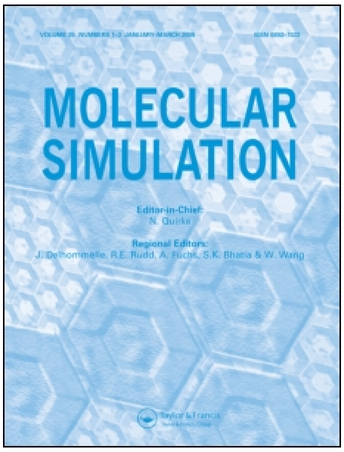

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Substitution effects on the optical spectra of diarylethene photochroms: *ab initio* insights

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Substitution effects on the optical spectra of diarylethene photochroms: *ab initio* insights

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Using a time-dependent density functional approach and taking into account the bulk solvent effects, we study the modification of the optical properties of maleic anhydride diarylethenes induced by structural changes. Our results reproduce the auxochromic shifts described by experiments. We show that the closed forms of diarylethene molecules are much more sensitive to heteroatom substitution of the cyclopentadienyl rings than the open forms. The addition of electro-active groups to the reactive carbon atoms is also investigated. The major effect on the UV/visible spectra originates from the resonance effect as measured by the Hammett's factor.

Keywords: diarylethenes; photochromism; optical spectra; UV/vis absorption; TD-DFT

1. Introduction

Diarylethene derivatives are among the most well-known and investigated molecular photochroms. These compounds possess two structures with very distinct electronic properties: a conjugated closed-ring form and a less conjugated open-ring form (Figure 1). While the cyclisation occurs under UV irradiation, the cycloreversion generally takes place upon visible light absorption.

Diarylethenes (DA) also satisfy the usual prerequisites for the design of efficient molecular switches: high-fatigue resistance, thermal stability (P-type photochroms [1]), as well as short response times. In short, DA are ideal building blocks for various applications such as optical memories, variable electrical current devices and even photomagnetic switches [1–5].

In order to improve the photochromic properties of DA, it is of prime importance to maximise the difference of the maximum absorption wavelengths ($\Delta\lambda_{\max}$) between the open and closed form, as larger $\Delta\lambda_{\max}$ considerably ease practical use of photochroms. Many previous investigations followed this track, identifying the most adequate DA, either by modifying the bridge linking the two parts (Figure 1) in the photochrom's open form [6–9] or by substituting the conjugated cycles [10,11].

In this paper, we perform a systematic study of the closed DA with the maleic anhydride forming the bridge (Figure 1) by means of quantum mechanical calculations. In order to quantify the substituting effects on these DA, we have (1) modified the nature of both heteroatoms (X_1 and X_2) included in the cyclopentadienyl cycles and (2) investigated the auxochromic effects of electron-withdrawing as well as electron-donating groups (R_1 and R_2) that can be grafted on the reactive carbon atoms (Figure 1).

2. Methodology

We have chosen the density functional theory (DFT) and its time-dependent counterpart (TD-DFT) for our calculations [12]. TD-DFT is well suited for our purpose as it yields an accurate yet fast description of the transition energies for most mono-determinental compounds [13] in various media. Concerning DA, several studies have been performed with TD-DFT, but only a few take into account the surrounding effects or use extended atomic basis set necessary to obtain reliable results [14–20].

The Gaussian 03 suite of program [21] was selected to perform our calculations on maleic anhydride DA derivatives (Figure 1). The PBE0 hybrid functional [22] has been chosen because it yields small mean absolute errors on $\lambda_{\max}$ prediction for many organic dyes [23] and anhydride DA as well [20]. Our results rely on a well-documented methodology [20], and the geometry optimisations were achieved with the 6-311G(d,p) basis set. The vibrational spectra were obtained with the same basis set, while the evaluation of the three-to-eight first low-lying excited states required a more extended basis set, namely 6-311 + G(2d,p). These basis sets have been shown adequate for DA [16,18,19]. At each computational stage, we have taken bulk solvent (heptane) effects into account by means of the polarisable continuum model (IEF-PCM [24]).

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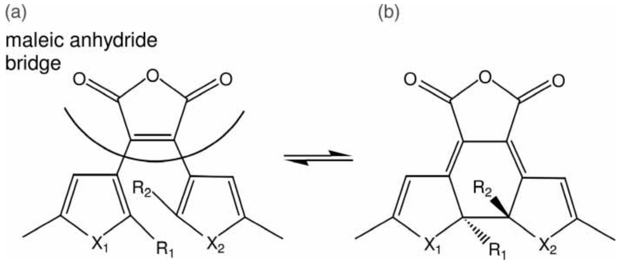

Figure 1. Representation of maleic anhydride DA in its open-ring (a) and closed-ring (b) forms.

3. Results and discussion

Maleic anhydride DA derivatives (Figure 1) have initially been synthesised by Irie's group [7,25,26]. In these works, absorption spectra (λ_{max}values) of closed and open DA containing $X_{1,2} = $ Se, S, N—Me are reported, with some inconsistencies for the λ_{max} of the open form. For instance, for the $X_{1,2} = $ S structure, the reference data maximum UV/visible wavelength may be attributed to the first (405 nm [7]) or to the second (331 nm [25]) dipole-allowed transition. Direct comparisons might therefore be difficult as the selected experimental reference is not always clearly identified. For the sake of consistency, we report in the following the first transition with a significant oscillator strength ($f > 0.09$) for the closed forms. This transition corresponds to an electron promotion from the HOMO to the LUMO, and according to the experimental data, it is associated to the first peak of open forms. For open DA, an additional strong absorption ($f > 0.3$) appears, which corresponds to the second peak sometimes listed by experimentalists. We note that the oscillator strength ratio (1:3) determined by means of theoretical calculations is totally in line with the experiment.

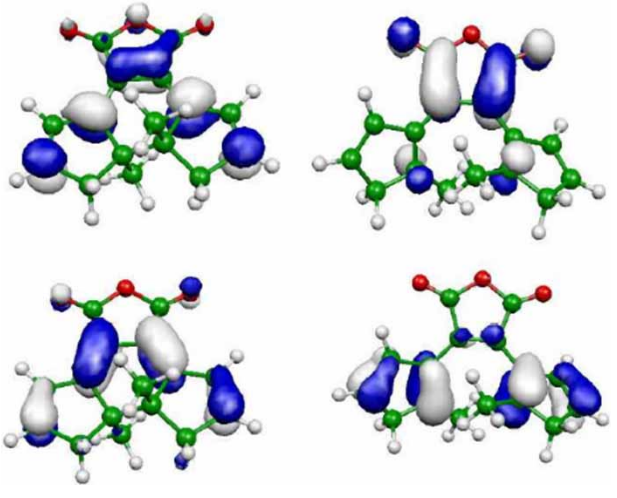

Figure 2. HOMO (bottom) and LUMO (top) of the closed (left) and open (right) forms for $X_{1,2} = CH_2$ and $R_{1,2} = CH_3$ (Figure 1).

The topology of the frontier orbitals of both the closed and open forms (Figure 2, with $X_{1,2} = CH_2$ and $R_{1,2} = CH_3$) demonstrates that the related electronic density (e.d.) is not similarly located for the two forms. For the HOMOs, the e.d. is centred on the double bonds of the two cycles for both forms, while the LUMO orbitals are spread differently for each forms the e.d. of the closed (open) form is mainly located on the cyclopentadienyl (delocalised on the maleic bridge) moieties. Since the LUMO generally guides the cycloreversion and the photoreactivity [18], it does not modify the absorption spectra of DA (λ_{max} value). In this paper, we only discuss the absorption spectra of the closed forms, as neither the modifications of cyclopentadienyl nor chemical substitution on the reactive carbons will strongly influence the absorption spectra of the open form. For the record, the theoretical values of λ_{max} for open DA are given as Supplementary information, available online.

3.1 Closed forms

3.1.1 Influence of the heteroatoms

In Table 1, we report the maximum absorption wavelengths of closed DA featuring different heteroatoms. First, let us note that we accurately reproduce the measured shifts [27–29]. For instance, we obtain for the $X_1 = CH_2$ series the same evolution as Yamaguchi and Irie [27]: going from $X_2 = $ O and to $X_2 = $ S yields a bathochromic displacement of +34 nm, in good agreement with our estimate (+43 nm). When X_1 is O, S or Se, the experimental shifts of the reference DA ($X_1 = CH_2$ and $X_2 = $ S) are +24, + 48 and +77 nm, respectively [27–29], whose values are adequately reproduced by our PCM-TD-DFT calculations: +24, + 64 and +76 nm.

As can be deduced from Table 1, the largest λ_{max} are reached for compounds containing at least one pyrol, thiophene or selenophene cycle, using two such cycles being optimal. Consequently, these compounds are the most interesting and are good candidates for designing switches with the desired properties. The values listed in

Table 1. λ_{max} (in nm) of the closed form of DA (Figure 1) with $R_1 = R_2 = CH_3$ featuring heteroatoms X_1 and X_2.

	X_1						
X_2	CH_2	NH	O	SiH_2	PH	S	Se
CH_2	413						
NH	480	527					
O	444	508	478				
SiH_2	413	488	446	408			
PH	449	508	474	432	480		
S	487	539	511	493	520	551	
Se	504	549	525	512	536	563	575

Note: All values were obtained with the PCM(C_7H_{16})-TD-PBE0/6-311+G(2d,p)//PCM(C_7H_{16})-PBE0/6-311G(d,p) level of theory.

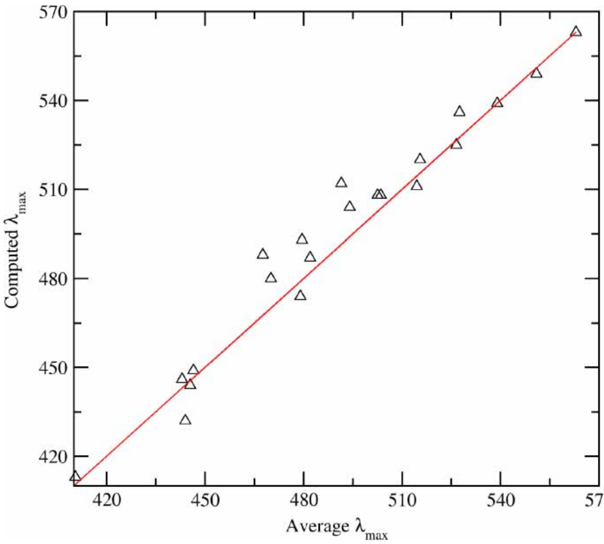

Figure 3. Comparison between the average λ_{max} (calculated with the two λ_{max} of symmetric unit) and the computed λ_{max} obtained for asymmetric DA. These values are obtained with different heteroatoms in the cyclopentadienyl. The diagonal corresponds to the perfect agreement between the two values.

Table 1 allow an extra conclusion: a DA possessing different heterocycles ($X_1 \neq X_2$) systematically presents a λ_{max} value in between the wavelengths listed for the symmetric DA. For example, the DA derivative with a pyrol and a selenophene cycle absorbs at 549 nm, which is very close to the average of 527 nm ($X_{1,2}$ = N—H) and 575 nm ($X_{1,2}$ = Se). Figure 3 shows the relation between the 'exact' average for asymmetric structures determined as the computed λ_{max} of two symmetric DAs and the results theoretically obtained for asymmetric compounds. Apart for only one case (X_1 = PH and X_2 = SiH_2), the computed values are always higher or very close (agreement is within few nanometres) to the average values, showing a clear cooperative enhancement effect.

3.1.2 *Substitution effects on the reactive carbon atoms*

We have designed DA with thiophene cycles (X_1 = X_2 = S) with various functional groups (R_1 and R_2) attached to the reactive carbon atoms (Figure 1 and Table 2). For the typical structure (R_1 = R_2 = CH_3), we notice that the theoretical λ_{max} (551 nm) correctly produces Irie's reference of 551 nm (in hexane [25]). For R_1 = R_2 = CN, CH_3, OCH_3 series, the trend is similar to the bathochromic effect experimentally observed [30]. Starting from R_1 = R_2 = CN and going to CH_3 and OCH_3, a +23 and a +105 nm red shift is obtained theoretically, whereas +30 and +80 nm displacements are measured for similar (perfluoro) DA.

Table 2. λ_{max} (in nm) of the closed forms of DA (Figure 1), with X_1 = X_2 = S and substitution of the reactive carbons (R_1 and R_2).

	R_1						
R_2	CH_3	OCH_3	OH	CN	CF_3	Cl	F
CH_3	551						
OCH_3	579	633					
OH	570	612	590				
CN	538	568	561	528			
CF_3	552	597	581	540	563		
Cl	563	628	610	554	574	608	
F	563	628	618	557	579	615	626

Note: All values were obtained with the PCM(C_7H_{16})-TD-PBE0/6-311+G(2d,p)//PCM(C_7H_{16})-PBE0/6-311G(d,p) level of theory.

We note that the largest λ_{max} are reached for compounds possessing at least one F atom. Also, compounds with one CN group exhibit the smallest λ_{max}, and hence are less useful. We observe that values obtained with different R_1 and R_2 groups lie in between those of the corresponding symmetric part (Figure 4). This effect is slightly different from that observed with different heteroatoms (see above), as in this case several computed values (R_1 = CH_3, CN, CF_3 with R_2 = F and R_1 = CH_3 with R_2 = Cl) for asymmetric units are 15–20 nm lower than the average.

We can decompose the electronic effect of substituents into two contributions: an inductive effect and a resonance term, though it is not easy to distinguish which one predominates. According to Hansh [31], it is noteworthy that the effects on λ_{max} follow a dual substituent parameter

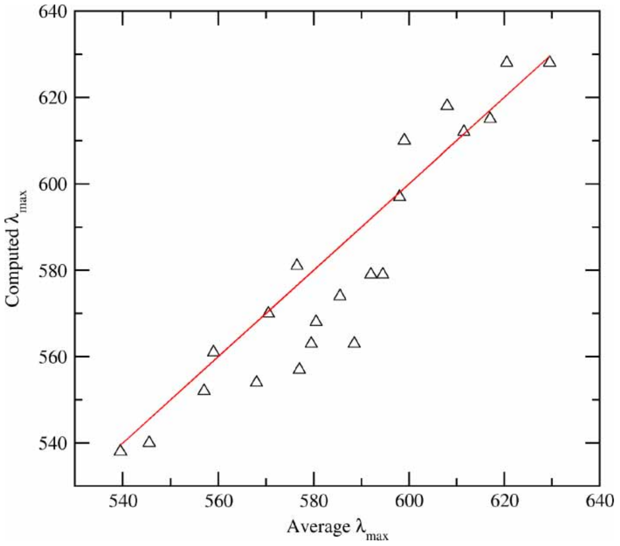

Figure 4. Comparison between the average λ_{max} (calculated with the two λ_{max} of symmetric unit) and the computed λ_{max} obtained for asymmetric DA. These values are obtained for different substitution at the reactive carbons. The diagonal corresponds to the perfect agreement between the two values.

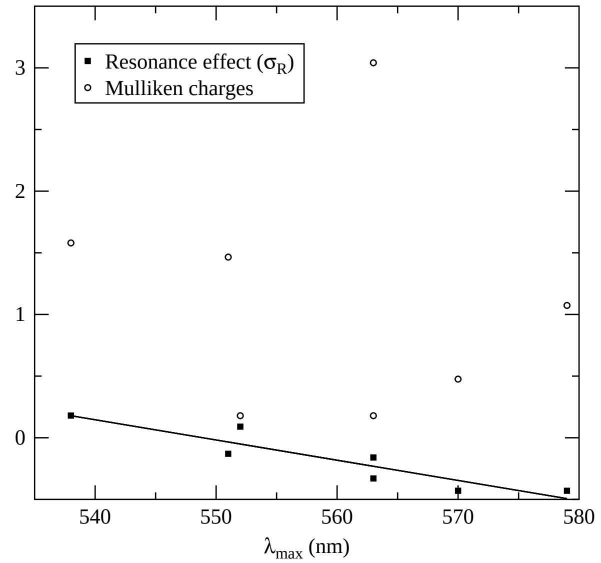

Figure 5. Relation between the maximal absorption wavelengths (λ_{max}) and Mulliken charges, or σ_R, corresponding to the substitution of R_2 of maleic anhydride DA when R_1 is fixed (CH_3).

equation, where only the resonance part turns out to be active (σ_R [31]), as commonly observed for UV/visible properties. Figure 5 shows the approximate linear relation between the maximum absorption wavelength and the σ_R factor, with a correlation coefficient of 0.92. On the contrary, a large dispersion is observed for the Mulliken charges borne by the reactive carbon atoms. As these can be used as a crude estimate of the inductive effect, one can conclude that the resonance effect is the major contribution, as expected.

4. Conclusions

The optical properties of maleic anhydride DA derivatives have been investigated, with an approach combining both TD-DFT and bulk solvent effect. The main electronic transition presents a systematic HOMO → LUMO character, and is associated with an oscillator strength ≥ 0.09. Preliminarily, we have shown that different heterocycles do not significantly influence the open form transition because the e.d. of the LUMO is located on the maleic bridge. The same remark is valid when various groups are grafted on the reactive carbon atoms. The λ_{max} of the closed form guides the $\Delta\lambda_{max}$ parameter and is therefore the most useful descriptor for practical applications.

For each case, the experimental shifts are nicely reproduced by our theoretical procedure, and prediction of maximum absorption wavelength of new compounds can consequently be considered as reliable. In particular, we propose compounds containing at least one ring with NH or S or Se atom. If atoms are attached to the reactive carbons, the λ_{max} also increases. We have shown that an approximate relation exists between the wavelength and the resonance Hammett factor, whereas no significant inductive effects on the reactive carbon atoms could be unravelled.

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Note

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Supplementary information

Two tables are available online presenting the $\lambda_{\max}$ for open forms of the studied DA. The first one contains the $\lambda_{\max}$ for different heteroatoms (X_1 and X_2), and the second one gives the maximun absorption wavelength induced by various substitutions on the reactive carbons (R_1 and R_2).