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Bridging effect on structural and optoelectronic properties of oligothiophene

S.M. Bouzzine [a,b], A. Makayssi [b], M. Hamidi [a,*], M. Bouachrine [b,*]

[a] *Laboratoire de Chimie Théorique Appliquée, FST, B.P. 509, Boutalamine, 5200 Errachidia, Morocco*
[b] *Laboratoire de Recherche sur les Macromolécules et Modélisation, FST, B.P. 509, Boutalamine, 5200 Errachidia, Morocco*

Abstract

In this paper, we report on a theoretical study of structural and electronic properties of some oligothiophenes based on cylopentadithiophene (CPDT) dimers in which both 3,3′ positions were bridged with (CH_2, SiH_2, $C(CN)_2$, S, C=O, C=S, $C=CH_2$, and $C=C(CN)_2$). The important reduction of the gap energy observed for the whole series of the bridged compounds studied here, is explained on the basis of an orbital interaction analysis. Computations were performed by using density functional theory (DFT) calculations. The compounds bridged by C=S and $C=C(CN)_2$ have small Eg = LUMO–HOMO gaps suggesting that these compounds have optoelectronic application.
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1. Introduction

Oligothiophenes possess extensive π-electron delocalization along the molecular backbone, which makes them interesting for various optoelectronic applications [1–5]. Due to this applicative interest and to the fact that they can be used as model compounds for the parent polymer (polythiophene), they have been extensively studied [6,7]. Also, due to their chemical stability, ease of functionalization and intrinsic electronic properties, α-linked oligothiophenes are the most extensively investigated oligomers for conducting polymers in recent years [8]. Due to their controllable and precisely defined structure, physical properties can be followed and correlated with the chain and conjugation length. With the implementation of these results to polymer design, conjugated oligothiophenes were recognized as a novel and independent class of materials in their own right. Moreover, suitable modifications on their

molecular structures by functionalization at the terminal α or side β positions permit their application as molecular materials in organic field-effect transistors [9], light-emitting devices [10], photovoltaic cells [11], or even as molecular wires for information storage or transfer [12].

Polymers with low band gaps are expected to show not only good intrinsic conductivity but also nonlinear optical properties [13]. For their successful design, it is necessary to have a complete understanding of the relation between the chemical structure of polymers and its electronic properties. Various routes are presently followed for designing novel conducting polymers, one is provided by donor–acceptor polymers, based on the approach suggested by Havinga et al. [14]. The study of conjugated oligomers is very attractive due to the fact that finite-size systems can be obtained with high purity and a well-defined chemical structure, thus opening the way for the investigation of electronic properties as a function of chain length and extent of the π-electron system. The results display two most stable conformation ($\theta = 28°$ and $\theta = 180°$) in the neutral case. The gap energy calculated decreases as function of the increase of the chain length from the dimer to

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octamer. The gap energy value of octathiophenes (8T) (2.41 eV) is close to those of polythiophene. The octathiophene is the useful model to understand electronic properties of the parent polymers [15]. With the aim of reducing gap energy in oligothiophenes, it is interesting to reduce the angle of torsion between two thiophenes rings from 28° to 0° by bridging thiophenes rings by various groups.

In this contribution, we present a DFT (B3LYP/6-31(d)) study of series of bithiophenes in which inter-ring torsional angles have been blocked by chemical bridging. Fig. 1a

shows the types of adjacent ring bridging studied here; this rigid bridge contains CH_2, SiH_2, S, $C(CN)_2$, $C=CH_2$, $C=O$, $C=S$, $C=C(CN)_2$ groups. We focus on the electronical properties and geometric structure of these compounds and their parent unsubstituted oligomers. We will first investigate the influence of bridging on bithiophene (BT); then we will discuss the structural changes generated by bridging quaterthiophene (QT), starting from a conformational analysis of QTX (X: CH_2, SiH_2, S, $C(CN)_2$, $C=CH_2$, $C=O$, $C=S$, $C=C(CN)_2$). Finally, we will try to understand the effect of

a

$X=CH_2, SiH_2, S, C(CN)_2, C=CH_2, C=O, C=S, C=C(CN)_2$

b

4H-cyclopenta [2,1-b; 3,4-b']dithiophène

(BTCH₂)

4H-dithenisilole cyclopentadithiophène

(BTSiH₂)

4,4'-dicyano-cyclopenta[2, 1-b; 3, 4-b']dithiophène

(BTC(CN)₂)

4H-dithieno[2, 3-b; 2', 3'-b']dithiophène

(BTS)

4H-dicyanomethlene–cyclopentadithiophène

(BTC=C(CN)₂)

4H-cyclopenta[2, 1-b; 2, 4-b']dithiophène -4-thione

(BTC=S)

4-methylene– cyclopentadithiophène

(BTC=CH₂)

4H-cyclopenta [2, 1-b; 3, 4-b']dithiophène-4-one
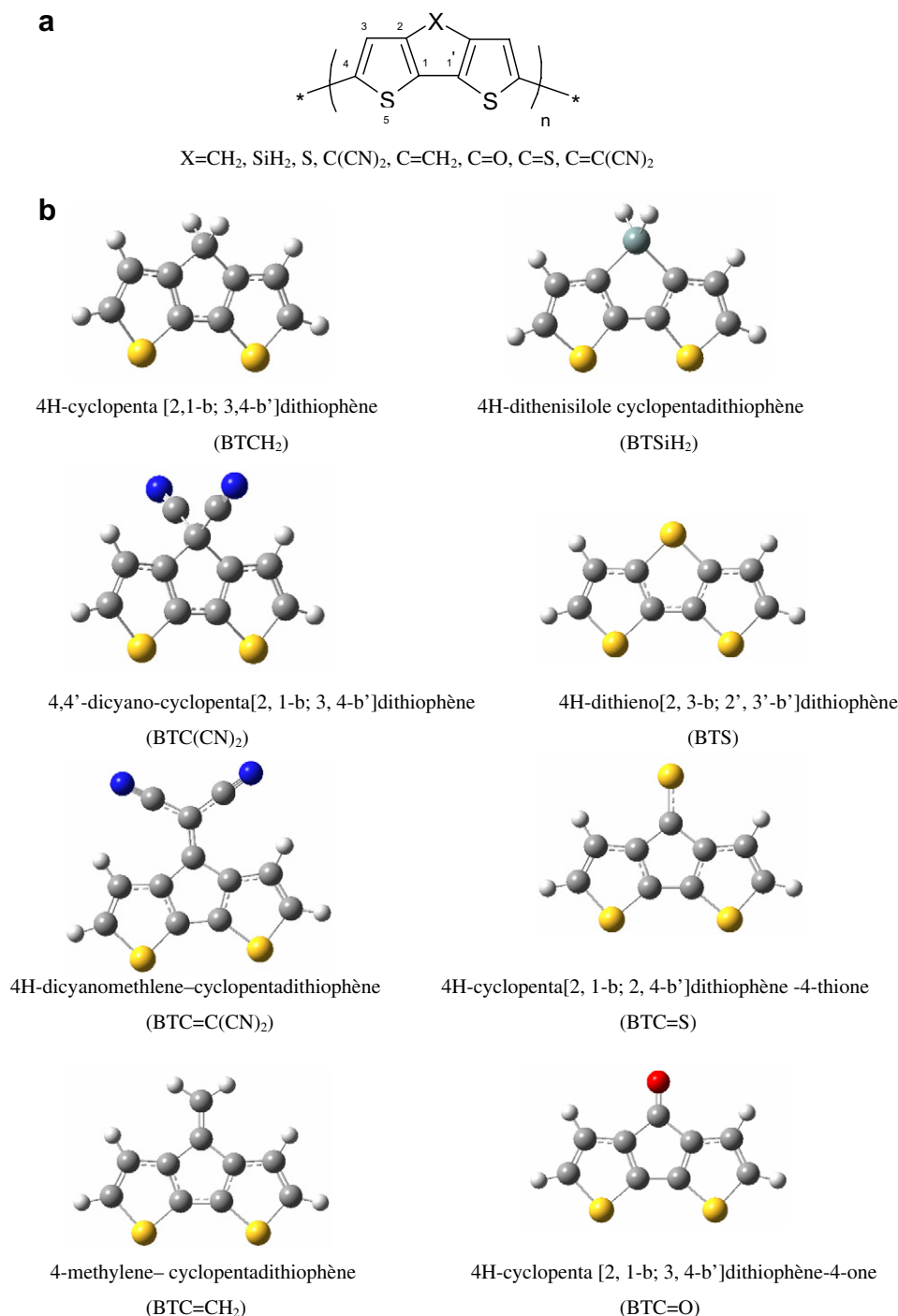
(BTC=O)

Fig. 1. (a) Chemical structures of compounds under investigation. (b) The theoretical geometric structure of studied compounds.

Table 1
Optimized structural parameters (bond length (in Å), angle (in degree)) of bridged bithiophene obtained at B3LYP/6-31G(d)

Parameters	X: C=O	X: C=S	X: C=CH$_2$	X: C=(CN)$_2$	X: S	X: CH$_2$	X: C(CN)$_2$	X: SiH$_2$	BT
C$_1$C$_2$	1.383	1.389	1.389	1.391	1.392	1.384	1.380	1.389	1.378
C$_2$C$_3$	1.417	1.420	1.421	1.424	1.424	1.420	1.417	1.425	1.424
C$_3$C$_4$	1.372	1.370	1.370	1.370	1.366	1.372	1.371	1.370	1.367
C$_1$S$_5$	1.719	1.716	1.726	1.715	1.741	1.730	1.725	1.743	1.757
C$_4$S$_5$	1.752	1.754	1.752	1.751	1.751	1.750	1.749	1.736	1.736
C$_1$C$_1'$	1.461	1.456	1.446	1.451	1.422	1.444	1.445	1.455	1.45
C$_1$X	1.506	1.478	1.481	1.474	1.759	1.517	1.540	1.425	–
C$_1$XC$_4$	104.1	104.6	104.6	105.9	90.1	101.8	101.1	.92.4	–
XC$_1$C$_2$	108.5	109.0	108.8	108.1	112.3	109.6	109.6	106.7	–
C$_1$C$_2$C$_3$	109.3	108.5	108.8	108.9	112.5	109.2	109.7	116.9	120

the bridging on the structural and optical properties of these bridged oligomers and corresponding polymers.

2. Methodology

The calculations on the geometries of both oligomers chains have been performed under density functional theory (DFT) at the B3LYP level of theory and the 6-31G(d) basis set [16]. The notation B3 indicates a three-parameter Becke exchange functional [17] and LYP indicates the Lee–Yang–Parr [18]. Calculations were carried out using the Gaussian 03 program package [19]. The conformational analysis of all dimers was done by changing the torsional angles θ between the bridged bithiophenes rings monomer by 20° steps in the same direction. The geometries were fully optimized for each group. To obtain the final torsional angles of the conformers in each minimum calculation of these geometries were performed without constraint on the dihedral angles. The general abbreviation of our bridged compounds is BTX (monomer), QTX (dimer), and OTX (quatermer) where X: CH$_2$, SiH$_2$, S, C(CN)$_2$, C=CH$_2$, C=O, C=S, and C=C(CN)$_2$ where n, the number of bridged bithiophenes, varies between 1 and 4.

3. Results and discussion

3.1. Geometric structure results

The unit-cell geometries of the compounds BTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$), and (X: CH$_2$, SiH$_2$, S,

Table 2
Calculated HOMO, LUMO, and gap energies (eV) of the studied compounds

Dimer	E_{HOMO}	E_{LUMO}	Eg
BT (unabridged)	−5.524	−1.195	4.329
BT (anti planar)	−5.475	−1.246	4.229
BTCH	−5.220	−0.985	4.235
BTSiH	−5.488	−1.483	4.005
BTS	−5.605	−1.087	4.518
BTC (CN)$_2$	−5.488	−1.482	4.006
BTC=CH$_2$	−5.271	−1.725	3.546
BTC=O	−5.263	−2.813	3.216
BTC=S	−5.714	−3.171	2.543
BTC=C (CN)$_2$	−6.047	−3.425	2.622

C(CN)$_2$) are presented in Fig. 1b. For both systems, we observe major differences in the optimized bond lengths and angles when we change compounds bridging. We present in Table 1 the optimized structural parameters of
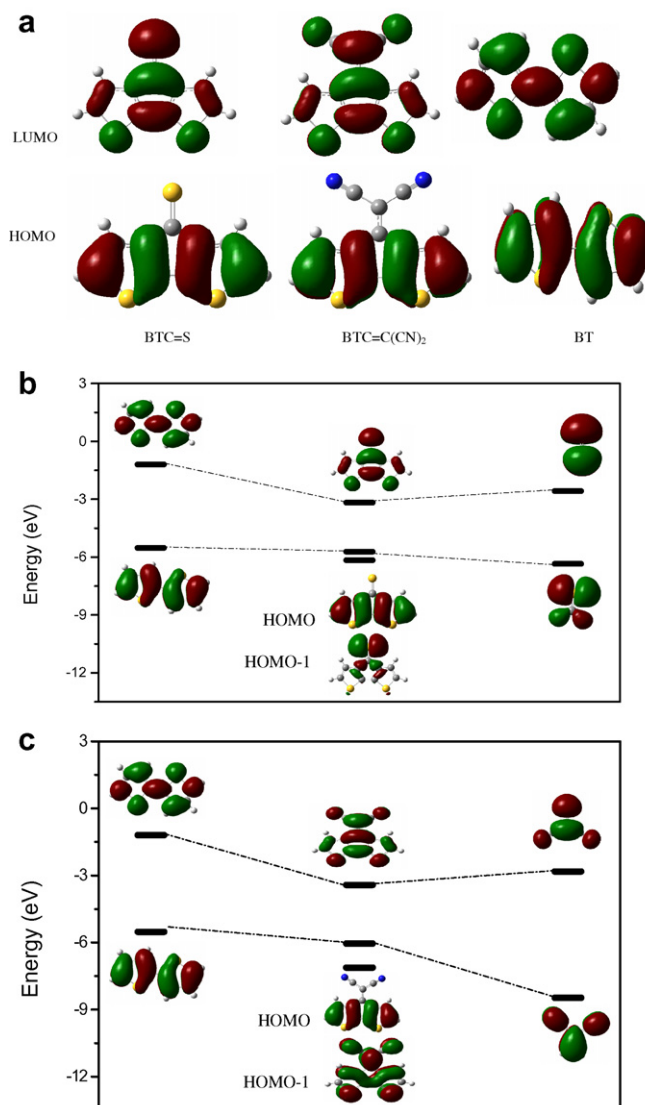

Fig. 2. (a) Orbital molecular of the HOMO and LUMO of BTC=S and BTC=C(CN)$_2$. (b) Contour plots of the frontier orbitals of BT, BTC=S, and H$_2$C=S (contour value 0.06 (e/bor^3)$^{1/2}$). (c) Contour plots of the frontier orbitals of BT, BTC=C(CN)$_2$, and H$_2$C=C(CN)$_2$ (contour value 0.06 (e/bor^3)$^{1/2}$).
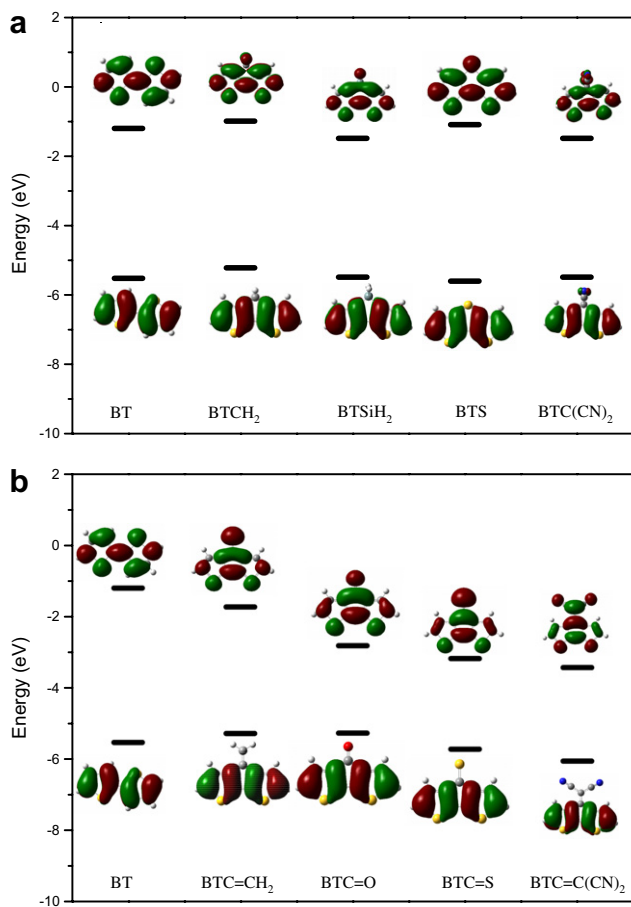
Fig. 3. (a) Contour plots of the HOMO and LUMO of BT, BTCH$_2$, BTSiH$_2$, BTS, BTC(CN)$_2$, (contour value 0.06 (e/bor^3)$^{1/2}$). (b) Contour plots of the HOMO and LUMO of BT, BTC=CH$_2$, BTC=O, BTC=S, and BTC=C(CN)$_2$ (contour value 0.06 (e/bor^3)$^{1/2}$).

bridged and unbridged dithiophenes as computed at B3LYP/6-31G(d) level. The structural analysis shows that the geometries of compounds are plan (Fig. 1b).

The C—S bond lengths do not show a significant change for all compounds, we note that the C$_1$S$_5$ show the particularity of having smaller values than C$_4$S$_5$ by (0.015 Å) (Table 1). The values of C$_1$XC$_4$ angle decrease when we pass from the sp^2 (C=CH$_2$, C=O, C=S, C=C(CN)$_2$) bridged groups to sp^3 bridged groups (X: CH$_2$, SiH$_2$, S, C(CN)$_2$).

3.2. Electronic properties of bithiophene bridged by C=CH$_2$, C=O, C=S, C=C(CN)$_2$, CH$_2$, SiH$_2$, S, C(CN)$_2$

In order to study the influence of bridging effects on the electronic properties, calculations were performed using B3LYP/6-31(d) method. Table 2 shows calculated values of HOMO, LUMO, and energy gaps (Eg) for bridged and unbridged bithiophene. Comparing the values obtained after bridging, we find the known result that bridging by the substituted sp^2 carbon atom reduces the gaps energy in all cases. We notice that the values of energy gap decrease when we pass from the BTX (X: CH$_2$, SiH$_2$, S,

C(CN)$_2$) to BTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$). The gap energy values of the latter compounds are nearly similar to that of planar bithiophene, therefore the reaction of these compounds causes the bithiophene adjacent ring to be blocked.

The orbital patterns of the highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO calculation, for both BTC=O and BTC=C(CN)$_2$, are shown in Fig. 2a. It is interesting to note that the contribution of the electron accepting group X: C=S and 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 these two compounds by visualizing their formation (Fig. 2b and c) via the interaction of a bithiophene skeleton with an electron accepting group X terminated by H atoms (X: CH$_2$=S, CH$_2$=C(CN)$_2$).
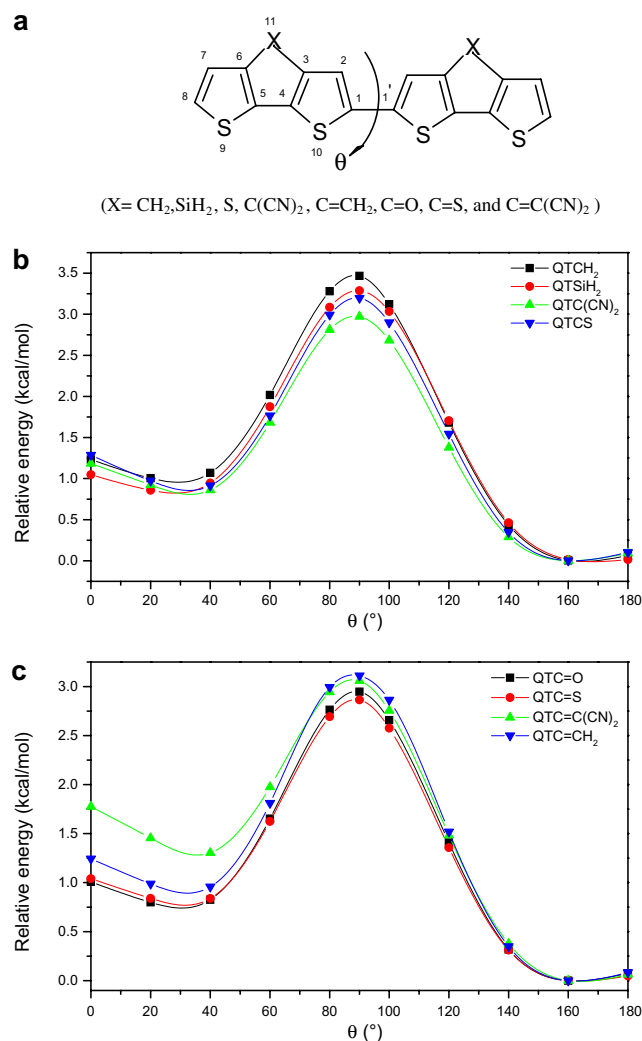

(X= CH$_2$, SiH$_2$, S, C(CN)$_2$, C=CH$_2$, C=O, C=S, and C=C(CN)$_2$)

Fig. 4. (a) Torsional angle between the two bridged bithiophenes. (b) Torsional potential curves for QTCH$_2$, QTSiH$_2$, QTS, QTC(CN)$_2$ obtained at B3LYP/6-31G(d) level. (c) Torsional potential curves for QTC=CH$_2$, QTC=O, QTC=S, and QTC=C(CN)$_2$ obtained at B3LYP/6-31G(d) level.

Table 3
Torsional angle of stationary point (degree) and relative energy en eV

QTX	θ_{syn}	θ_{anti}
4T	28.8/23.8 (0.11)[a]	162.7 (0.00)
CH$_2$	28.8 (0.93)	162.0 (0.00)
SiH$_2$	28.1 (0.80)	166.6 (0.00)
C(CN)$_2$	32.4 (0.86)	158.6 (0.00)
S	32.0 (0.84)	159.0 (0.00)
C=O	29.9 (0.72)	159.7 (0.00)
C=S	30.8 (0.76)	161.3 (0.00)
C=CH$_2$	32.3 (0.87)	160.0 (0.00)
C=C(CN)$_2$	34.5 (1.27)	160.9 (0.00)

[a] Relative energies of state.

The band gap of BTC=S and BTC=C(CN)$_2$ are determined by strength of bonding interaction between the LUMO of the bithiophene skeleton and LUMO of the electron accepting group X. The smaller band gap of BTC=S as compared to that of BTC=C(CN)$_2$ is due the lower-lying value of LUMO (-2.575 eV) of H$_2$C=S compared with that of H$_2$C=C(CN)$_2$ (-2.820 eV).

The orbital HOMO and LUMO bridged compounds are shown in Fig. 3a and b. The formation of these dimers are realized by interaction of bithiophene orbital with electron donating group (X: CH$_4$, SiH$_4$, H$_2$S, and H$_2$C(CN)$_2$) and electron accepting group (X: H$_2$C=CH$_2$, H$_2$C=O, H$_2$C=S, H$_2$C=C(CN)$_2$). For the electron donating, we note that SiH$_4$ group presents a lower LUMO. The LUMO of accepting C=S group is much lower in energy. This energy decreases when passing from C=CH$_2$, C=O, C=S, and C=C(CN)$_2$. The decrease of energy is due to the combined effects of small energy lowering of π^* molecular orbital of the group X and the slight increase of the X weight in the LUMO of species [20]. The orbital of the HOMO for both species are found to be nearly similar.

3.3. Conformational analysis and geometric consideration of QTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$, CH$_2$, SiH$_2$, S, C(CN)$_2$)

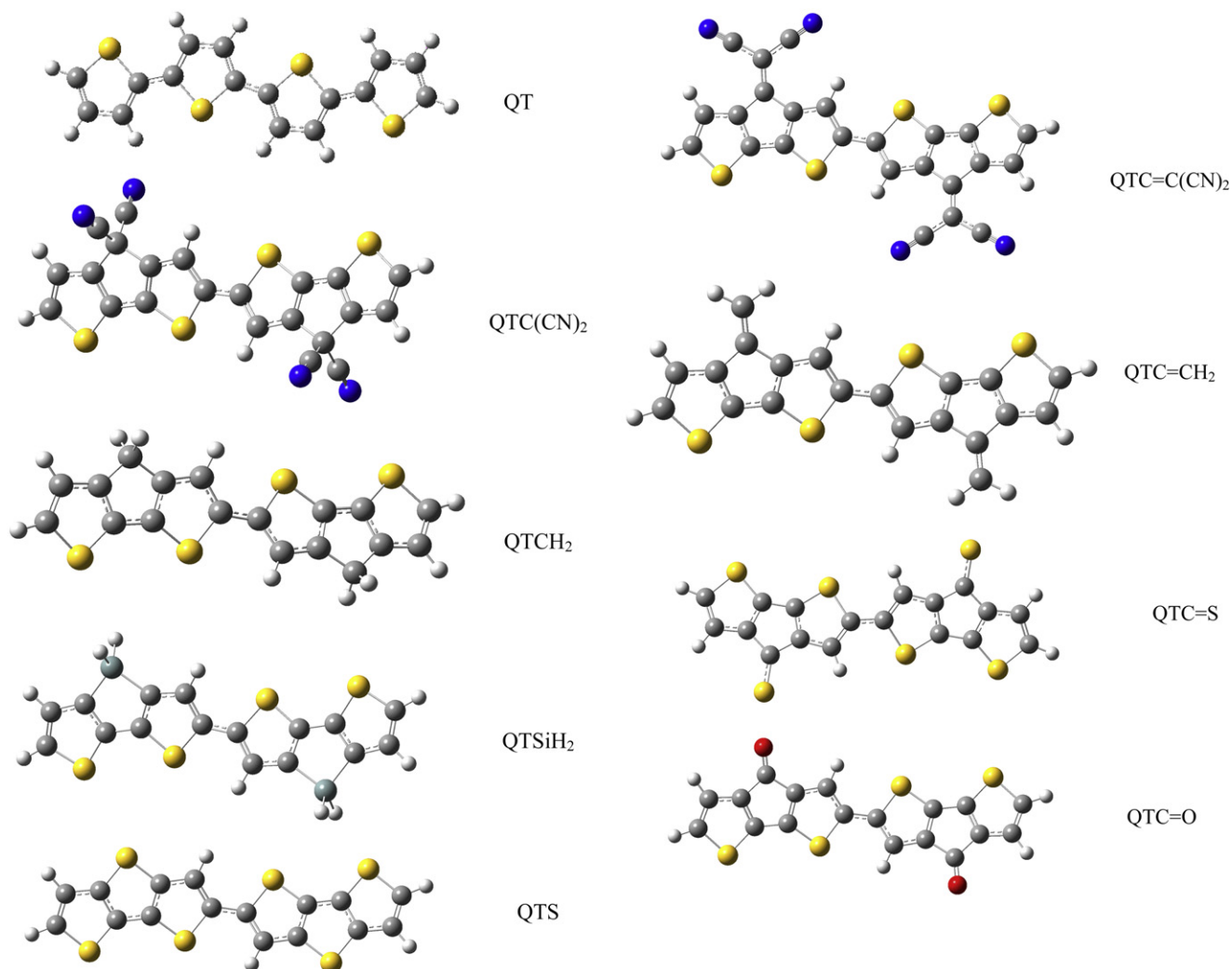In this section, we present and discuss the conformational behavior calculated for QTX (X: CH$_2$, SiH$_2$, S,

Fig. 5. Optimized bond lengths (in Å) and bond angles in QT, QTCH$_2$, QTSiH$_2$, QTS, QTC(CN)$_2$, QTC=CH$_2$, QTC=O, QTC=S, QTC=C(CN)$_2$ obtained by B3LYP/6-31G(d).

C(CN)$_2$) and QTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$) (Fig. 4a). The energy potential curves obtained by B3LYP/6-31G(d) show the existence of two stable conformations: a syn conformation and anti conformation (the most stable) for all oligomers (Fig. 4b and c). The dihedral angle of the most stable conformation is around 160° for all oligomers (Table 3). The energy barrier towards anti planar conformation for QTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$) is slightly less than that for QT (X: CH$_2$, SiH$_2$, S, C(CN)$_2$) (about 0.5 kacl/mol). The segment, in bridged bond between two adjacent thiophenes in five-membered ring in these polymers, is twisted slightly. Their average in the oligomers is 0.2°. The same observations are obtained for polyfluorene (0.13° and 0.3°) [21].

The optimized geometries of anti planar-bridged and -unbridged quaterthiophenes compounds are displayed in Fig. 5.

We present in Table 4 the optimized structural parameters (corresponding to global minimum optimized structure) of the quaterthiophenes bridged QTX (X: CH$_2$, SiH$_2$, S, C(CN)$_2$, C=CH$_2$, C=O, C=S, C=C(CN)$_2$) as computed at B3LYP/6-31G(d) level. The structure analysis of all compounds revealed that the molecule had an inversion center with high planarity (Fig. 5). The two bridged rings adopted an anti conformation. Planar anti conformation has also been observed for quaterthiophene and oli-

gothiophenes [15,22]. Since geometric parameters remain unchanged when we change group X. In the twisted conformation, the bond lengths differ only very slightly (the maximum deviation is 0.002 Å) from those calculated for the anti planar oligothiophenes. Both bond length and angle data are consistent with the quaterthiophene previously reported [15,22].

3.4. Electronic structures of bridged octamers

The gap energy value of octathiophene is close to that of polythiophene [15]. This value has permitted to take the octamer as parent polymer since it reflects properties of polythiophenes. Therefore in this part, we examine the highest occupied orbitals and the lowest virtual orbitals for these oligomers because the relative ordering of the occupied and virtual orbitals provide a reasonable qualitative indication of the excitation properties [23] and of the ability of electron transitions or hole transport. We have plotted the contour plots of the HOMO and LUMO orbitals of OTX (X: CH$_2$, SiH$_2$, S, C(CN)$_2$) and OTX (X: C=O, C=S, C=CH$_2$, C=C(CN)$_2$) in their completely optimized conformation B3LYP/6-31G(d) in Fig. 6.

Analysis of Fig. 6 reveals that for both HOMO and LUMO orbitals, the same appearance is observed for all compounds except for OTX (X: C=O, C=S, C=C(CN)$_2$).

Table 4
Optimized structural parameters (bond length (in Å), angle (in degree)) of bridged quaterthiophene obtained at B3LYP/6-31G(d)

Parameters	QTCH$_2$	QTS	QTSiH$_2$	QTC(CN)$_2$	QTC=O	QTC=H$_2$	QTC=S	QTC=C(CN)$_2$	4T
C$_1$C$_2$	1.386	1.380	1.384	1.385	1.387	1.385	1.385	1.385	1.380
C$_2$C$_3$	1.411	1.416	1.416	1.408	1.408	1.413	1.411	1.413	1.419
C$_3$C$_4$	1.386	1.393	1.390	1.382	1.384	1.391	1.390	1.391	1.380
C$_4$C$_5$	1.440	1.418	1.451	1.441	1.456	1.442	1.451	1.446	1.441
C$_5$C$_6$	1.386	1.394	1.391	1.382	1.385	1.391	1.392	1.391	1.379
C$_6$C$_7$	1.419	1.423	1.424	1.415	1.416	1.420	1.419	1.420	1.422
C$_7$C$_8$	1.372	1.367	1.371	1.372	1.372	1.371	1.372	1.371	1.367
C$_6$C$_{11}$	1.516	1.759	1.879	1.540	1.504	1.480	1.419	1.480	–
C$_3$C$_{11}$	1.517	1.759	1.881	1.540	1.509	1.482	1.411	1.482	–
C$_8$S$_9$	1.750	1.751	1.743	1.748	1.751	1.752	1.754	1.752	1.786
C$_5$S$_9$	1.730	1.741	1.737	1.725	1.719	1.726	1.716	1.726	1.758
C$_4$S$_{10}$	1.730	1.740	1.736	1.724	1.719	1.726	1.717	1.726	1.757
C$_1$S$_{10}$	1.775	1.774	1.767	1.773	1.776	1.776	1.778	1.776	1.758
C$_1$C$_1'$	1.441	1.444	1.443	1.443	1.442	1.442	1.442	1.442	1.442
C$_1$C$_2$C$_3$	112.9	111.8	114.0	111.8	112.3	112.8	112.4	112.8	113.8
C$_2$C$_1$S$_{10}$	110.8	111.2	110.4	111.2	110.8	110.9	110.8	110.9	110.0
C$_2$C$_3$C$_4$	113.1	114.9	112.0	114.3	113.7	113.0	113.5	113.0	113.9
C$_1$S$_{10}$C$_4$	90.8	90.9	91.1	90.4	91.0	90.9	91.0	90.9	92.1
C$_3$C$_4$S$_{10}$	112.2	111.5	112.3	111.5	111.9	112.1	112.0	112.1	110.0
C$_3$C$_4$C$_5$	109.2	109.8	116.9	109.8	109.3	108.9	108.6	108.9	129.1
C$_4$C$_5$C$_6$	109.2	109.7	116.9	109.7	109.4	108.9	108.6	108.9	129.0
C$_4$C$_3$C$_{11}$	109.8	109.6	106.8	109.6	108.5	108.7	109.0	108.7	–
C$_5$C$_6$C$_{11}$	109.8	109.7	106.8	109.7	108.5	108.8	109.1	108.8	–
C$_3$C$_{11}$C$_6$	101.8	101.0	92.3	101.0	104.1	104.6	104.5	104.6	–
C$_5$C$_6$C$_7$	112.8	114.0	111.7	114.0	113.4	112.7	113.1	112.7	113.6
C$_6$C$_7$C$_8$	112.0	110.9	113.1	110.9	111.5	111.9	111.6	111.9	112.9
C$_7$C$_8$C$_9$	112.5	112.8	112.0	112.8	112.3	112.5	112.4	112.5	111.6
C$_8$C$_9$C$_5$	90.5	90.6	90.8	90.6	90.8	90.6	90.8	90.6	91.7
C$_9$C$_5$C$_6$	112.1	111.4	112.1	111.4	111.8	112.0	111.9	112.0	110.0

They have a delocalized character over all the backbone, and do not differ in respect with unbridged octathiophenes. Those of bridged OTC=S, OTC=O, and OTC=C(CN)$_2$ are delocalized at the innermost ring with a clear participation of C=S, C=O, and C(CN)$_2$ in LUMO orbital.

In Table 5, we present the bridging oligomers leading to reduction of the band gap. This is possibly due to the stabilization of the LUMO in the bridged octamers caused by the planarization of the octamers skeletons. Besides we

notice that the gaps energy of C=S and C=C(CN)$_2$ bridged derivatives are weaker than the other compounds. The possible reason of this decrease is certainly the electronic character of the C=S and C=C(CN)$_2$ groups. The values of the band gap are 1.87 and 1.51 eV for OTC=O and OTC=C(CN)$_2$, respectively. These values are in accordance with that measured experimentally for polythiophene bridged with C=O and C=C(CN)$_2$ 1.2 and 0.8 eV, respectively [24,25]; which are lower than the unbridged oligothiophene (2.41 eV).
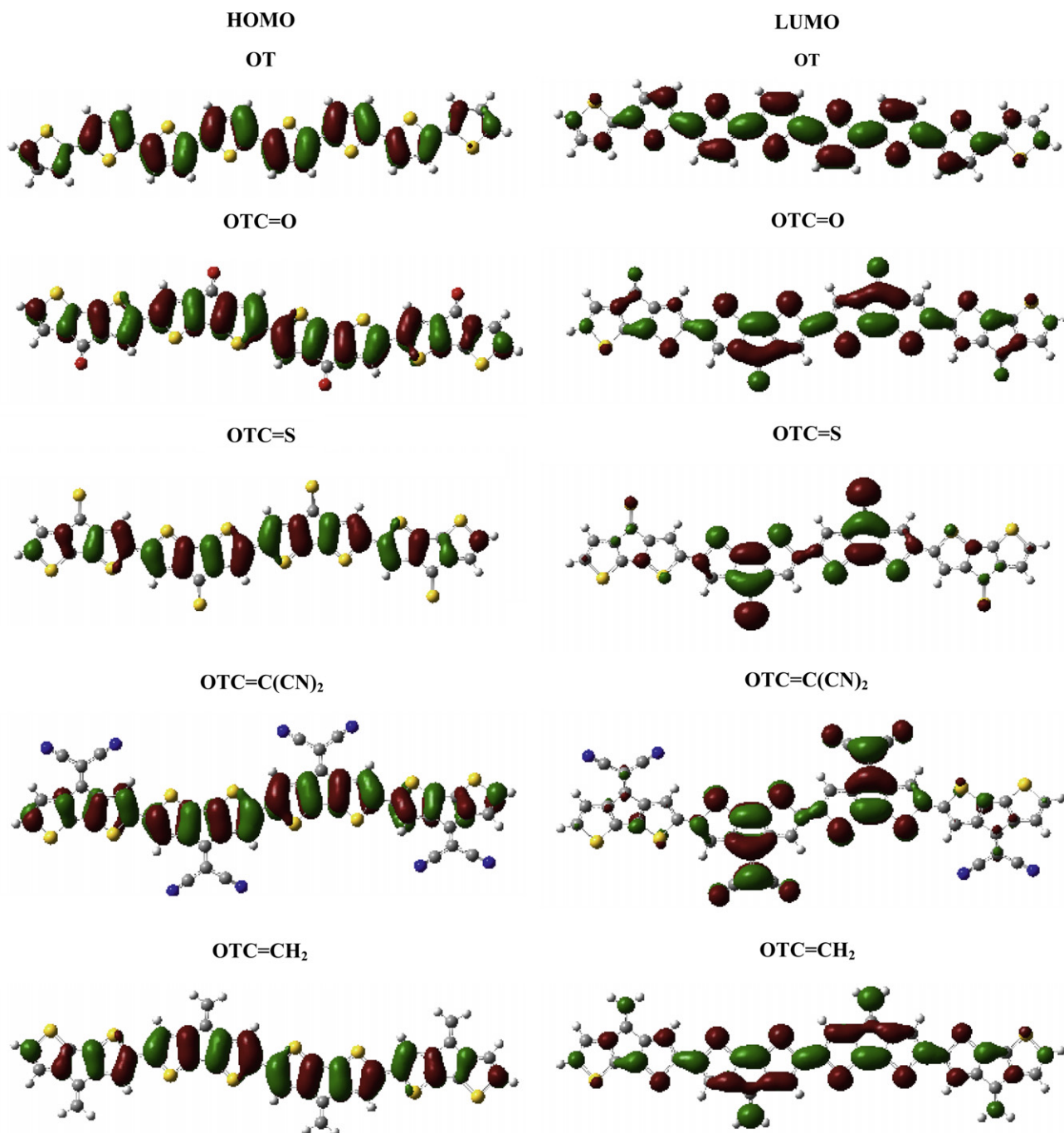

Fig. 6. The HOMO and LUMO orbitals of OTX (X: C=CH$_2$, C=O, C=S, C=C(CN)$_2$, CH$_2$, SiH$_2$, S, C(CN)$_2$) obtained by B3LYP/6-31G(d).

HOMO

OTCH$_2$

OTSiH$_2$

OTS

OTC(CN)$_2$

LUMO

OTCH$_2$

OTSiH$_2$
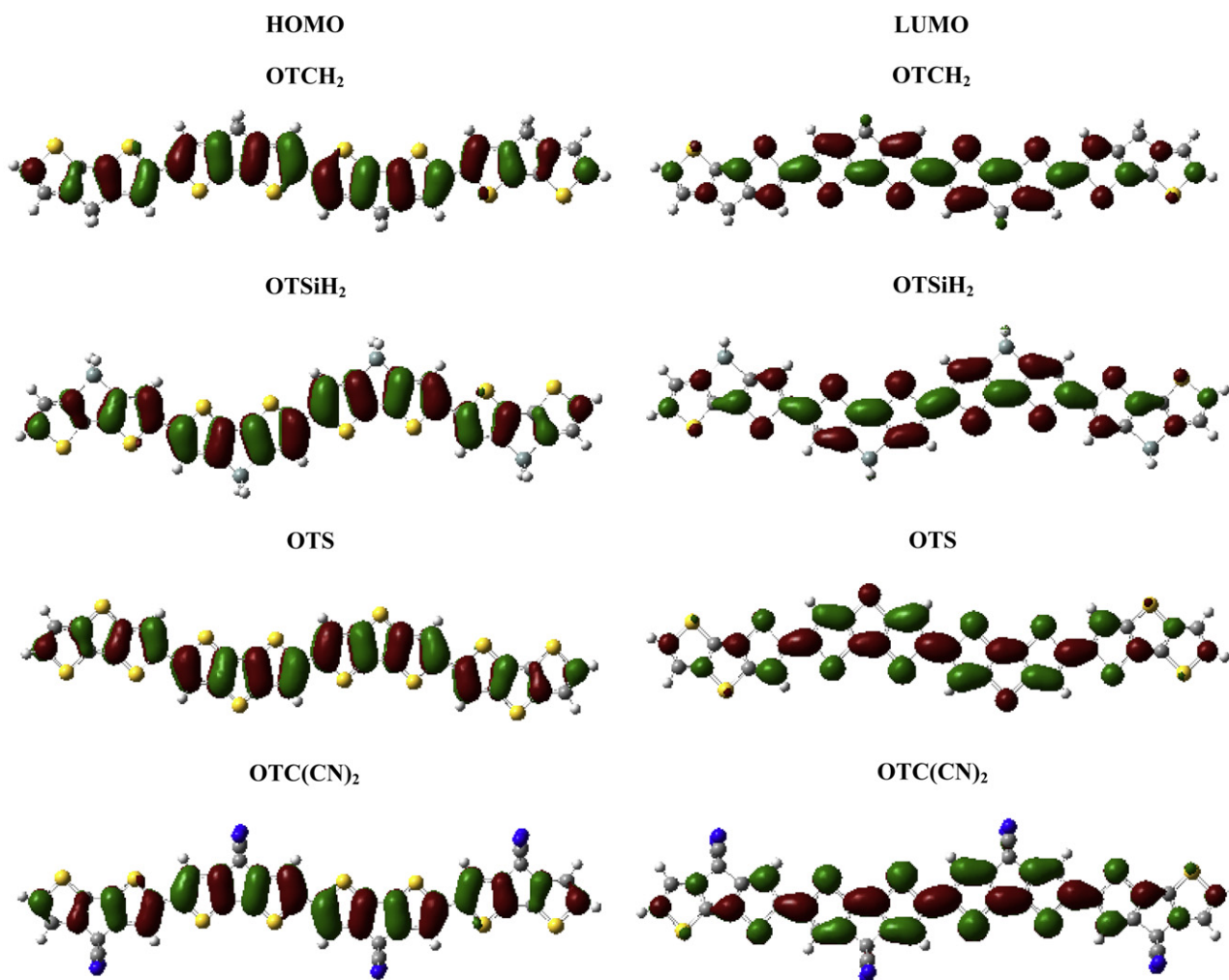

OTS

OTC(CN)$_2$

Fig. 6 (*continued*)

Table 5
Calculated values of HOMO, LUMO, and Eg of bridge octathiophene (OT) derivatives (eV)

Polymers	E_{HOMO}	E_{LUMO}	Eg	Eg$_{exp}$
OT (unbridged)	−4.72	−2.31	2.41	2.3–2 [26]
OTC (CN)$_2$	−5.54	−3.26	2.28	
OTCH$_2$	−4.32	−2.09	2.23	
OTSiH$_2$	−4.66	−2.39	2.27	
OTS	−4.83	−2.33	2.50	
OTC=CH$_2$	−4.39	−2.36	2.03	
OTC=O	−4.98	−3.12	1.86	1.2 [24,25]
OTC=S	−4.95	−3.52	1.43	
OTC=C(CN)$_2$	−5.40	−3.84	1.56	0.8 [24,25]

4. Conclusion

The torsional potentials for oligobithiophene bridged by (X: CH$_2$, SiH$_2$, S, C(CN)$_2$) and (X: C=CH$_2$, C=O, C=S, and C=C(CN)$_2$) were obtained by B3LYP/6-31G(d) calculations. The most stable conformation is anti planar conformation. The gap energy calculated with the same method decreases when we pass from compounds with (X: CH$_2$, SiH$_2$, S, C(CN)$_2$) to those with (X: C=CH$_2$; C=O, C=S, and C=C(CN)$_2$). The insertion of a bridging group between two rings leads to a reduction of the HOMO–LUMO energy gaps. This is mainly due to the stabilization of the LUMO level of several compounds. Concerning the C=C(CN)$_2$ and C=S derivatives, the lowering of the energy gap observed is likely to insure the better electronic properties for the corresponding polymers. These results indicated that the bridged C=S and C=C(CN)$_2$ polymers are promising materials for optoelectronic application.

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