these molecules. The calculated frontier orbital energies HOMO, LUMO and gap energy (Egap) showed a slight difference in the gap energy values of the studied molecules and depending on the electron acceptor groups added, these values arein the range of 1.10 -2.06 eV.
- The calculated values of Voc of the studied molecules range from 0.45 eV to 1.03 eV in the case of PCBM, these values are sufficient for a possible efficient electron injection.
- The UV–Vis absorption properties have been obtained by using TD/DFT calculations. The obtained absorption maximums are in the range of 398–522 nm.

Finally, using theoretical methodologies, we showed that is possible to predict reasonably the optical and electronic properties of conjugated systems, to orientate the synthesis efforts and help in understanding the structure-properties relation of conjugated materials for photovoltaic applications.

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