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Photochromic properties of dithienylazoles and other conjugated diarylethenes

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Abstract

Using an *ab initio* approach explicitly taking into account bulk solvent effects, we have investigated open- and closed-ring diarylethenes derivatives presenting conjugated bridging units. It turns out that the topology of the open-ring form's LUMO is correlated to the (non-)photochromic character. In addition, the visible spectra of 29 closed-ring compounds have been investigated. After statistical correction, the average (maximal) theory/experiment discrepancy is limited to 6 nm (13 nm), allowing an accurate theoretical colour design for this class of diarylethenes. It is also demonstrated that no simple correlation does exist between the ground-state dipole moment or the bond length alternation and the λ_{max}.

Keywords: Diarylethenes; Photochromism; Density-functional theory; Colour; Electronic spectra

1. Introduction

Diarylethene (DA) derivatives, originally proposed by Irie and Lehn [1,2], probably constitute the most well-known class of photochromic molecules. They can show a conjugated closed-ring form or a less conjugated open-ring form (Fig. 1), the direct or reverse conversion being achieved by irradiation at well-separated wavelengths. Most DA present high fatigue-resistance, large quantum yield and small response times. Consequently, they are ideal basic units for optical-storage and photo-switching applications [3–8]. One can classify DA according to their bridge unit, that is, the group linking the two parts in the photochrom's open-form. DA with cyano [1,9], maleic [1,10], perfluoro-cycloalkanes [11], maleimide [12], cyclopentene [13,14], dihydrothiophene [15] and dihydropyrrole [16,17] bridging units have been synthesised. Quite recently, Krayushkin et al. have proposed new structures with π-delocalised bridges: oxazoles (Fig. 1) [18], thiazoles [18], imidazoles [18], furanones [19] and related derivatives [20–23]. Groups from Perugia and Marseille have also proposed closely-related DA structures [24–26]. Using a π-conjugated bridge results in an original way to tune the photo-coloration properties of the closed-form without substituting the (reactive) side thiophene rings. However, for some substitution patterns (the *R* group in Fig. 1), it appears that photocyclization is impeded. In the present contribution, we thoroughly study these DA derivatives in order to clarify the parameters required for photo-reactivity. In addition, extensive comparisons with experimental data have been carried out for closed-ring systems.

It is worth to point out previous calculations of the electronic transition energies of DA that used semi-empirical [9,27] or *ab initio* approaches [28–39], but to the best of our knowledge none addressed the families of DA tackled here, neither did they predict any reactivity from simple structural considerations. In fact, several investigations aimed at determining the reaction path relating the closed and open forms [30,40–44], but due to the complexity of the problem (excited-state surfaces), they have been limited to simplified structures. In addition, apart from our previous methodological works focussed on the closed form [37,38] all these *ab initio* investigations have been performed with rather limited basis set, 6–31 G or 6–31 G(d) (or similar), and they did not incorporate any modelling of the environmental effects. The present work reports the very first computations of open-ring forms, taking into account solvation effects. We selected the Time-Dependent density-functional theory (TD-

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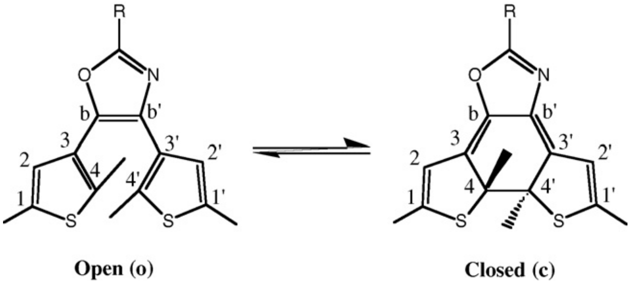

Fig. 1. Sketch of photocyclization process for oxazole-DA.

DFT) that was originally proposed more than two decades ago by Runge and Gross [45], as main theoretical resource. TD-DFT has become the most widely used tool for theoretically evaluating excited-state energies and geometries. Indeed, TD-DFT often provides an accurate, yet rapid, description of transition energies for both gas-phase and solvated species [46]. In practice, TD-DFT uses approximated functionals and some limitations do appear, but they are well understood and generally foreseeable. In the framework of excited-state studies, TD-DFT tends to underestimate the transition energies for charge-transfer states. In other words, the TD-DFT tend to agree with UV–vis experimental spectra when chromophoric units are centred on a few atoms [47–49], but might fail for some biological complexes [50], or cyanine derivatives [51,52].

This paper is organised as follows: Section 2, briefly describes our computational procedure, while Sections 3.1–3.3 respectively present results dealing with the nature and reactivity of the excited-state, the colour of closed-ring derivatives, and the structure-property relationships.

2. Methodology

The geometry optimisations, vibrational analysis and excited-state evaluations of DA derivatives have been performed with the Gaussian 03 program [53], using the PBE0 hybrid [54,55] that is successful for cyano and maleic DA [37,38] and often allows accurate excited-spectra evaluations [49,56–60]. PBE0 has been designed on the basis of purely theoretical considerations, that is a quite exceptional fact amongst the available hybrid functionals.

For each molecule, the ground-state geometry has been optimised by a standard force-minimisation process and the vibrational spectrum has been determined in order to check the absence of imaginary-frequency modes. A triple-ζ polarised basis set, namely 6–311G(d,p), was selected at this stage as it provides converged ground-state structural parameters for the largest majority of organic molecules [61–63]. Then, the three to ten first low-lying excited-states of DA are evaluated with TD-DFT using the 6–311 + G(2d,p) atomic basis set that has been found adequate and accurate for thioindigo dyes, which similarly possess five member sulphur rings in their chromogenic unit [64]. It is also known that a further extension of the basis set does not alter the λ_{max} of DA [37,38], that is, 6–311 + G(2d,p) provides *theoretically converged* transition energies, at least for the low-lying state(s) of interest. Note that, it has been shown in Ref. [36] that TD-DFT and (very accurate) SAC-CI results are in good agreement with each other for neutral DA structures.

As DA UV–vis spectra are measured in solution, it is crucial to include surroundings effects in our simulations [56–58,65]. Therefore, at each stage, the bulk solvent effects are evaluated by means of the polarisable continuum model (IEF-PCM) [66]. To build the cavity, we have used the so-called UA0 radii, but for some geometry optimisations for which the UAKS radii have been found necessary to obtain converged ground-state geometries. IEF-PCM returns valid solvent effects when no specific interactions link the solute and the solvent molecules. In this paper, we have selected the so-called non-equilibrium procedure for TD-DFT calculations that has been specifically designed for the study of absorption processes [46].

3. Results and discussion

3.1. Photochromic properties of oxazole-based DA

Experimentally, the oxazoles-DA drawn in Fig. 1 are active photochroms as long as no nitro-substituted aryl group is used [18]. In this section, we develop a theoretical procedure to predict their (non-) photoreactivity without the tedious computations of excited-state surfaces. In fact, such computation would be a nearly impossible task for the large non-planar structures treated here. In general most diarylethenes cyclise/cyclorevert through a reaction involving singlet excited-states of the open/closed forms [44]. Notable exceptions involving a crucial role of triplet state(s) do exist [26,67], but to the best of our knowledge, there is no evidence of the implication of triplet states in the photochromic reactivity of the oxazoles-DA synthesised by Krayushkin et al.

In Table 1, we compare the experimental and theoretical absorption wavelengths for the six oxazole DA of Ref. [18]. For the four photochromic molecules (*R* = Ph, p-Me-Ph, p-Cl-Ph and p-OMe-Ph), theory is able to mimic the major experimental findings with, on the one hand, the correct auxochromic ordering of the λ_{max} for both forms and, on the other hand, a nearly quantitative agreement, although the wavelengths are overestimated by theory, especially in the closed-ring form (see Section 3.2). The typical variation of λ_{max} upon photocyclization (210 nm) is therefore, slightly overshot by TD-DFT (~250 nm).

Table 1
λ_{max} (nm) for the diarylethene of Fig. 1

Substitution R	Open form		Closed form	
	Theo.	Exp.	Theo.	Exp.
Ph	331 (0.52)	314	577 (0.21)	525
p-Me-Ph	330 (0.59)	313	571 (0.22)	523
p-NO_2-Ph	468 (0.42)	379	837 (0.12)	–
p-Cl-Ph	341 (0.59)	320	589 (0.20)	530
3,5-NO_2-Ph	466 (0.08), 346 (0.38)	362	784 (0.06), 593 (0.14)	–
p-OMe-Ph	327 (0.66)	312	560 (0.23)	513

Oscillator strengths are given between brackets. All theoretical values have been obtained with the PCM(CH_3CN)-TD-PBE0/6-311 + G(2d,p)//PCM(CH_3CN)-PBE0/6-311G(d,p) approach. The experimental data have been taken in Ref. [18].

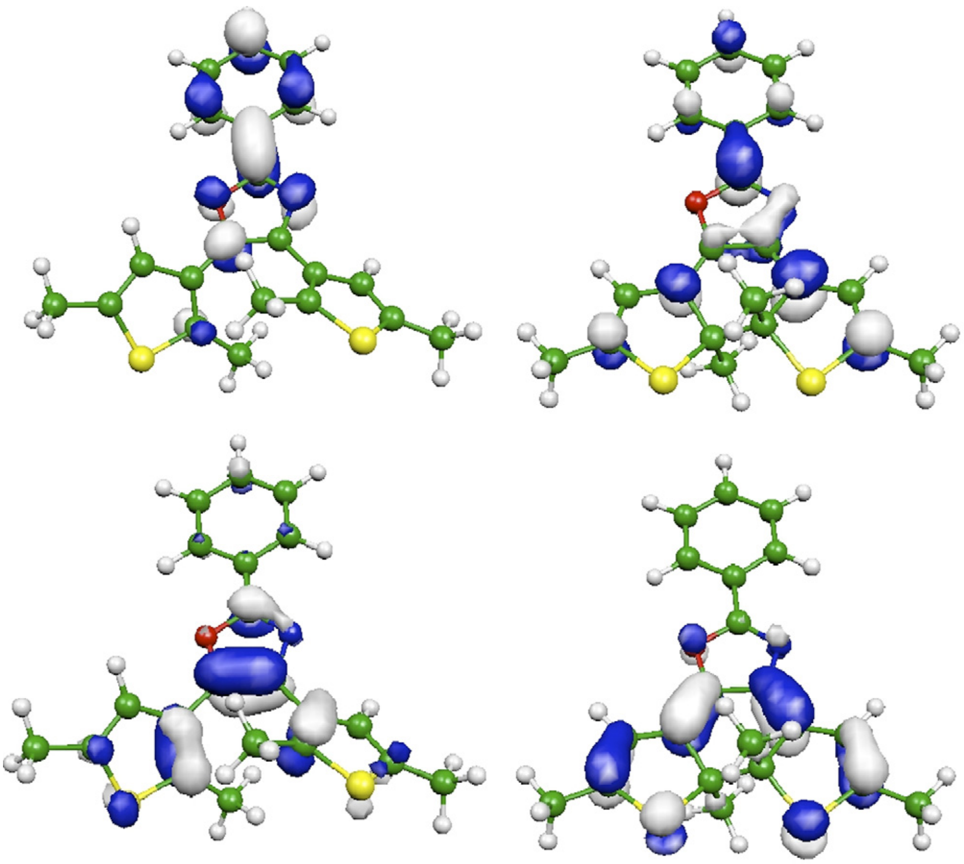

Fig. 2. HOMO (bottom) and LUMO (top) of the open (left) and closed (right) forms for the $R = \mathrm{Ph}$ DA of Table 1.

The C_4–$C_{4'}$ distance always amounts to 3.64 Å (1.54 Å) in the open- (closed) forms. These values are in the line with Perrier, Maurel and Aubard's results [39], as they reported distances of 3.62 ± 0.05 Å (1.54 Å) for typical DA. The $\tau_{\mathrm{b'b34}}$ ($\tau_{\mathrm{bb'3'4'}}$) dihedral angles are −40° (−43°) and −8° (−9°) for the open and closed DA, respectively. For all these four molecules, the $\lambda_{\max}$ transition corresponds to a HOMO → LUMO excitation in both forms. The topology of these frontier orbitals is sketched in Fig. 2 for the $R = \mathrm{Ph}$ system, the three other compounds displaying completely similar patterns. For comparison, Fig. 3 provides the same information for a perfluoro-bridge molecule synthesised by the Irie group [29]. For this latter compound, the shapes of the orbitals are quite comparable to these reported in Ref. [39], with (i) HOMOs mainly centred on the double bonds of the core photochromic unit, (ii) an open-ring LUMO displaying a significant density on the reactive carbon atoms and, (iii) a closed-ring LUMO showing the typical π^* state shape of conjugated DA [35,37]. The HOMOs of the oxazole-DA in Fig. 2 are comparable to those depicted in Fig. 3, but for an enhanced contribution on the $C_\mathrm{b} = C_{\mathrm{b'}}$ doubly bond in the open form. While the closed-ring LUMO is more delocalised than in Fig. 3 (with additional densities on the oxazoles and aryl rings), the more striking differences occur for the open-ring LUMO, which is mostly centred on the top of the bridge unit, but for a small contribution on C_4. This means that a small component on one of the reactive carbon atom is sufficient to allow photocyclization. It also suggests that the photochromic efficiency is decreased when using conjugated bridges instead of saturated bridges. Unfortunately, no experimental quantum yields are given in Ref. [18].

Plugging nitro groups impedes any photochromic activity: only the open-ring form exists experimentally. The calculated geometrical parameters of the two nitro DA are exactly in line with the reactive compounds: a C_4–$C_{4'}$ distance of 3.64 Å, and $\tau_{\mathrm{b'b34}}$ ($\tau_{\mathrm{bb'3'4'}}$) dihedral angles of −40° (−43°). For the p-NO_2-Ph molecule, the first allowed transition displays a HOMO → LUMO character, and these frontier orbitals are sketched in Fig. 4. The topology of the open-ring HOMO is completely comparable to the one of Fig. 2, but the LUMO is displaced towards the acceptor group with no residual density on C_4 or $C_{4'}$. This most probably explains the absence of photocyclization for the $R = NO_2$ derivative. Therefore, our calculations confirm the suggestion of the experimental group: "Apparently, the presence of electron-withdrawing substituents leads to a decrease in the electron density at the [reactive] carbons of the thiophene rings" [18]. Note that the enhanced charge transfer nature of the excited-state also explains the substantial theory/experiment $\lambda_{\max}$ discrepancy (90 nm versus 20 nm). For the di-nitro-DA, the situation is more complex: we obtain several transitions displaying negligible oscillator strengths ($f < 0.005$) in the domain spanning from 517 nm (HOMO → LUMO) to 376 nm. Of course, due to the limitations of TD-DFT, some of these states could be unrealistic ghost states [50]. The 466 nm transition given in Table 1 is the sec-

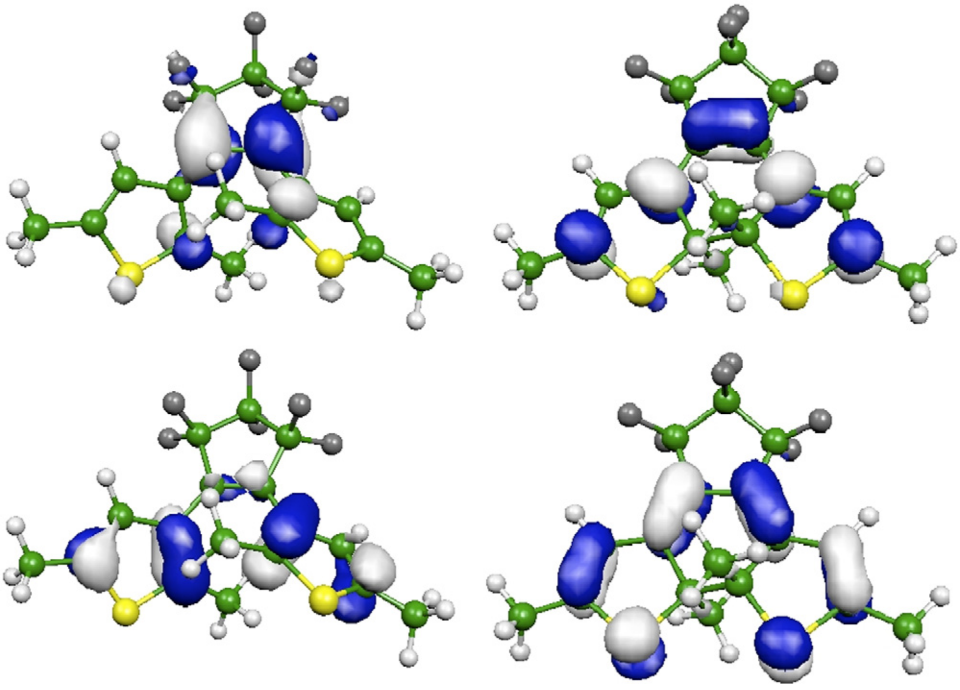

Fig. 3. HOMO (bottom) and LUMO (top) of the open (left) and closed (right) forms of a typical perfluoro-DA photochrom.

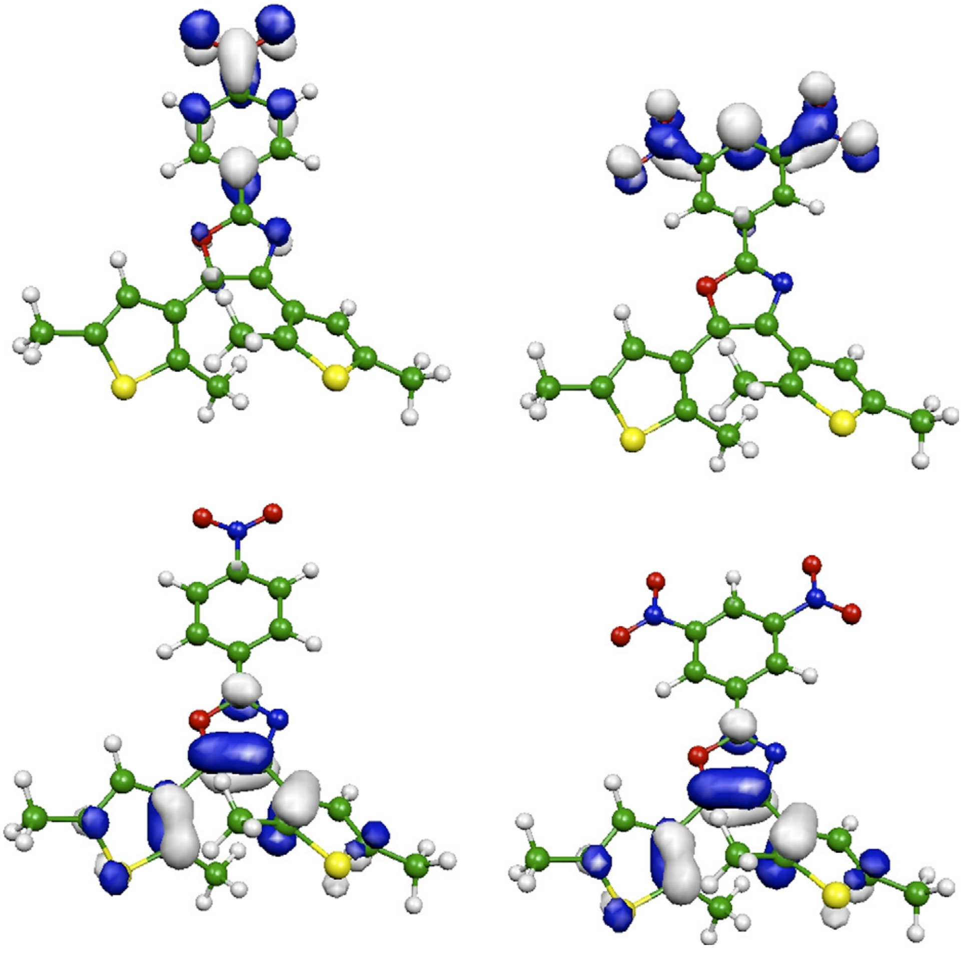

Fig. 4. Left: HOMO (bottom) and LUMO (top) of the open $R = \text{p-NO}_2\text{-Ph}$ ox-azole photochrom. Right: HOMO (bottom) and LUMO + 1 (top) of the open $R = 2,5\text{-NO}_2\text{-Ph}$ system.

Table 2
Comparison between experimental and theoretical λ_{max} (nm) for the compounds depicted in Fig. 5

System	X_1	X_2	R	Solvent	Theo.	Exp.	Ref.
I	S	O	H	CH_3CN	511	473	[23]
	S	NMe	H	CH_3CN	520	489	[23]
	O	S	H	CH_3CN	491	467	[23]
	O	O	H	CH_3CN	475	442	[21]
	O	O	COMe	CH_3CN	460	447	[21]
	O	NMe	H	CH_3CN	481	450	[21]
	O	NMe	COMe	CH_3CN	467	445	[21]
II	–	–	H	CH_3CN	492	464	[21]
	–	–	COMe	CH_3CN	478	462	[21]
	–	–	COPh	CH_3CN	457	450	[21]
III	S	–	–	3-Me-pentane	548	520	[25]
	S	–	–	Cyclohexane	549	522	[24]
	O	–	–	CH_3CN	490	460	[23]
IV	–	–	–	CH_3CN	492	460	[22]
V	O	C–C	NH_2	CH_3CN	508	483	[20]
	O	N	Ph	CH_3CN	577	525	[18]
	O	N	*p*-Me-Ph	CH_3CN	571	523	[18]
	O	N	*p*-Cl-Ph	CH_3CN	589	530	[18]
	O	N	*p*-OMe-Ph	CH_3CN	560	513	[18]
	S	N	NH_2	CH_3CN	514	485	[18]
	NH	N	Ph	CH_3CN	610	568	[18]
	NH	N	*p*-Br-Ph	CH_3CN	625	570	[18]
	NH	N	*p*-Me-Ph	CH_3CN	603	558	[18]
	NH	N	*o*-OH-Ph	CH_3CN	603	544	[18]
	NH	N	*o*-Cl-Ph	CH_3CN	595	554	[18]
	NH	N	*p*-Cl-Ph	CH_3CN	622	570	[18]
VI	–	–	–	CH_3CN	535	505	[20]
VII	–	–	–	CH_3CN	560	506	[20]
VIII	–	–	–	CH_3CN	555	515	[20]

ond excited-state, possesses a HOMO → LUMO + 1 character, and probably corresponds to the 366 nm experimental transition. Indeed, we expect a slightly larger error on the λ_{max} than for the p-NO_2 system so we have to honestly state that it is unlikely that our 346 nm peak could be assigned to the 366 nm measurement. The HOMO and LUMO + 1 of the di-nitro DA are displayed in Fig. 4 that shows an LUMO + 1 completely centred on the acceptor groups. No contribution is found on the reactive carbons, or on the oxazole bridge. By looking at higher lying unoccupied orbitals, one could find orbitals presenting shapes comparable to the open-ring LUMO of Fig. 2, but it is well known that a reactive first excited-state is often the essential prerequisite for the design of the most efficient photo-switches.

As an intermediate conclusion, our calculations gave clear hints that a small but non-zero "LUMO density" should be detected at (at least) one of the reactive carbons of the open-ring form to allow a photocyclization.

3.2. Colour of closed-ring systems

In Table 2, the theoretical and experimental λ_{max} of 29 DA dyes presenting bridge units including π electrons (see Fig. 5) are listed. A graphical comparison can be found in Fig. 6. The experimental wavelengths span over about 130 nm (from 442 to 570 nm), indicating that modifications of the bridge unit only can efficiently tune the colour of the closed-ring isomer. For this set of photochroms, the mean signed error (MSE, experiment-theory) amounts to −36 nm (0.16 eV) and the mean absolute error (MAE) is 36 nm (0.16 eV), that is, TD-DFT systematically undershoots the transition energies. This is due to the spatial extension of the chromophoric unit involving a significant electron transfer from the thiophene rings to the bridging moiety (see Fig. 2). Indeed, as underlined in Section 1 the charge transfer excited states are often poorly described by TD-DFT relying on conventional hybrid functionals [68]. Consequently, for other DA dyes possessing similar side groups but less delocalized bridges, the MAE are smaller: 26 nm for cyano derivatives [37] and 9 nm for maleic bridges [38]. However, a 0.16 eV error still matches the expected TD-DFT accuracy. Indeed, we are aware of four studies using a wide panel of organic compounds belonging to several dye families: two reported a MAE 0.29 eV and 0.24 eV for $\pi \rightarrow \pi^*$ transitions in sulphur-free and sulphur-bearing molecules, respectively [52,69]; one obtained a MAE of 0.19 eV for an extended set of organic dyes [51]; whereas the fourth gave an average error of 0.14 eV for 47 singlet-triplet transitions [70].

In practice, one is interested in the auxochromic effects, not in the absolute λ_{max} values. As can be seen in Table 2, these effects are often satisfactorily reproduced by theory. For instance, in series **I** with X_1=O, going from X_2=O to X_2=S (X_2=NMe) shifts the experimental spectra by 25 nm (8 nm), and these values are well reproduced by theory: 16 nm (6 nm). Likewise, replacing the oxygen atom by an amine group at X_1 in **V** (with *R*=Ph), leads to a computed 33 nm bathochromic shift, in good agreement with the 43 nm measured value. In addition, from Fig. 6, it is quite clear that the larger the experimental λ_{max}, the larger the theory/experiment discrepancy (in nm), and a simple statistical correction could therefore, be of high benefit. For the present set of DA derivatives, we obtained:

$$\lambda_{max}^{corr} = 83.061 + 0.778\lambda_{max}^{TD-DFT} \tag{1}$$

This fitting yields an excellent R^2 (0.97) and allows to drastically decrease the MAE: 6 nm (0.03 eV), that is an error amounting to only 5% of the 130 nm of the λ_{max} window studied. Simultaneously, the largest discrepancy is reduced to a tiny 13 nm (0.07 eV). The striking impact of Eq. (1) is illustrated by Fig. 6, showing that efficient design of photochromic bridges is at hand: one can accurately predict the visible properties from *ab initio* calculations.

3.3. Structure-property relationships

In Table 3, structural and energetic parameters are reported for the closed-ring DA listed in Table 2. It is often useful to establish relationships between these parameters and the absorption wavelengths. First, let us consider the bond length alternation (BLA) that is often viewed as the main geometrical parameter for quantifying elec-

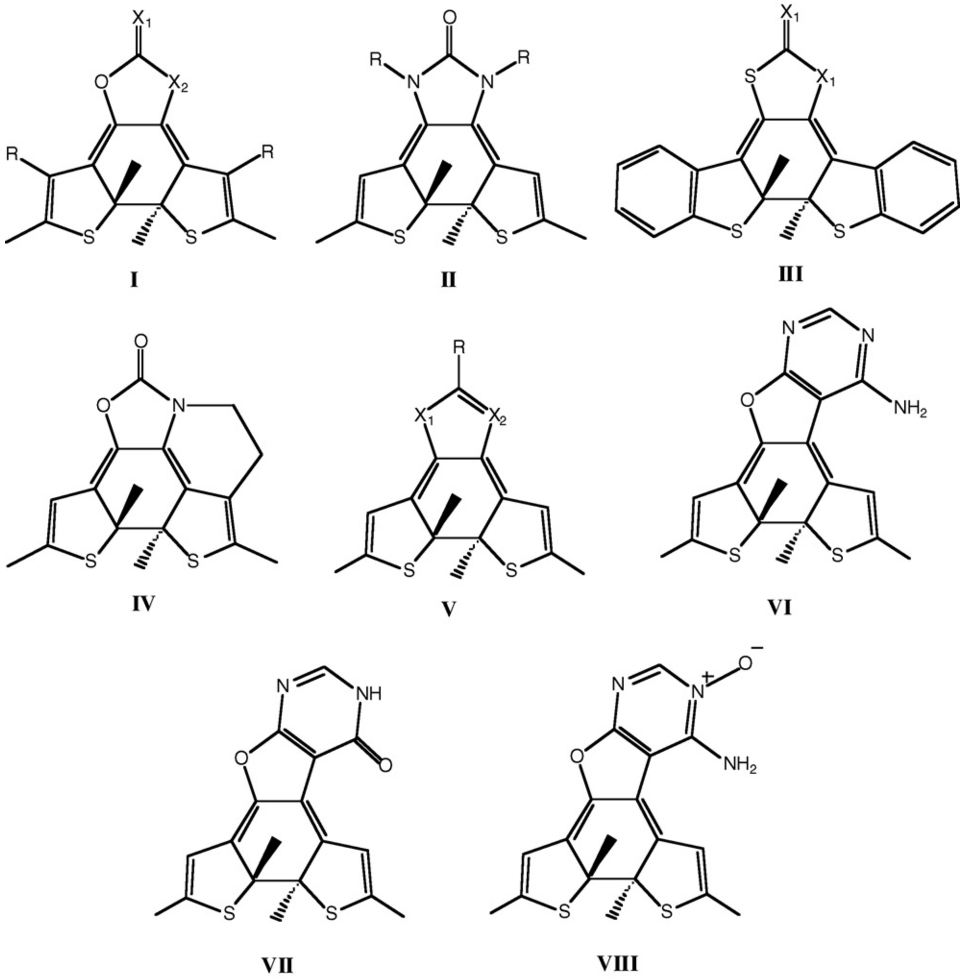

Fig. 5. Sketch of the closed-ring diarylethenes investigated in Table 2.

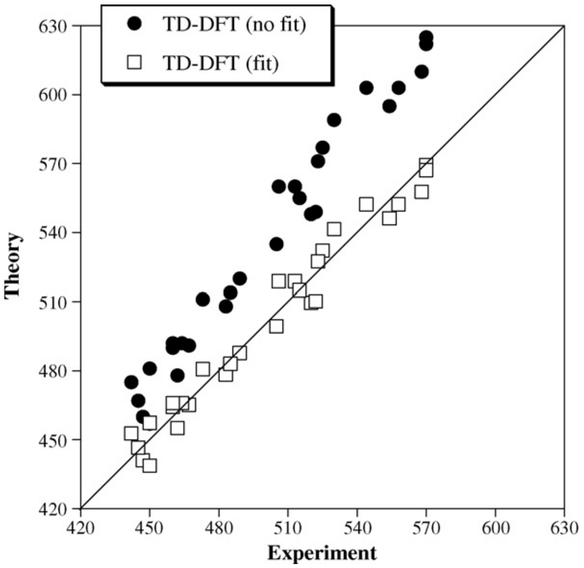

Fig. 6. Comparison between experimental and theoretical $\lambda_{\max}$ (nm) for closed-ring DA. The closed circles are the raw TD-DFT data whereas the open squares have been obtained after correction by Eq. (1). The central line indicates a perfect theory/experiment agreement.

tron delocalisation in π-conjugated molecules. Following Perrier et al. [39], the BLA has been chosen as the (normalised) difference of the single and double bond lengths involved in the HOMO of the closed-ring forms (see Figs. 1 and 2):

$$\mathrm{BLA} = \frac{1}{3}(d_{2-3} + d_{2'-3'} + d_{b-b'}) - \frac{1}{4}(d_{1-2} + d_{i'-2'} + d_{3-b} + d_{3'-b'}) \qquad (2)$$

A graphical comparison is shown in Fig. 7 and demonstrates the lack of correlation between the BLA and the $\lambda_{\max}$: the R^2 obtained for a linear regression is meaningless (0.15) and does absolutely not compared to the $R^2 = 0.94$ reported in Ref. [39] for DA with saturated bridges. This difference originates in the topologies of the LUMO (see Figs. 2 and 3), as for the perfluoro photochroms, it is centred on the bonds included in Eq. (2). This is not the case for the compounds of Table 2. To circumvent this shortcoming, one would probably need to include the bond lengths of the conjugated bridges in Eq. (2). But, as the structural variety is large (check Fig. 5), such description could hardly be general or transferable. In addition, we note that the ground-state dipole moments are absolutely not indicative of the absorption

Table 3
Structural and energetic parameters for molecules listed Table 2

System	X_1	X_2	R	Solvent	BLA	$\lvert\vec{\mu}\rvert$	E^{H}	E^{L}
I	S	O	H	CH_3CN	0.0777	5.82	−0.197	−0.083
	S	NMe	H	CH_3CN	0.0805	6.05	−0.191	−0.080
	O	S	H	CH_3CN	0.0837	4.73	−0.193	−0.075
	O	O	H	CH_3CN	0.0815	4.74	−0.196	−0.074
	O	O	COMe	CH_3CN	0.0892	6.23	−0.211	−0.084
	O	NMe	H	CH_3CN	0.0858	4.08	−0.188	−0.068
	O	NMe	COMe	CH_3CN	0.0952	10.62	−0.203	−0.078
II	–	–	H	CH_3CN	0.0887	0.87	−0.179	−0.062
	–	–	COMe	CH_3CN	0.0908	2.26	−0.193	−0.071
	–	–	COPh	CH_3CN	0.0862	3.39	−0.190	−0.079
III	S	–	–	3-Me-pentane	0.0723	3.39	−0.209	−0.100
	S	–	–	Cyclohexane	0.0723	3.42	−0.209	−0.100
	O	–	–	CH_3CN	0.0684	3.13	−0.208	−0.088
IV	–	–	–	CH_3CN	0.0752	3.90	−0.185	−0.068
V	O	C-CN	NH_2	CH_3CN	0.0844	7.92	−0.180	−0.067
	O	N	Ph	CH_3CN	0.0788	3.24	−0.182	−0.082
	O	N	*p*-Me-Ph	CH_3CN	0.0792	4.10	−0.181	−0.081
	O	N	*p*-Cl-Ph	CH_3CN	0.0788	1.17	−0.183	−0.084
	O	N	*p*-OMe-Ph	CH_3CN	0.0792	5.49	−0.181	−0.078
	S	N	NH_2	CH_3CN	0.0873	5.43	−0.175	−0.063
	NH	N	Ph	CH_3CN	0.0803	6.57	−0.171	−0.076
	NH	N	*p*-Br-Ph	CH_3CN	0.0799	4.71	−0.172	−0.079
	NH	N	*p*-Me-Ph	CH_3CN	0.0803	7.09	−0.171	−0.075
	NH	N	*o*-OH-Ph	CH_3CN	0.0805	5.93	−0.174	−0.079
	NH	N	*o*-Cl-Ph	CH_3CN	0.0791	6.32	−0.172	−0.075
	NH	N	*p*-Cl-Ph	CH_3CN	0.0800	4.86	−0.172	−0.079
VI	–	–	–	CH_3CN	0.0863	5.07	−0.187	−0.078
VII	–	–	–	CH_3CN	0.0818	4.44	−0.183	−0.080
VIII	–	–	–	CH_3CN	0.0853	5.82	−0.189	−0.084

BLA is defined by Eq. (2) (Å), $\lvert\vec{\mu}\rvert$ is the norm of the dipole moment (Debye). E^{u} and E^{L} are the energies of the HOMO and LUMO (a.u.).

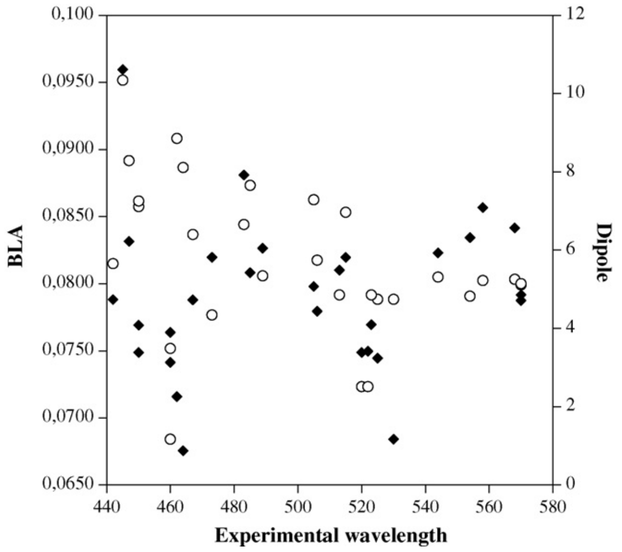

Fig. 7. Comparison between experimental $\lambda_{\max}$ (nm) and computed bond length alternation (Å, open circles) and norm of the dipole moment (D, closed diamonds) for the compounds of Table 3.

wavelengths: the linear correlation coefficient could hardly be weaker ($R^2 = 0.004$).

The energies of both the HOMO and LUMO are listed in Table 3. As expected, the LUMO is slightly more sensitive to the substitution pattern than the HOMO, but individual correlations with the $\lambda_{\max}$ remain small (R^2 of 0.37 for the E^{H} and 0.08 for E^{L}). Hopefully, there exists a direct correlation between the HOMO-LUMO gap and the experimental $\lambda_{\max}$ (see Fig. 8):

$$\lambda_{\max}^{\mathrm{estim}} = 916.7 - 140.76\Delta E^{\mathrm{H-L}} \qquad (3)$$

which yields a R^2 of 0.90. This constitutes a satisfactory result though R^2 remains under Perrier et al. value (0.99) [39]. Using Eq. (3) instead of Eq. (1) in order to estimate the $\lambda_{\max}$ would results in a MAE of 10 nm and a maximal deviation of 41 nm, significantly above the values calculated in Section 3.2. This illustrates that TD-DFT provides a more consistent approximation to the experimental absorption wavelengths than single structural and/or energetic molecular descriptors.

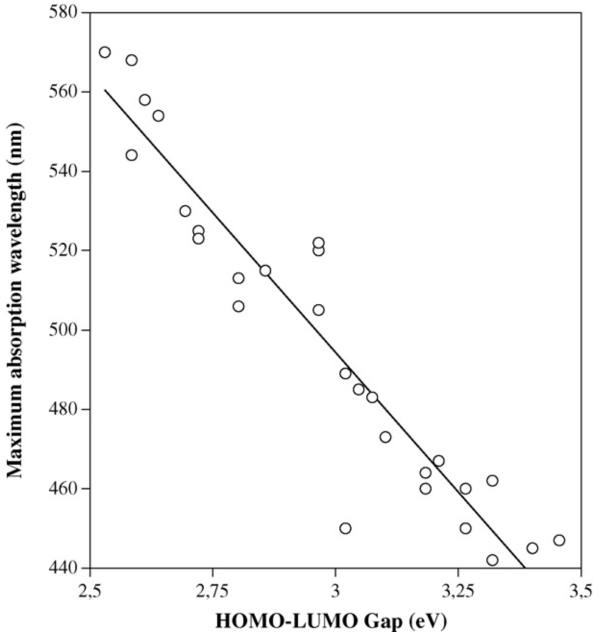

Fig. 8. Correlation between the HOMO-LUMO gap (eV) and the experimental maximum absorption wavelength (in nm). The fitting line represented corresponds to Eq. (3).

4. Conclusions and outlook

The open- and closed-ring forms of oxazole-based DA have been investigated using a state-of-the-art TD-DFT approach that includes modelling of environmental effects. It has been found that a small electronic density at one of the reactive carbon atoms is sufficient to allow photocyclization. On the contrary, adding electron acceptor groups impedes photochromic reactivity because either the density is negligible on C_4 and $C_{4'}$ in the LUMO, and/or because the reactive excited state is not the first singlet excited state. For sure, other phenomena might hamper photocyclization of DA. For instance, the open-ring form could decompose upon irradiation, a fact that is not foreseeable with the present approach. The colours of a large panel of closed-ring DA possessing a variety of conjugated bridges have been investigated. The use of Eq. (1) allows a consistent and accurate prediction of the λ_{max} with a MAE limited to 6 nm and a maximal error of 13 nm. Such an accuracy cannot be attained just by using HOMO-LUMO gaps as descriptors. In addition, due to the delocalized nature of the excited-state, there is no correlation between the bond length alternation (or the dipole moments) and the λ_{max}, in strong contrast with DA based on saturated bridges.

We are currently investigating other classes of DA derivatives to test the transferable character of these conclusions.

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