

Theoretical Studies on the Structural, Electronic and Optical Properties of the New π -conjugated Copolymers Based on Carbazole and Thiophene

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Abstract

This work reports a theoretical investigation of π -conjugated oligomers constituted by n units ($n = 1-4$) based on carbazole and ethylenedioxythiophene. The molecular geometry, torsional potential, electronic and optical properties of the oligomers [Cbz-(Edot) _{n} -Cbz] ($n = 1-4$) are investigated using DFT (B3LYP/3-21G*) calculations. The discussion is focused on the influence of chain length on the properties of these copolymers. The analyses of torsional angles for [Cbz-(Edot)₄-Cbz] reveal that the structure has a anti-planar conformation. The electronic properties of the molecules, HOMO, LUMO and E_g (HOMO-LUMO), are studied using B3LYP functional. The results have been compared with those of thiophene and ethylenedioxythiophene. The lowest excitation energies (E_{ex}) and the maximal absorption wavelength (λ_{abs}) are studied using the TD/DFT, ZINDO and CIS methods. The electronic transitions of the absorption spectrum derived by TD/DFT method give useful structural and electronic information for designing novel conducting organic polymer materials. The bridging effect by C=C(CN)₂ on the optoelectronic properties of the (carbazole-thiophene-carbazole) comonomer is investigated.

Keywords: Conducting polymer; Carbazole-(Ethylenedioxythiophene) _{n} -Carbazole comonomers; DFT Optoelectronic properties; absorption coefficient; Bridging effect.

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1. Introduction

Electrically conducting polymers have been considered for numerous applications including charge dissipation coatings [1], organic thin-film transistors [2], and conducting textiles [3].

In the last year, the poly(3,6-carbazole) and derivatives have been synthesized [4, 5]. Luminescent materials spanning the entire visible range have been prepared from these polymers [6], and can be used in organic light electronic devices (OLED) [7]. The

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polyvinylcarbazole (PVK) have significant specific properties (photoconductivity, photoluminescence and hole transport properties) [8, 9]. One of the most important factors of controlling physical properties is the bandgap, which is a current topic of research. The polymers with a low bandgap are desired in optoelectronic applications. Leclerc *et al.* [4, 5] have reported the spectroscopic and photophysical properties of carbazole-based molecules in solution. The absorption and emission energies of these copolymerized derivatives were correlated with their electronic transitions, as computed by ZINDO calculations performed on optimized HF/6-31G(d) geometries, and first relaxed excited state as obtained by RCIS/6-31G(d) calculations [10, 11]. The results demonstrated a good agreement between computed electronic transitions and the optical data. The geometric structures and electronic properties of the carbazole-based oligomers, were recently studied by Yang *et al.* [12, 13] and Surmtir *et al.* [14].

On the other hand, the poly(3,4-ethylenedioxythiophene) (PEDOT) showed a remarkable high stability, high electrical conductivity and a low optical band gap [15, 16] of approximately 1.6 eV, making this material to be a candidate for many industrial applications. As antistatic material, PEDOT is already being used industrially in a large scale. In this polymer the oxygen atoms of the dioxane ring are directly attached at the 3- and 4-positions. PEDOT homopolymer is widely used as a conducting and hole-injecting electrode in organic light emitting diodes (OLEDs) [17]. Several EDOT based donor-acceptor conjugated polymers with small band gaps have been reported [18-20]. Dkhissi *et al.* [21] have investigated the relative stability of the aromatic and quinoid-like structures for neutral PEDOT using *ab initio* SCF and DFT (density functional theory) calculations at the HF and B3LYP levels, respectively. Materials that combine properties of these two monomers (Cbz and EDOT) are attractive materials for a variety of applications in the electronic devices. Recently, the copolymer based carbazole and ethylenedioxythiophene was synthesized by Sarac *et al.* [22]. In the present study, we report a theoretical study of the structural, electronic, and optical properties of (carbazole-(3,4-ethylenedioxythiophene)_n-carbazole) [Cbz-(Edot)_n-Cbz]. The model compound of the molecular structure is shown in Fig. 1. We will examine the insertion effect of bridging by C=C(CN)₂ groups on the energy gaps and the electronic properties of the (Carbazole-Bithiophene-Carbazole) (Cbz-BThi-Cbz) and (Carbazole-Quaterthiophene-Carbazole) (Cbz-QThi-Cbz) comonomers. These properties will be compared with those of the studied comonomers. Bridging is one of several chemical modifications which have been intensively used by several groups that aim at decreasing the band gaps of the systems [23, 24].

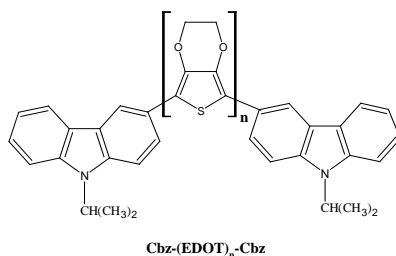


Fig. 1. Chemical structure of the oligomers [Cbz-(Edot)_n-Cbz].

2. Computational Methods

The molecular geometries of the several oligomers [Cbz-(Edot)_n-Cbz] ($n = 1-4$), were fully optimized using the DFT method of three-parameter compound of Becke (B3LYP) [25]. All calculations in this work were carried out using Gaussian 03 program package [26]. The 3-21G* basis set was used for all calculations [27-30]. The conformational analysis of all oligomers was done by changing the torsional angles between adjacent carbazole and ethylenedioxythiophene rings by 20° steps in the same direction in order to obtain the final torsional angles of the conformers in each minimum. The HOMO, LUMO and gap (HOMO-LUMO) energies were also deduced for the stable structures. We employed the linear extrapolation technique in this research, which has been successfully employed to investigate several series of polymers [31-34]. Electronic transition energies and oscillator strengths of oligomers were obtained by using various methods (semi-empirical ZINDO [35], configuration interaction singles (CIS) [36] and time dependent density functional theory (TD/DFT) [37]).

3. Results and Discussion

3.1. Conformation and structural properties

3.1.1. Conformational analysis

The results of the torsion potential of the several oligomers obtained with B3LYP/3-21G* level, are presented in **Fig. 2**. All the curves obtained for the oligomers have the same behavior and they present four extrema, two maxima situated at 0 and 90° and two minima located at about 20 and 180°. The potential energy curves show the existence, for

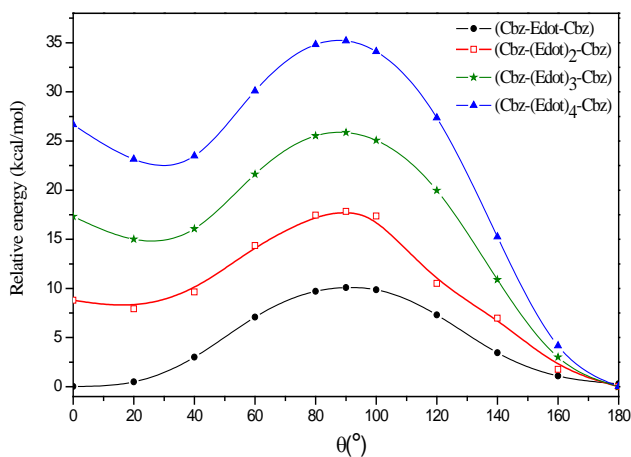


Fig. 2. Potential energy curves of [Cbz-(Edot)_n-Cbz] ($n = 1-4$) obtained by B3LYP/3-21G* level.

all oligomers, of two stable conformations: a syn-conformation and anti-conformation with the anti-one being the most stable (Table 1). The anti-conformation becomes nearly anti-planar for [Cbz-(Edot)₃-Cbz] and [Cbz-(Edot)₄-Cbz] oligomers. The syn-planar and perpendicular conformations energy barriers increase with the chain length while anti-planar energy barriers remain identical for all the oligomers (Table 2). The steric effect felt for anti-planar conformation remains unaltered with the increase of the number of rings. Similarly, HF/6-31G(d) optimizations of *n*-EDOT oligomers [38, 39] and B3LYP/6-31G(d) optimization of *n*-THP oligomers [40-42] provided an anti-conformation in all cases.

Table 1. Angle of torsion cisoide and transoide (°) conformation of copolymers [Cbz-(Edot)_{*n*}-Cbz] (*n* = 1-4), obtained by B3LYP/3-21G* level.

No of rings	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4
θ ₁ (syn)	4.81	2.00	3.37	1.90
θ ₁ (anti)	177.51	175.37	177.40	178.29
θ ₂ (syn)	3.08	37.56	38.11	37.96
θ ₂ (anti)	177.71	179.88	179.84	179.81
θ ₃ (syn)	-	4.69	37.67	38.10
θ ₃ (anti)	-	179.94	179.89	179.73
θ ₄ (syn)	-	-	5.38	38.34
θ ₄ (anti)	-	-	179.70	179.27
θ ₅ (syn)	-	-	-	5.92
θ ₅ (anti)	-	-	-	174.33

Table 2. Relative energy (eV) of all conformations of all oligomers [Cbz-(Edot)_{*n*}-Cbz] (*n* = 1-4), calculated by B3LYP/3-21G* level.

Oligomer	Plane (0°)	Syn-plane	Perpendicular (90°)	Anti-gauche	Anti-plane (180°)
[Cbz-Edot-bz]	0.001	0.00	0.437	0.012	0.013
[Cbz-(Edot) ₂ -Cbz]	0.381	0.286	0.773	0.00	0.0005
[Cbz-(Edot) ₃ -Cbz]	0.750	0.565	1.121	0.00	0.0003
[Cbz-(Edot) ₄ -Cbz]	1.156	0.877	1.526	0.00	0.001

3.1.2. Geometric properties

We present in Table 3, the optimized structural parameters (corresponding to the global minimum optimized structure) for all oligomers (Cbz-(Edot)_{*n*}-Cbz] (*n* = 1-4) as calculated

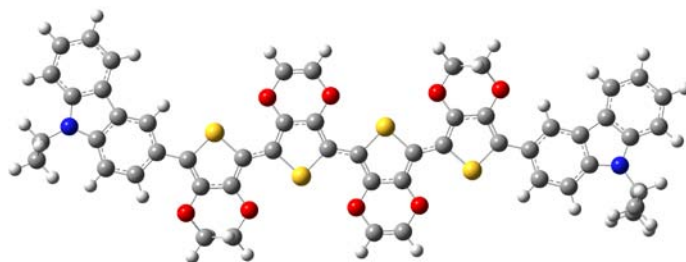
by B3LYP/3-21G* level. The optimized geometric model for [Cbz-(Edot)₄-Cbz] with B3LYP/3-21G* method is shown in Fig. 3. There are no significant differences among the bond lengths obtained for all oligomers in their ground state. Concerning the rotational angle, the results obtained for [Cbz-Edot-Cbz] show that the stable conformation is syn-planar, on the other hand, from n = 2 and up, the structures exhibits the anti-planar conformation. The results with the change in rotational angle are similar to that obtained for oligothiophenes [43] and PRODOT (poly(3,4-propylenedioxothiophene)) [44] ($\theta_1 \approx 178^\circ$), which all adopt anti-planar conformation.

Table 3. Optimized structural parameters, bond length (in Å) and inter-ring twisting angle (°) of oligomers [Cbz-(Edot)_n-Cbz] (n = 1-4) obtained by B3LYP/3-21G* level.

No. of rings	1	2	3	4
C ₁ C ₂	1.393	1.393	1.393	1.393
C ₂ C ₃	1.396	1.396	1.397	1.396
C ₃ C ₄	1.452	1.451	1.451	1.451
C ₄ C ₅	1.391	1.391	1.391	1.391
C ₅ C ₆	1.407	1.405	1.405	1.405
C ₆ C ₇	1.461	1.460	1.460	1.460
C ₇ C ₈	1.377	1.380	1.380	1.380
C ₈ C ₉	1.431	1.423	1.422	1.422
C ₉ C ₁₀	1.377	1.375	1.375	1.375
C ₁₀ C ₁₁	1.461	1.427	1.427	1.427
C ₁₁ C ₁₂	1.408	1.369	1.372	1.372
C ₁₂ C ₁₃	1.392	1.421	1.413	1.413
C ₁₃ C ₁₄	1.452	1.373	1.371	1.372
C ₁₄ C ₁₅	1.396	1.461	1.428	1.428
C ₁₅ C ₁₆	1.392	1.405	1.369	1.372
C ₁₆ C ₁₇	-	1.391	1.422	1.413
C ₁₇ C ₁₈	-	1.451	1.373	1.372
C ₁₈ C ₁₉	-	1.396	1.461	1.427
C ₁₉ C ₂₀	-	1.392	1.405	1.376
C ₂₀ C ₂₁	-	-	1.391	1.421
C ₂₁ C ₂₂	-	-	1.451	1.380
C ₂₂ C ₂₃	-	-	1.396	1.460
C ₂₃ C ₂₄	-	-	1.392	1.407
C ₂₄ C ₂₅	-	-	-	1.391
C ₂₅ C ₂₆	-	-	-	1.451
C ₂₆ C ₂₇	-	-	-	1.396
C ₂₇ C ₂₈	-	-	-	1.393

Table 3 (contd.)

θ_1	4.81	175.37	177.40	178.29
θ_2	3.08	179.88	179.84	179.81
θ_3	-	179.94	179.89	179.73
θ_4	-	-	179.70	179.27
θ_5	-	-	-	174.33

Fig. 3. Optimized structure of [Cbz-(Edot)₄-Cbz] obtained by B3LYP/3-21G* level.

3.2. HOMO, LUMO and band gaps

There are two theoretical approaches for calculating the energy gap. One way is based on the ground-state properties, from which the band gap is estimated from the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [45, 46], when $n = \infty$, termed the HOMO–LUMO gaps (Δ_{H-L}). The TD/DFT, which has been used to study systems of increasing complexity due to its relatively low computational cost and also to include in its formalism the electron correlation effects, is also employed to extrapolate energy gap of polymers from the calculated first dipole-allowed excitation energy of their oligomers. The HOMO, LUMO, ΔE_n (between HOMO and LUMO) are computed and the results are given in Table 4. The obtained results for (EDOT)_n and (THP)_n [39], are presented also for comparison. When we compare the various values of calculated gap of the longest oligomer, we note that the energy gaps in [Cbz-(Edot)_∞-Cbz] (1.83 eV) are dramatically lower than those in (EDOT)_∞ (2.17 eV) and (THP)_∞ (2.34 eV), which indicates that, the additive conjugated monomers, facilitate the decreasing of the energy gaps. As is usual in π -conjugated systems, with the increasing conjugation lengths the HOMO energies increase, whereas the LUMO energies decrease in all series. The HOMO–LUMO gaps (Δ_{H-L}) and lowest singlet excited energies (E_{ex}) are both listed in Table 5 together with the results obtained for (Cbz)_n [13]. Comparing the calculated values, we can find the

superiority of carbazole-based ethylenedioxythiophene and the influence of the introduction of charge carriers.

Table 4. The HOMO, LUMO, ΔE_n (HOMO-LUMO), values of energy (in eV) of [Cbz-(Edot) $_{n-2}$ -Cbz], (EDOT) $_n$ [39] and (THP) $_n$ [39] ($n = 3-8$).

No. of rings	[Cbz-(Edot) $_{n-2}$ -Cbz]			(EDOT) $_n$ [39]			(THP) $_n$ [39]		
	HOMO	LUMO	ΔE_n	HOMO	LUMO	ΔE_n	HOMO	LUMO	ΔE_n
3	-4.532	-0.925	3.607	-4.54	-0.87	3.67	-5.31	-1.49	3.82
4	-4.477	-1.301	3.176	-4.32	-1.02	3.30	-5.15	-1.71	3.44
5	-4.435	-1.490	2.945	-4.18	-1.11	3.07	-5.07	-1.84	3.23
6	-4.287	-1.526	2.761	-4.09	-1.16	2.92	-5.01	-1.93	3.08
7	-4.147	-1.561	2.586	-4.02	-1.20	2.82	-4.98	-2.00	2.98
8	-4.144	-1.651	2.493	-3.99	-1.23	2.76	-4.95	-2.04	2.91
∞	-	-	1.83	-	-	2.17	-	-	2.34

Table 5. The HOMO-LUMO gaps (Δ_{H-L}) (eV) obtained by B3LYP/3-21G* level and the lowest excitation energies (E_{ex}) (eV) obtained by TD/DFT of [Cbz-(Edot) $_{n-2}$ -Cbz] and (Cbz) $_n$ [13] ($n = 3-8$).

Oligomer	Δ_{H-L}	E_{ex} (TD)
(Cbz) $_n$ [13]		
n = 3	3.90	3.58
n = 4	3.75	3.42
n = 5	3.67	3.34
n = 6	3.63	3.31
n = 7	3.61	3.27
n = ∞	3.42	3.08
Cbz-(Edot) $_{n-2}$ -Cbz		
n = 3	3.61	3.29
n = 4	3.17	2.88
n = 5	2.94	2.65
n = 6	2.76	2.46
n = 7	2.58	2.30
n = 8	2.49	2.21
n = ∞	1.83	1.57

3.3. Absorption spectra

We present in Table 6 the calculated absorption (λ_{\max}) (nm), the oscillator strength (f) and the excitation energy (E_{ex}) (eV) for the different studied oligomers. These values are calculated by ZINDO, TD/DFT and CIS methods starting with optimized geometry obtained at B3LYP/3-21G* level. λ_{\max} increases asymptotically as the number of aromatic nuclei increases. The oscillator strength values (f) show that the transition probability [47], increases with the chain length. Comparing with the wavelengths λ_{\max} of the Poly(THP) ($\lambda_{\max} = 318.58$ nm) and Poly(EDOT) ($\lambda_{\max} = 322.62$ nm) [48], we can note that the superiority of the proposed copolymer is in the long chain [Cbz-(Edot)₆-Cbz] ($\lambda_{\max} = 561.72$ nm), and also the influence of the introduction of charge carriers (Table 6). Therefore, the theoretical calculations give a good description of optoelectronic properties of studied oligomers and can be employed to predict the electro-luminescence characteristics of other materials.

Table 6. Calculated absorption λ_{\max} (nm), excitation energy E_{ex} (eV) and oscillation strength (f) for all oligomers [Cbz-(Edot)_n-Cbz] ($n = 1-6$).

Method		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
Zindo	λ_{\max}	417.88	487.03	536.19	575.22	608.08	632.00
	E_{ex}	2.97	2.54	2.31	2.15	2.04	1.96
	f	1.22	1.32	1.57	1.87	2.13	2.37
TD/B3LYP/3-21G*	λ_{\max}	376.41	430.05	468.12	503.02	539.09	561.72
	E_{ex}	3.29	2.88	2.65	2.46	2.30	2.21
	f	1.48	1.62	1.91	2.39	2.73	3.10
CIS/3-21G*	λ_{\max}	291.35	327.00	349.88	368.95	386.47	398.21
	E_{ex}	4.25	3.79	3.54	3.36	3.21	3.11
	f	1.65	1.96	2.38	2.93	3.34	3.69

We list the excitation energies, oscillator strengths and configurations obtained by TD/DFT-B3LYP/3-21G* calculations for each oligomer [Cbz-(Edot)_n-Cbz] ($n = 1-6$) in Table 7. All electronic transitions are of the $\pi\pi^*$ type and involve both subunits of the molecule. The largest oscillator strengths (f) originate from $S_0 \rightarrow S_1$ electronic transition. Excitation to the S_1 state corresponds exclusively to the promotion of an electron from the HOMO to the LUMO. As in the case of the oscillator strengths, the absorption wavelengths arising from $S_0 \rightarrow S_1$ electronic transition increase progressively with the increase of the conjugation lengths. It is reasonable, since HOMO \rightarrow LUMO transition is predominant in $S_0 \rightarrow S_1$ electronic transition and as seen in the analysis above that with the extending molecular size, the HOMO-LUMO gaps decrease.

Table 7. Electronic transition data obtained by the TD/DFT-B3LYP/3-21G* calculation for all oligomers [Cbz-(Edot)_n-Cbz] (n = 1-6).

Electronic transitions	λ_{abs} (nm)	E_{ex} (eV)	f	MO/character	Coeff
[Cbz-(Edot)₁-Cbz]					
$S_0 \longrightarrow S_1$	376.41	3.29	1.48	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	348.15	3.56	0.03	HOMO \longrightarrow LUMO+1	0.66
$S_0 \longrightarrow S_3$	346.78	3.58	0.04	HOMO \longrightarrow LUMO+2	0.66
[Cbz-(Edot)₂-Cbz]					
$S_0 \longrightarrow S_1$	430.05	2.88	1.62	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	367.02	3.38	0.02	HOMO-1 \longrightarrow LUMO	0.64
$S_0 \longrightarrow S_3$	352.36	3.52	0.0009	HOMO \longrightarrow LUMO+2	0.46
[Cbz-(Edot)₃-Cbz]					
$S_0 \longrightarrow S_1$	468.12	2.65	1.91	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	399.15	3.11	0.03	HOMO-1 \longrightarrow LUMO	0.62
$S_0 \longrightarrow S_3$	375.33	3.30	0.08	HOMO-2 \longrightarrow LUMO	0.66
[Cbz-(Edot)₄-Cbz]					
$S_0 \longrightarrow S_1$	503.02	2.46	2.39	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	431.07	2.88	0.0009	HOMO-1 \longrightarrow LUMO	0.60
$S_0 \longrightarrow S_3$	389.88	3.18	0.06	HOMO-2 \longrightarrow LUMO	0.66
[Cbz-(Edot)₅-Cbz]					
$S_0 \longrightarrow S_1$	539.09	2.30	2.73	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	458.06	2.71	0.05	HOMO-1 \longrightarrow LUMO	0.57
$S_0 \longrightarrow S_3$	421.03	2.94	0.02	HOMO \longrightarrow LUMO+1	0.52
[Cbz-(Edot)₆-Cbz]					
$S_0 \longrightarrow S_1$	561.72	2.21	3.10	HOMO \longrightarrow LUMO	0.65
$S_0 \longrightarrow S_2$	475.00	2.61	0.004	HOMO-1 \longrightarrow LUMO	0.54
$S_0 \longrightarrow S_3$	442.81	2.80	0.02	HOMO \longrightarrow LUMO+1	0.49

3.4. Bridging effect on optoelectronic properties

In this part, we present a DFT (B3LYP/3-21G*) study of oligomers in which inter-ring torsional angles have been blocked by chemical bridging. This rigid bridge contains C=C(CN)₂ group. We will investigate the influence of bridging on (carbazole-bithiophene-carbazole) [Cbz-(BThi)-Cbz] and (carbazole-quaterthiophene-carbazole) [Cbz-(QThi)-Cbz]. We focus on the electronic properties of these compounds and we will try to understand the effect of the bridging on the optical properties of these oligomers. We present in Fig. 4 the theoretical geometric structure of studied compounds.

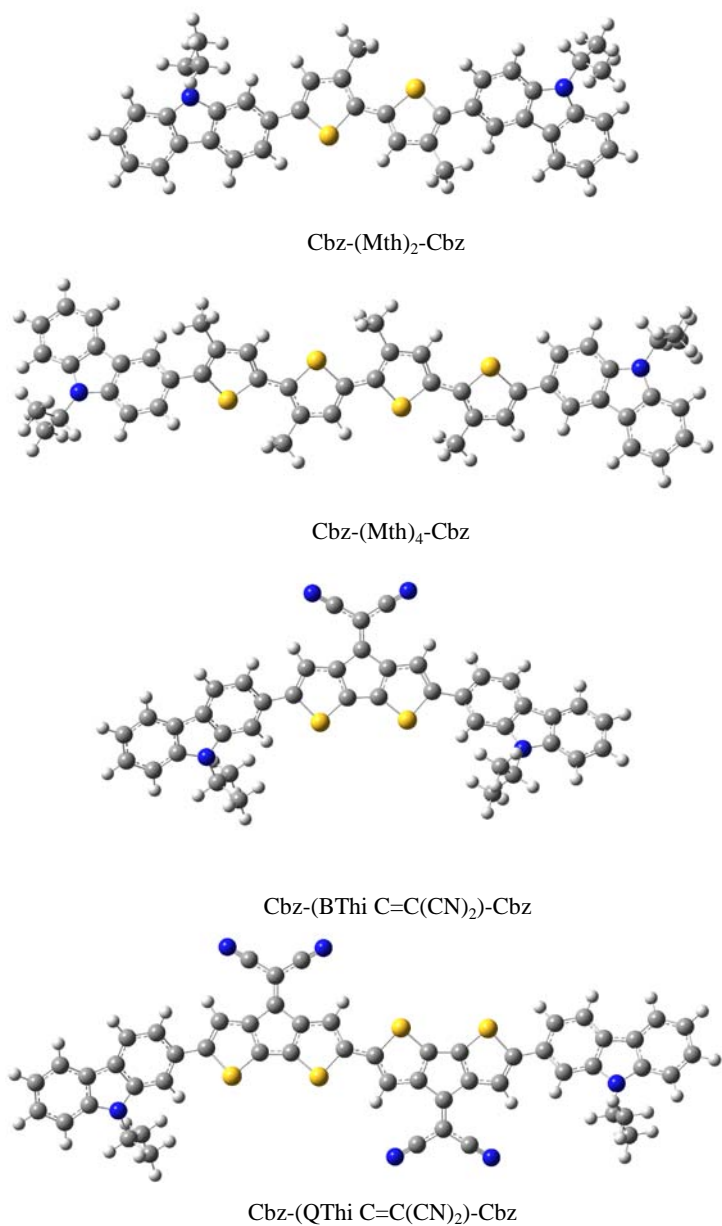


Fig. 4. The theoretical geometric structure of studied compounds.

In order to study the influence of bridging effects on the electronic properties, calculations were performed using B3LYP/3-21G* method. Table. 8 shows calculated values of HOMO, LUMO, and energy gaps (E_g) for bridged [Cbz-(BThiC=C(CN)₂)-Cbz], [Cbz-(QThiC=C(CN)₂)-Cbz] and unbridged [Cbz-(Mth)_n-Cbz] and [Cbz-(Edot)_n-Cbz] for

($n = 2$ and 4). Comparing the values obtained, we find that the bridging by the substituted sp^2 carbon atom reduces the gaps energy, similar results were obtained in the case of substituted oligobithiophene [24].

The orbital patterns of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO calculation, for bridged [Cbz-(BThiC=C(CN)₂)-Cbz], unbridged [Cbz-(Mth)₂-Cbz] and unbridged [Cbz-(Edot)₂-Cbz], are shown in Fig. 5. It is interesting to note that the contribution of the electron accepting group C=C(CN)₂ to the HOMO is negligibly small while it makes a significant contribution to the LUMO. In the light of these results, one can rationalize the small band gap values obtained in this compound.

Table 8. Calculated HOMO, LUMO, and gap energies (eV) of the compounds, unbridged [Cbz-(Mth)_n-Cbz], unbridged [Cbz-(Edot)_n-Cbz] for $n = 2$ and 4 , and bridged [Cbz-(BThiC=C(CN)₂)-Cbz] and [Cbz-(QThiC=C(CN)₂)-Cbz].

Polymers	E_{HOMO}	E_{LUMO}	E_g
[Cbz-(Mth) ₂ -Cbz] (unbridged)	-4.825	-1.373	3.452
[Cbz-(Edot) ₂ -Cbz] (unbridged)	-4.477	-1.301	3.176
[Cbz-(BThiC=C(CN) ₂)-Cbz]	-5.266	-3.263	2.003
[Cbz-(Mth) ₄ -Cbz] (unbridged)	-4.539	-1.671	2.868
[Cbz-(Edot) ₄ -Cbz] (unbridged)	-4.287	-1.526	2.761
[Cbz-(QThiC=C(CN) ₂)-Cbz]	-5.245	-3.496	1.749

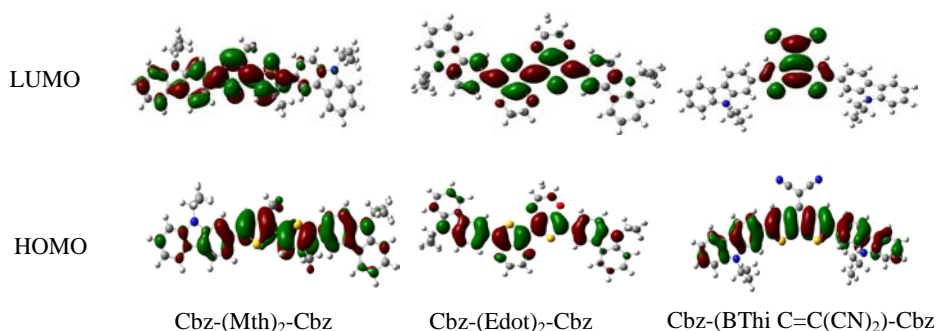


Fig. 5. HOMO and LUMO molecular orbital of the studied bridged [Cbz-(BThiC=C(CN)₂)-Cbz], unbridged [Cbz-(Edot)₂-Cbz] and unbridged [Cbz-(Mth)₂-Cbz].

To investigate the insertion effect of C=C(CN)₂ group on electronic properties of the [Cbz-(Thi)_n-Cbz] ($n = 2$ and 4), we presented in Table. 9 the calculated absorption λ_{max} values of the oligomers : bridged [Cbz-(BThiC=C(CN)₂)-Cbz], [Cbz-(QThiC=C(CN)₂)-Cbz], unbridged [Cbz-(Edot)_n-Cbz] and unbridged [Cbz-(Mth)_n-Cbz] ($n = 2$ and 4). The

values are calculated by TD/DFT method starting with optimized geometry obtained at B3LYP/3-21G*. Comparing the wavelengths λ_{\max} of the oligomers, we note that the bridged [Cbz-(BThiC=C(CN)₂)-Cbz] and [Cbz-(QThiC=C(CN)₂)-Cbz] exhibits the longest wavelengths values. Introducing the C=C(CN)₂ group into oligomers backbone affects the electronic structure by donating charge carriers thereby lowering the energy band gap and raising the conjugation length.

Table 9. Calculated absorption λ_{\max} (nm), excitation energy (eV) and oscillation strength (f) for bridged [Cbz-(BThiC=C(CN)₂)-Cbz], [Cbz-(QThiC=C(CN)₂)-Cbz], unbridged [Cbz-(Edot)_n-Cbz] and unbridged [Cbz-(Mth)_n-Cbz] (n = 2 and 4) by TD/DFT level.

Polymers	λ_{\max}	f	Excitation energy
[Cbz-(Mth) ₂ -Cbz] (unbridged)	397.80	1.64	3.12
[Cbz-(Edot) ₂ -Cbz] (unbridged)	430.05	1.62	2.88
[Cbz-(BThiC=C(CN) ₂)-Cbz]	884.27	0.08	1.40
[Cbz-(Mth) ₄ -Cbz] (unbridged)	478.75	2.35	2.59
[Cbz-(Edot) ₄ -Cbz] (unbridged)	503.02	2.39	2.46
[Cbz-(QThiC=C(CN) ₂)-Cbz]	991.21	0.22	1.25

4. Conclusion

The structural and electronic properties of 3, 4-ethylenedioxythiophene (EDOT) based carbazole (Cbz) were studied for ground state from the [Cbz-(Edot)_n-cbz] (n = 1-4), by B3LYP/3-21G* level. The behavior of torsional angles has been discussed in detail. The stable conformation of all oligomers is the anti-planar conformation. Our calculated results indicate that all the carbazole-based EDOT oligomers improve the hole injection due to the higher HOMO levels and the lower LUMO energies, which contribute to the highly improved electron-accepting and transporting properties. The gap energy calculated from all oligomers, decreases with the chain length, and the values of optical absorption λ_{\max} calculated by the three methods (ZINDO, TD/DFT et CIS), increase with the number of monomers. The first electronic transition gives rise to the largest values of the oscillator strength in each oligomer. The absorption spectra of all polymers indicates a strong π -electron delocalization along the oligomeric chain. These points are essential for light-emitting polymers, and provide the opportunity of tuning the electronic and optical properties of the oligomers. The insertion of a C=C(CN)₂ group into oligomers backbone affects the electronic structure, leading to a reduction of the energy gaps and to a raising of the conjugation length.

Finally, the theoretical results showed that, by modification of chemical structures could greatly modulate and improve the electronic and optical properties of pristine polymers. Furthermore, using theoretical methodologies, we showed that is possible to

predict reasonably the electronic properties of conjugated systems and we are convinced that the systematic use of those theoretical tools should contribute to orientate the synthesis efforts and help in understanding the structure-properties relation of these conjugated materials.

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