Theoretical investigation of the substituent effect on the electronic and optical properties of photochromic dithienylethene derivatives

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Abstract

We have studied the substituent effect on the optical properties of both the closed-ring and open-ring isomers of a series of dithienylethene photochromic molecules. We demonstrate that TDDFT method, in conjunction with moderate size basis set, provides an accurate tool for the determination of the lowest singlet excitation energies of dithienylethene compounds. We have seen that the absorption spectrum of both the closed-ring and open-ring isomers can be easily shifted to longer wave wavelengths by introducing (1) acetylenic groups at the 5-position of the thiophene rings and (2) electron-withdrawing substituents in the upper cyclopentene structure.
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1. Introduction

Dithienylethenes with heterocyclic aryl groups show photochromism, which is defined as the reversible transformation between two isomers having different absorption spectra by photoirradiation [1]. These molecules are fatigue resistant and thermally stable photochromic compounds [2] since they require light for isomerization. Dithienylethenes undergo the ring-closure reaction (cyclisation) under the UV irradiation, while the ring-opening reaction (cycloreversion) occurs under visible light irradiation (Scheme 1).

The high thermal- and photo-stabilities make the dithienyl-ethenes promising candidates for optoelectronic applications such as memories or switches [2,3]. Implementation of this type of molecules in an electronic device would not only miniaturize it, but also add the commutation property. To this purpose, photochromic molecular switches made of a dithienylethene derivative self-assembled on gold have been recently studied [4]. Both the electronic transport and spectroscopic properties of these molecular devices have been investigated by using break junction experiments and UV/vis spectroscopy. It was demonstrated that the photochromic properties of dithienylethene

switches between two gold electrodes are dramatically affected. Hence, the authors show that the cyclisation mechanism is inhibited and they attribute this to quenching of the first excited state of the open form of the molecule under the influence of gold. In these new dithienylethenes-based optical data storage or processing devices, a readout mechanism is necessary to determine the isomeric state of the molecule. Recently, surface plasmon resonance (SPR) was demonstrated to be an excellent technique for investigating the photoisomerization of photochromic dithienylethenes covalently linked to a chemically modified gold surface [5].

Using dithienylethenes molecules in these different devices requires a fine control of both the photochromic and the spectroscopic properties. To determine which dithienylethene-derivative may be the optimal candidate for use as an optical molecular switch, it is necessary to understand the influence of the molecular structure on the absorption maximum of both states of the photochromic equilibrium [2,6]. To this end, we are interested in studying the optical properties of a series of photochromic molecules with general formula depicted in Scheme 2. More precisely, we investigate the influence of the introduction of conjugated groups at the 5 and 5′ positions of the thiophene groups (Fig. 1). The influence of the cyclopentene ring on the optical properties of the photochrome is also examined. One can notice that, in order to potentially use these photochromic compounds inside hybrid electronic devices, thiol terminations are

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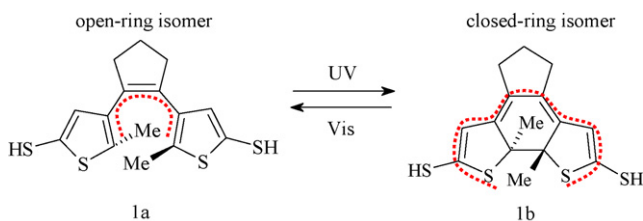
Scheme 1. Open and closed forms of molecule **1**. The dashed lines depict the π-electron conjugation path from inspection of the HOMO and LUMO.
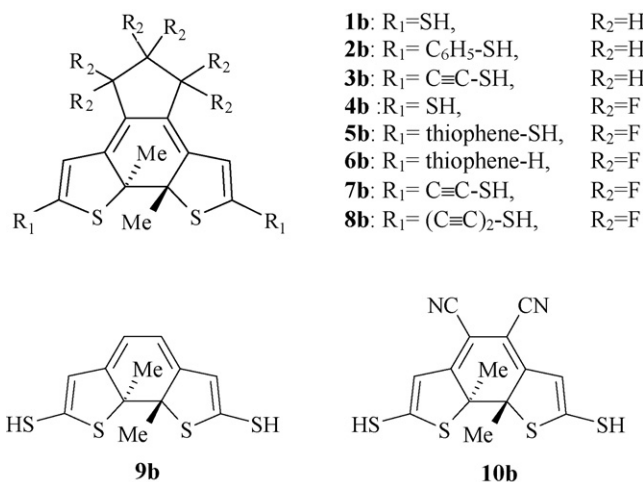
Scheme 2. Sketch of the considered photochromic molecules.

added. In this work, molecule **1** (Schemes 1 and 2) is considered as a reference compound and substituent effect on the optical properties of both the closed-ring isomer (**1b**) and the open-ring isomer (**1a**) is studied.

The paper is organised as follows. In Section 2, we present the computational details. Results concerning the reference molecule are presented in Section 3. The substituent effects on the closed-ring isomer and the open-ring isomer are, respectively, discussed in Sections 4 and 5. We conclude in Section 6.

2. Computational details

Geometry optimisations have been performed at the B3LYP/6-31G level of theory with Gaussian 03 [7] program
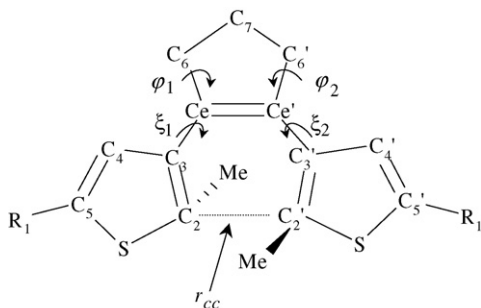

Fig. 1. Atom numberings. r_{cc} is the distance between the two reactive carbons, 2 and 2′. Torsion angles between the thiophene and cyclopentene rings, ξ_1 and ξ_2, are, respectively, defined as ∠4–3–e–6 and ∠4′–3′–e′–6′. The dihedral angles φ_1 and φ_2 are chosen as ∠3–e–6–7 and ∠3′–e′–6′–7.

package. For each molecule, geometry optimisation is followed by a vibrational spectrum analysis in order to check that all vibrational frequencies are real. The B3LYP/6-31G level has previously been used by Goldberg et al. [8] to determine the geometrical parameters of a series of diarylethenes. Calculated results were found to be in good agreement with X-ray data. In particular, the most important geometrical parameter, the reaction distance (r_{cc} in Fig. 1), is perfectly reproduced by calculations at this level of theory (1% error between experimental and calculated values).

The absorption spectra of both open-ring and closed-ring isomers were calculated by using time-dependent density-functional theory (TD-DFT) calculations with the B3LYP functional and the 6-31G basis set. TD-DFT was shown to be an efficient method to evaluate spectroscopic properties of large conjugated molecules [9–13] such as dithienylethenes [14–21]. TD-DFT at the B3LYP/6-31G level correctly reproduced the absorption wavelength and intensity of large organic dyes [13]. In the case of dithienylethenes [16], the calculated absorption maxima of a series of closed-ring isomers was found to be in good agreement with experimental values (2% of average error between experimental and theoretical values).

3. Reference molecule (molecule 1)

Initial C_2 symmetry was imposed. After symmetry restriction was removed, we found a C_1 minimum. Two similar but distinct dihedral angles are obtained. For the C_1 minimum, the cyclopentene is no longer planar as in C_2 structure but distorted at the optimised geometry. The calculated results for both the C_2 and C_1 symmetry are summarised in Table 1 for open-ring (**1a**) and closed-ring (**1b**) isomers. r_{cc} is the reaction distance between the two reactive carbons, ξ_1 and ξ_2 are the dihedral angles depicted in Fig. 1. One can notice that C_2 and C_1 geometrical parameters are close to each others, the main differences between these two conformers arising from the geometry of the cyclopentene (φ_1 and φ_2 angles). Some extra geometrical parameters for **1a** and **1b** molecules with C_1 symmetry are given in Fig. 2. The frequency analysis indicates that the C_2 minimum is a transition state connecting two C_1 minima.

The size and signs of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both open-ring and closed-ring isomers (C_1 symmetry) are illustrated in Fig. 3. The frontier HOMO and LUMO are distributed along the π-conjugation chains shown in Scheme 1. In the open-ring isomer, the π-path has severe distortion along the hexatriene center (between 2 and 2′ positions) due to the non-planar geometry (see Fig. 2). The frontier orbitals are mainly delocalized between the 2 and 2′ positions. In the closed-ring isomer, the frontier orbitals are more extended and coplanar along the polyene chain shown in Scheme 1: the HOMO and LUMO are delocalized between the 5 and 5′ positions.

The HOMO of **1a** and the LUMO of **1b** present a bonding character between the C_e and $C_{e'}$ atoms. On the opposite, the LUMO of **1a** and the HOMO of **1b** are bonding between C_3–C_e and $C_{3'}$–$C_{e'}$ positions. Therefore, one can notice that the HOMO (respectively, the LUMO) of the open-ring isomer correlates

Table 1
Ground state minima of molecule **1**: energy, geometrical parameters and maximum absorption wavelength

Compound	Symmetry	Energy (a.u.)	Relative energy (kJ mol^{-1})	r_{cc} (Å)	ξ_1/ξ_2 (°)	φ_1/φ_2 (°)	λ_{max} (nm)	Oscillator strength
1a	C_2	−2173.682832	1.67	3.667	−48.3/−48.3	−176.6/−176.6	291.9	0.0626
1a	C_1	−2173.683468	0.00	3.670	−50.9/−45.0	−164.6/171.9	294.0	0.0645
1b	C_2	−2173.676909	17.22	1.540	−6.1/−6.1	−171.5/−171.5	471.6	0.2413
1b	C_1	−2173.678621	12.73	1.540	−7.4/−7.4	−154.8/170.3	477.9	0.2462

with the LUMO (respectively, the HOMO) of the open-ring isomer. According to Woodward–Hoffman rules [22], the ground state cyclisation and cycloreversion are forbidden.

The excitation energies of both open-ring and closed-ring isomers are given in Table 1. The calculated wavelengths of C_1 and C_2 conformers are close to each other, thus showing that the maximum absorption band of both C_1 and C_2 conformers involve the same electronic excitations. For both the open-ring and the closed-ring isomers, the TD-DFT absorption spectrum shows that the transition with the highest oscillator strength corresponds to the HOMO → LUMO ($\pi \rightarrow \pi^*$) single excitation, that is to say to the excitation from the 1A to 1B state under C_2 symmetry. This is in agreement with previous CASSCF

calculations [6,8,23] which have shown that this electronic excitation is the first step of both the cyclisation and cycloreversion reactions.

Substituent effect on the spectroscopic properties of molecule **1** has been successively studied for closed-ring and open-ring isomers. Conjugated groups are introduced at the 5 and 5′ positions of the thiophene groups (compounds **2** and **3** in Scheme 2). The influence of the cyclopentene on the optical properties of the photochrome is also examined. This ring is respectively replaced by a perfluorocyclopentene in molecule **4** (as it is commonly done in experiment [2]) and two cyano substituents in compound **10**, while this ring is removed in compound **9**. Molecules **5**–**8** combine the replacement of the cyclopentene ring by a perfluorocyclopentene ring and the introduction of conjugated groups.

4. Substituent effect: closed form

4.1. Geometrical properties

For molecules **1b**–**10b**, the reaction distance r_{cc} between the two reactive carbons and the dihedral angles ξ_1 and ξ_2 are given in Table 2. One can notice that these geometrical parameters are scarcely affected by the introduction of conjugated groups (molecules **2b** and **3b**). In the same way, the replacement of the cyclopentene ring (molecules **4b**–**7b**) does not modify these structural parameters.

C–C bond lengths along the π-conjugation path (see Scheme 1) are given in Table 3. The averaged distance differences between consecutive C–C bonds of the conjugated path define the bond length alternation (BLA) parameter. For the series of considered molecules, the BLA parameter is defined as the difference between single bond and double bond lengths between the C_5 and $C_{5'}$ positions:

$$\text{BLA} = \sum r_{\text{single}} - \sum r_{\text{double}}$$
$$= r(C_3C_4) + r(C_eC_{e'}) + r(C_{3'}C_{4'}) - r(C_4C_5) - r(C_3C_e)$$
$$- r(C_{3'}C_{e'}) - r(C_{4'}C_{5'}) \tag{1}$$

Since there are three single bonds and four double bonds along the conjugated path, the BLA parameter is negative. If the conjugation of the molecule increases, the single bond length decreases while the double bond length increases. Accordingly, the BLA parameter decreases. On the opposite, for a π-localized system, the value of the BLA parameter gets closer to zero. Table 3 shows that the BLA parameters of the different molecules are really close (−1.189 to −1.108). For a matter of
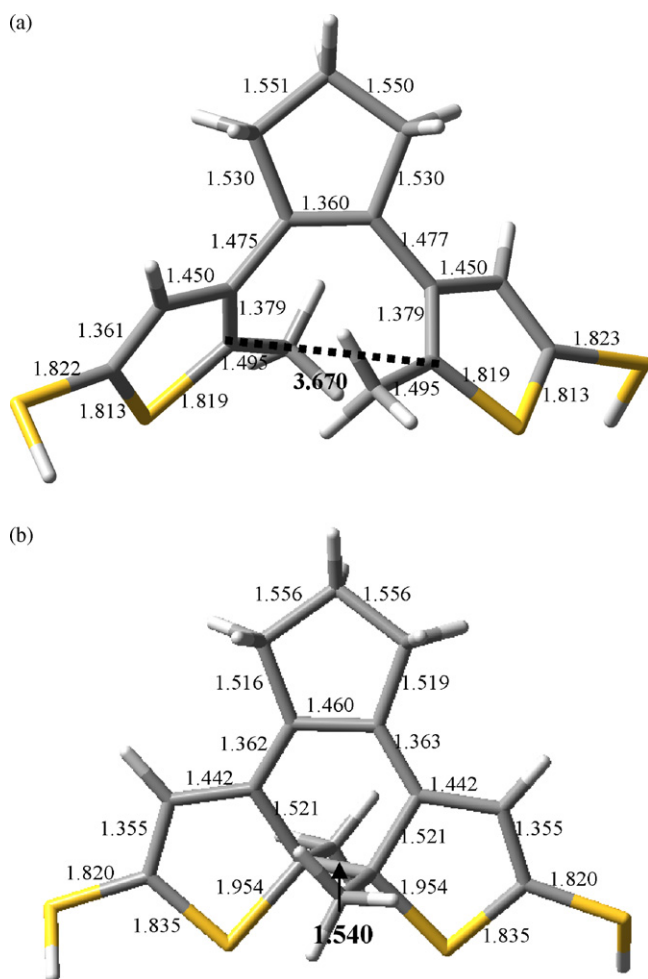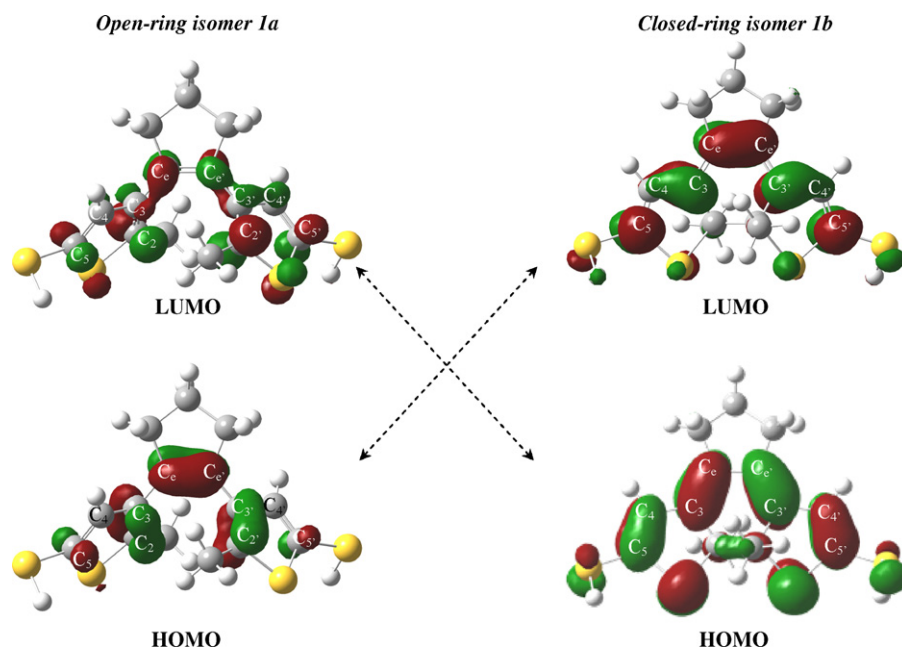

Fig. 2. optimized structures of open-ring and closed-ring isomers (C_1 symmetry) of molecule **1**.

Open-ring isomer 1a   **Closed-ring isomer 1b**

Fig. 3. HOMO and LUMO orbitals of molecules **1a** and **1b** (isodensity = 0.03 a.u.).

Table 2
Energy and structural parameters of open-ring and closed-ring isomers

Compound	Symmetry	r_{cc} (Å)	ξ_1/ξ_2 (°)	Compound	Symmetry	r_{cc} (Å)	ξ_1/ξ_2 (°)
1a	C_1	3.670	−50.9/−45.0	**1b**	C_1	1.540	−7.4/−7.4
2a	C_1	3.647	−50.8/−44.3	**2b**	C_1	1.541	−6.3/−6.0
3a	C_1	3.662	−51.0/−44.8	**3b**	C_1	1.542	−6.8/−7.3
4a	C_1	3.640	−50.4/−41.2	**4b**	C_1	1.543	−4.6/−9.3
5a	C_1	3.658	−51.2/−41.0	**5b**	C_1	1.543	−5.5/−9.7
6a	C_1	3.656	−51.3/−41.0	**6b**	C_1	1.544	−5.2/−9.3
7a	C_1	3.663	−51.6/−41.6	**7b**	C_1	1.544	−4.9/−9.4
8a	C_1	3.657	−51.3/−42.0	**8b**	C_1	1.544	−4.9/−9.6
9a	C_2	3.626	−41.1/−41.1	**9b**	C_2	1.539	−5.1/−5.1
10a	C_2	3.572	−45.7/−45.7	**10b**	C_2	1.538	−4.8/−4.8

convenience, we thus introduce the scaled BLA parameter:

$$BLA_{scaled} = (BLA + 1) \times 10 \qquad (2)$$

Introducing conjugated groups at positions 5 and 5′ (molecules **2b** and **3b**) results in a decrease of the BLA param-

eter (as compared to molecule **1b**). Therefore, the electronic π density tends to delocalize over the lateral groups.

While replacing the cyclopentene ring by a perfluorocyclopentene ring (molecule **4b**), the value of the BLA parameter decreases. The introduction of this electron-withdrawing sub-

Table 3
Closed-ring isomers: bond lengths along the π-conjugation path and bond length alternation parameter (BLA) in Å

Compound	C_4–C_5 ($C_{4'}$–$C_{5'}$)	C_3–C_4 ($C_{3'}$–$C_{4'}$)	C_3–C_e ($C_{3'}$–$C_{e'}$)	C_e–$C_{e'}$	BLA[a]	BLA_{scaled}[b]
1b	1.363 (1.364)	1.438 (1.439)	1.363 (1.363)	1.458	−1.118	−1.18
2b	1.365 (1.365)	1.435 (1.435)	1.366 (1.366)	1.456	−1.136	−1.36
3b	1.367 (1.368)	1.432 (1.432)	1.367 (1.368)	1.454	−1.152	−1.52
4b	1.360 (1.360)	1.434 (1.433)	1.363 (1.364)	1.454	−1.126	−1.26
5b	1.371 (1.372)	1.424 (1.423)	1.368 (1.369)	1.448	−1.185	−1.85
6b	1.371 (1.372)	1.424 (1.423)	1.368 (1.369)	1.449	−1.184	−1.84
7b	1.371 (1.371)	1.427 (1.425)	1.367 (1.368)	1.450	−1.175	−1.75
8b	1.374 (1.373)	1.424 (1.425)	1.369 (1.369)	1.447	−1.189	−1.89
9b	1.355 (1.355)	1.442 (1.442)	1.365 (1.365)	1.448	−1.108	−1.08
10b	1.360 (1.360)	1.434 (1.434)	1.377 (1.377)	1.474	−1.132	−1.32

[a] See Eq. (1).
[b] See Eq. (2).

Table 4
Closed-ring isomers: maximum absorption wavelength ($S_0 \rightarrow S_1$ transition), oscillator strength, HOMO and LUMO levels, and HLG's (HOMO and LUMO gaps)

Compound	λ_{max} (nm)	Description	Oscillator strength	HOMO (eV)	LUMO (eV)	HLG (eV)
1b	477.9	HOMO → LUMO	0.246	−4.75	−1.85	2.90
2b	563.5	HOMO → LUMO	0.661	−4.62	−2.14	2.48
3b	554.5	HOMO → LUMO	0.441	−4.77	−2.30	2.47
4b	512.0	HOMO → LUMO	0.235	−5.73	−3.00	2.73
5b	636.7	HOMO → LUMO	0.737	−5.47	−3.32	2.15
6b	620.3	HOMO → LUMO	0.523	−5.34	−3.14	2.20
	Exp: 605.0[a]					
7b	589.8	HOMO → LUMO	0.423	−5.50	−3.16	2.34
8b	645.9	HOMO → LUMO	0.694	−5.49	−3.28	2.11
9b	461.6	HOMO → LUMO	0.259	−5.04	−2.02	3.02
10b	505.5	HOMO → LUMO	0.194	−5.78	−3.00	2.78

[a] [24].

stituent leads to a delocalization of the electron density over the perfluorocyclopentene.

For molecules combining the replacement of the cyclopentene by a perfluorocyclopentene and the introduction of conjugated groups (molecules **5b** and **7b**), the value of the BLA parameter strongly decreases. The π-electron density becomes delocalized across the overall molecule. One can notice that a way to diminish the BLA parameter and thus to increase the delocalization of the π-electron density is to increase the number of conjugated units on the lateral chains (molecule **8b**).

For molecule **9b**, the BLA and thus the repartition of the π-electron density are close to molecule **1b**. Similarly, Table 3 shows that the value of the BLA parameter of molecule **10b** is close to molecule **4b**. A careful examination of molecule **10b** bond lengths shows that there is a large increase of both the double C_3–C_e bond and the single C_e–$C_{e'}$ bond while compared to the reference molecule. This arises from the mesomer effect induced by the cyano groups.

4.2. Spectroscopic properties

For each closed-ring isomer, the wavelength, the corresponding transition and the oscillator strength of the maximum absorption band are given in Table 4.

As previously seen, introducing conjugated substituents at positions 5 and 5′ of the thiophene rings (molecules **2b** and **3b**) increases the conjugation across the overall molecule. As compared to molecule **1b**, we thus have a diminution of the BLA parameter and a large bathochromic shift of the absorption band of the closed-ring isomer. These trends are illustrated in Fig. 4 where the maximum absorption wavelength is depicted as a function of the BLA parameter. As a matter of fact, the electron density is relatively high at positions 5 and 5′ for the LUMO of molecule **1b** (Fig. 3). Consequently, introducing a conjugated substituent at positions 5 and 5′ stabilizes the LUMO, leading to a decrease of the HOMO–LUMO gap (HLG) (see Table 4 and Fig. 5) and to a parallel increase of the maximum absorption wavelength. This is shown in Fig. 6 where the variation of the maximum absorption wavelength is represented a function of the HLG.
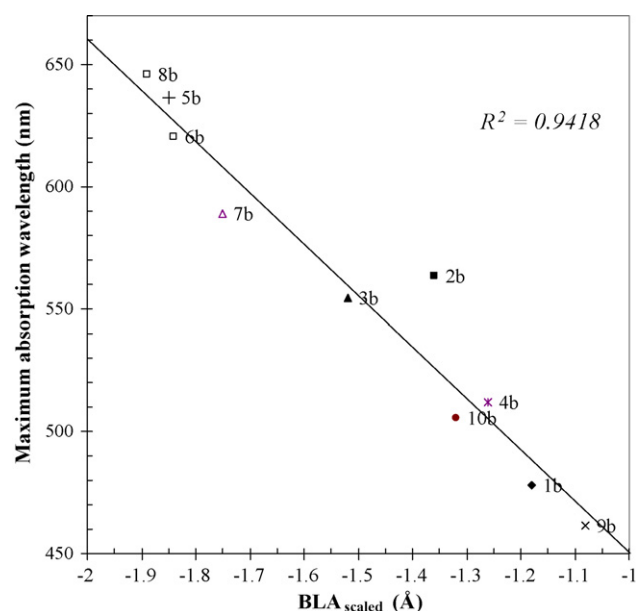

Fig. 4. Closed-ring isomers: value of the maximum absorption wavelength (nm) as a function of the bond length alternation parameter (BLA) parameter in Å.
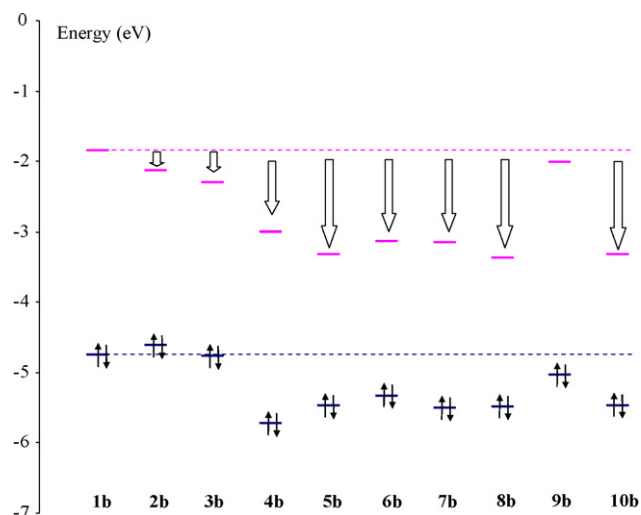

Fig. 5. Closed-ring isomers: HOMO and LUMO energies. The large arrows show the major substituent effect.
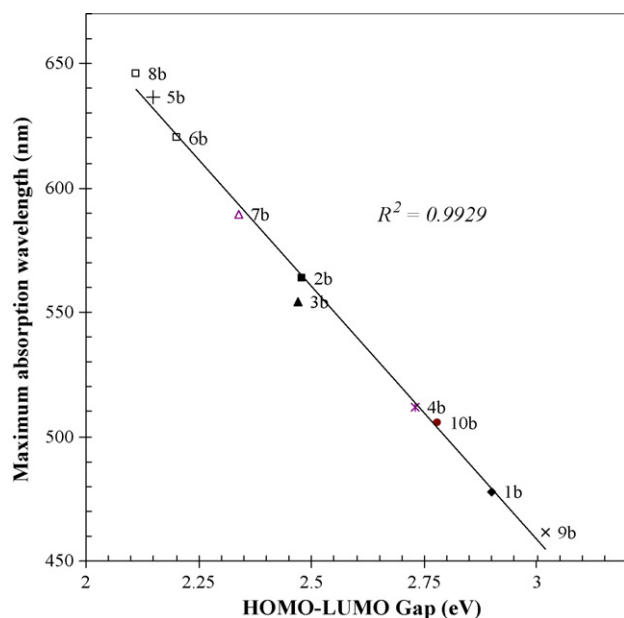
Fig. 6. Closed-ring isomers: value of the maximum absorption wavelength (nm) as a function of the HOMO–LUMO gap (eV).

Removing the cyclopentene ring (molecule **9b**) does not lead to significant change in the excitation energy (see comparison between **1b** and **9b** in Table 4). On the opposite, replacing the cyclopentene with a perfluorocyclopentene ring (molecule **4b**) leads to a strong bathochromic effect. Table 4 and Fig. 5 show that this electron-withdrawing substituent stabilizes both the HOMO and the LUMO orbitals. The LUMO stabilization being the major effect, both the HLG and the excitation energy decrease. Examination of the HOMO and LUMO orbitals of molecule **1b** (Fig. 3) can account for this result: introducing an electron-withdrawing substituent both decreases the antibonding character of the C_e–$C_{e'}$ bond in the HOMO orbital and the antibonding character of the C_e–C_2 and $C_{e'}$–C_2 bonds in the LUMO. In the same way, the replacement of the cyclopentene with two electron-withdrawing cyano substituents increases the maximum absorption wavelength. Table 4 and Fig. 5 show that the stabilization of both HOMO and LUMO orbitals of molecule **1b** induced by the cyano substituents is similar to the effect induced by the perfluorocyclopentene.

Accordingly, molecule **1b** absorption bands can be easily shifted towards larger wavelength by considering two different substituent effects: (1) a conjugated substituent should be introduced at the 5 and 5′ positions of the thiophene rings and (2) the cyclopentene ring should be replaced by an electron acceptor group such as a perfluorocyclopentene ring or cyano substituents. As a consequence, the optical properties of molecules **5b** and **7b** were examined (Scheme 2). These molecules combine the replacement of the cyclopentene by a perfluorocyclopentene and the introduction of conjugated groups (thiophenyl groups for molecule **5b** and acetylenic groups for molecule **7b**). In both cases, Table 4 shows large bathochromic effects arising from a large stabilization of the LUMO: the excitation energy of molecule **5b** (respectively, **7b**) is 636.7 nm (respectively, 589.8 nm) while the excitation energy of molecule **1b** is

477.9 nm. Molecule **6b** (SH terminations of molecule **5b** are removed) has been synthesized by Yassar [24]. The calculated maximum absorption wavelength is in good agreement with experimental observations (Table 4) thus confirming the accuracy of the B3LYP/6-31G level of theory to study the optical properties of this series of compounds.

For molecule **7b**, the maximum absorption band can be shifted to larger wavelength by increasing the number of conjugated units. Hence, for dithienylethene compound presenting two acetylenic units on both sides of the molecule (molecule **8b**), the value of the maximum absorption wavelength is 645.9 nm. This strong bathochromic effect can be explained by the strong π-electron density delocalization across the overall molecule (shown by the diminution of the BLA parameter). By increasing the number of acetylenic groups, the LUMO is more and more stabilized and the HLG decreases.

For this series of dithienylethenes, one can notice that there is a strong correlation between the HLG and the maximum absorption wavelength. As depicted in Fig. 6, as the HLG decreases, the maximum absorption wavelength decreases. This thus shows that, for this series of compounds, the maximum absorption band is perfectly described in terms of single electronic excitation from the HOMO to the LUMO. The red shift of the maximum absorption band can also be described in terms of π electron delocalization. Fig. 4 shows the correlation between the BLA parameter and the maximum absorption wavelength. Actually, the correlations depicted in Figs. 4 and 6 are linked: introducing conjugated or electron-withdrawing substituents gives rise to a delocalization of the π-electron density and to a stabilization of the LUMO. Therefore, both the BLA parameter and the HLG decrease while the absorption maximum shifts to longer wavelength.

The regression correlation coefficient ($R^2 = 0.9418$) between the BLA parameter and the maximum absorption wavelength (Fig. 4) is smaller than the regression correlation coefficient ($R^2 = 0.9929$) between the HLG and the maximum absorption wavelength (Fig. 6). The HLG is thus a better descriptor and predictor index of the maximum absorption wavelength than the BLA parameter. As a matter of fact, we only consider the central part of the molecule (positions 5 to 5′) to calculate the BLA parameter while the HOMO and LUMO energies give information about the electronic structure of the complete molecule. The BLA parameter should thus be calculated along the complete conjugated path of each molecule to provide a more accurate estimation of the π-electron delocalization.

5. Substituent effect: open form

As indicated in Scheme 1, the conjugation path of the open-ring isomer completely differs from that of the closed form. It involves the hexatriene system (C_2–C_3–C_e–$C_{e'}$–$C_{3'}$–$C_{2'}$ path), namely the photochromic part of the molecule. From now on, the "photochrome orbitals" will correspond to the orbitals involved in the cyclisation/cycloreversion reactions that is to say to the orbitals delocalized over the hexatriene system.

When introducing a large conjugated molecule (molecule **2a**), the substituent effect differs from the closed-ring isomer

Table 5
Open-ring isomers **2a** and **5a** absorption spectrum: calculated wavelength, description of the electronic excitation and oscillator strength

Compound	λ (nm)	Description	Oscillator strength
2a	331.9	HOMO (orb. 125) → LUMO (orb. 126)	0.2111
	327.1	HOMO (orb. 125) → LUMO + 1 (orb. 127)	0.0655
	303.9	HOMO − 1 (orb. 124) → LUMO + 1 (orb. 127)	1.1435
	301.8	HOMO − 1 (orb.124) → LUMO (orb. 126)	0.0630
	289.1	**HOMO (orb. 125) → LUMO + 2 (orb. 128)**	**0.0434**
5a	409.6	HOMO (orb. 151) → LUMO (orb. 152)	0.0088
	389.9	HOMO − 1 (orb. 150) → LUMO (orb. 152)	0.0070
	344.6	HOMO (orb. 151) → LUMO + 2 (orb. 154)	0.5031
	343.0	HOMO (orb. 151) → LUMO + 1 (orb. 153)	0.0174
	331.6	HOMO − 1 (orb. 150) → LUMO + 1 (orb. 153)	0.9503
	320.2	HOMO − 1 (orb. 150) → LUMO + 2 (orb. 154)	0.0247
	294.7	**HOMO − 2 (orb. 149) → LUMO (orb. 152)**	**0.1551**

The bolded transition corresponds to the excitation involved in the cyclisation reaction.

case: the chromophores (that is to say the lateral groups) orbitals interact with the photochrome ones. The low-lying excited states come in almost degenerate pairs (Table 5). The first two excited states arise from charge transfer from the central bond $C_e–C_{e'}$ HOMO orbital to the LUMO and LUMO + 1 orbitals localized on the chromophores side chains (Table 5 and Fig. 7) [25]. The HOMO and the two first unoccupied orbitals of molecule **2a** are located in different parts of the molecule thus leading to weak oscillator strength. The following two excited states arise from HOMO–LUMO transitions in the chromophores themselves. The transition involved in the cyclisation reaction corresponds to the transition between the HOMO and (LUMO + 2) orbitals. The corresponding wavelength (289.1 nm) is close to the value of the electronic excitation of the reference molecule **1a** (294 nm).

Similarly, the absorption spectrum of molecule **5a** is given in Table 5. The thiophene chains orbitals interact with the photochrome ones as depicted in Fig. 8. The transition with the largest oscillator strength ($λ = 331.6$ nm; see Table 5) corresponds to a transition in the chromophores themselves. The cyclisation reaction may proceed through the $(HOMO − 2) → LUMO$ transition $(λ = 294.7$ nm), these two orbitals being located over the central $C_e–C_{e'}$ bond.

Accordingly, for molecules **2a** and **5a**, the absorption spectrum of the open-ring isomer is modified by electronic transitions in the chromophores themselves. These excitations may compete with the electronic excitation leading to the ring-closure. At the same time, for the reactive carbons C_2 and $C_{2'}$, the value of the $π$ coefficient of the orbitals involved in the cyclisation reaction (the LUMO + 2 orbital for molecule **2a** and the LUMO for molecule **5a**) decreases when compared to molecule **1a** (see Table 6). This may lead to important consequences on the photochromic reactivity. Hence, molecules **2** and **5** may not be the optimal photochromic candidates for use as optical molecular switches.

If we introduce acetylenic groups at the 5 and 5′ positions (molecule **3a**), the HOMO and LUMO character of the photochromic molecule are not modified. The maximum absorption wavelength still corresponds to the transition involved in the cyclisation reaction, i.e. to the HOMO → LUMO electronic excitation within the photochromic unit. Besides, acetylenic

Orbital n°124
E= -5.62 eV

Orbital n°125 (HOMO)
E= -5.36 eV

Orbital n°126 (LUMO)
E= -1.22 eV

Orbital n°127
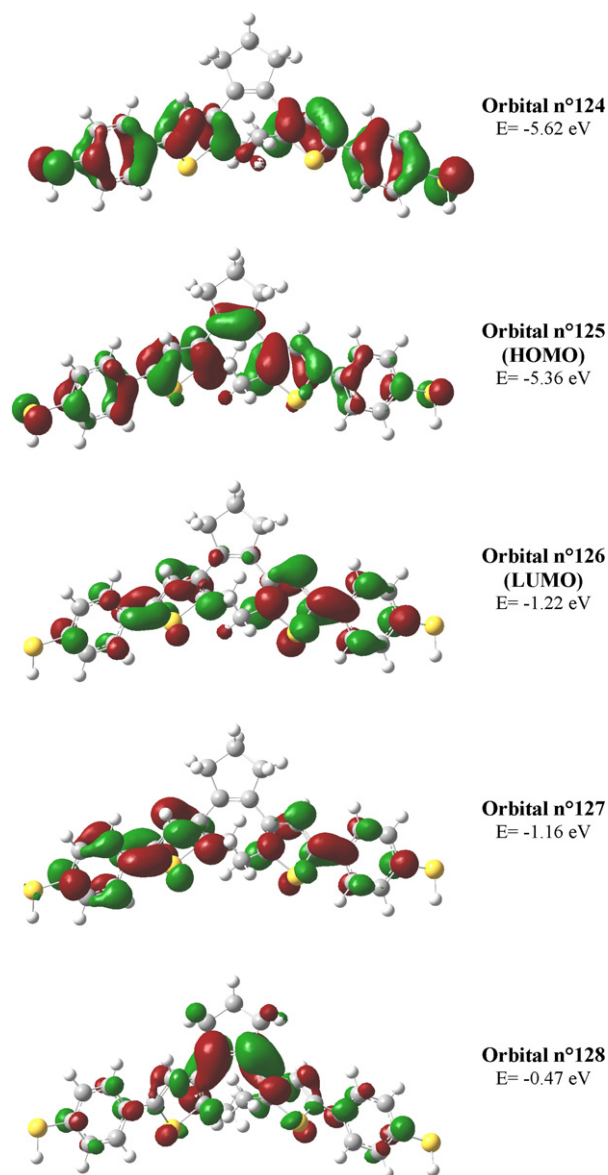E= -1.16 eV

Orbital n°128
E= -0.47 eV

Fig. 7. Molecule **2a**: representation and energy levels of some molecular orbitals (isodensity = 0.03 a.u.).
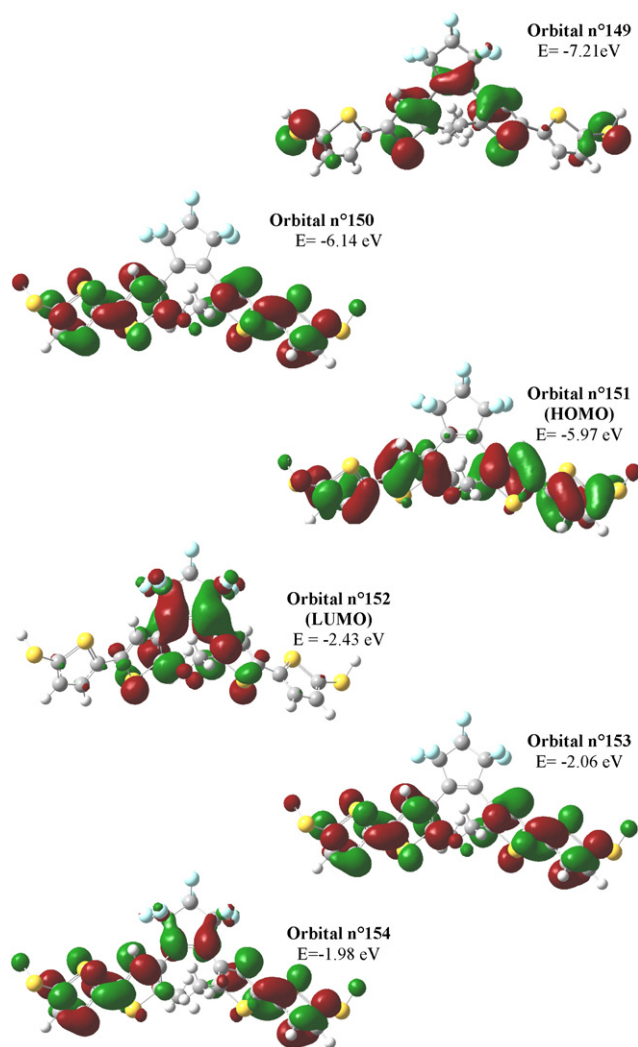
Fig. 8. Molecule **5a**: representation and energy levels of some molecular orbitals (isodensity = 0.025 a.u.).

conjugated substituents decrease the antibonding character of the C_5–S and $C_{5'}$–S bonds in the LUMO of molecule **1a** (see Fig. 3). This thus leads to a stabilization of the LUMO, a reduction of the HLG and a red shift of the maximum absorption band (Table 6).

Let us now consider the influence of the cyclopentene ring on the spectroscopic properties of the open-ring isomer. Removing the cyclopentene ring (molecule **9a**) does not lead to significant changes in the excitation energy (Table 6): the maximum wavelength of compound **9a** is close to molecule **1a**. Both open-ring and closed-ring isomers of molecule **9** can thus be used as a simplified theoretical model of molecule **1** while studying larger systems (such as dithienylethene molecules sandwiched between two gold electrodes [4]).

Replacing the cyclopentene with a perfluorocyclopentene (molecule **4a**) induces a bathochromic effect (Table 6). This electron-withdrawing substituent leads to a decrease of the antibonding character of the C_e–$C_{e'}$ bond in the LUMO (Fig. 3). The LUMO is thus stabilized and the HLG decreases (Table 6).

In molecule **10a**, the first excited state corresponds to a charge transfer from the central bond C_e–$C_{e'}$ HOMO to the LUMO of the cyano substituents (Table 6 and Fig. 9). The interaction of the cyano orbitals with the photochrome ones thus leads to strong modification of the absorption spectrum. While the absorption spectrum of the closed-ring molecule **10b** was similar to molecule **4b**, the behaviour of molecule **10a** strongly differs from molecule **4a**.

As a conclusion, the absorption spectrum of molecule **1a** can be shifted to larger wavelength without being perturbed by (1) introducing acetylenic substituents on the 5–5' positions and (2) replacing the cyclopentene by a perfluorocyclopentene. One can notice that in both cases, the maximum absorption wavelength remains in the UV domain. Accordingly, the spectroscopic properties of molecule **7a** were investigated. Table 6 shows a large bathochromic effect arising from a large stabilization of the LUMO: the excitation energy of molecule **7a** is 363.3 nm while the excitation energy of molecule **1a** is 294.0 nm. At the mean time, the nature of the absorption bands is not modified and the value of the π coefficient of the LUMO on the reactive carbon is conserved. Therefore, the photochromic reactivity and the ring-closure reaction should not be perturbed by the simultaneous introduction of the acetylenic groups and the perfluoro-substituted group. Besides, the maximum absorption band can be easily shifted towards larger wavelength by increasing the number of acetylenic units on both sides of the photochrome (see Molecule **8a** in Table 6).
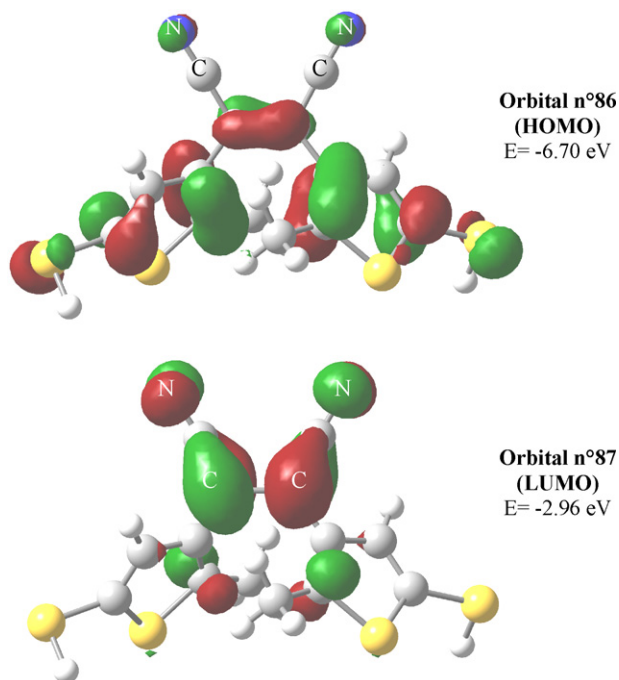
Table 6

Open-ring isomers: maximum absorption wavelength ($S_0 \rightarrow S_1$ transition), oscillator strength, HOMO and LUMO levels, and HLG's (HOMO and LUMO gaps) p_z (i.e. π) coefficient of the LUMO on the reactive C_2 carbon is also given (B3LYP/STO-3G single point calculation)

Compound	λ_{max} (nm)	Description	Oscillator strength	HOMO (eV)	LUMO (eV)	HLG (eV)	p_z^{LUMO} (C_2)
1a	294.0	HOMO → LUMO	0.065	−5.80	−1.06	4.74	0.46
2a[a]							0.30[b]
3a	325.4	HOMO → LUMO	0.050	−5.68	−1.41	4.27	0.40
4a	336.7	HOMO → LUMO	0.102	−6.72	−2.48	4.24	0.42
5a[a]							0.37
7a	363.3	HOMO → LUMO	0.063	−6.42	−2.44	3.98	0.47
8a	385.2	HOMO → LUMO	0.044	−6.24	−2.50	3.74	0.46
9a	292.4	HOMO → LUMO	0.112	−5.95	−1.24	4.71	0.47
10a	385.4	HOMO → LUMO	0.108	−6.70	−2.96	3.74	0.27

[a] See Table 5.
[b] Coefficient of the LUMO + 2 orbital (see text).

Fig. 9. Molecule **10a**: representation of HOMO and LUMO orbitals (isodensity = 0.04 a.u.).

6. Conclusion

Using dithienylethenes molecules in optical molecular switches will require a fine control of the photochromic spectroscopic properties. To this end, we have studied the substituent effect on the optical properties of both the closed-ring and open-ring isomers of a series of photochromic molecules. We demonstrate that density functional theory calculations may contribute to the design of molecular component in functional material. It has been shown that TDDFT method in conjunction with moderate size basis set provides an accurate tool for the determination of the lowest singlet excitation energies of dithienylethene compounds.

We have seen that the absorption spectrum of the closed-ring isomer can be easily shifted to longer wavelengths by modifying the substituents compounds. Both introducing large conjugated substituents at the 5–5′ positions of the photochromic molecule and replacing the cyclopentene by a perfluorocyclopentene lead to large bathochromic effect.

The absorption wavelength of the corresponding open-ring isomers remains in the UV domain. Nevertheless, for phenyl (molecule **2a**) and thiophene (molecule **5a**) substituted molecules, the absorption spectra of the open-ring molecules are modified by electronic transitions in the chromophores themselves. These excitations may compete with the electronic excitation leading to the ring-closure and the photochromic reactivity can thus be strongly affected. On the opposite, for acetylenic substituted molecules (molecules **3a** and **7a**), both the open-ring and closed-ring isomers show a bathochromic effect without any influence of the chain orbitals in the open form maximum absorption band. Moreover, the absorption maximum of both open-ring and closed-ring isomers can be shifted to longer

wavelength by increasing the number of acetylenic units on both sides of the photochrome (molecule **8b**). Acetylenic substituted photochromes can thus be considered as good candidates to be used in optical molecular switch. A complete study of the cyclisation and cycloreversion mechanisms of these molecules should confirm these preliminary results on their photochromic reactivity.

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