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RESEARCH ARTICLE

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 anhydre 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 heteroatoms 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

Diarylethenes (DA) derivatives are one of 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). Whilst the cyclisation occurs under UV irradiation, the cycloreversion generally takes place upon visible light absorption.

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 maximize 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].

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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 (i) modified the nature of both heteroatoms (X_1 and X_2) included in the cyclopentadienyl cycles, and (ii) 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 (see 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-determinantal compounds [13] in various media. Concerning DA, several studies have been performed with TD-DFT but only a few take into account 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 (MAE) 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 optimizations 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].

3 Results and Discussion

Maleic anhydride DA derivatives (Figure 1) have initially been synthesized by Irie's group [7, 25, 26]. In these works, absorption spectra ($\lambda_{\max}$ values) of closed and open DA containing $X_{1,2} = \text{Se}, \text{S}, \text{N-Me}$ are reported, with some inconsistencies for the $\lambda_{\max}$ of the open form. For instance, for the $X_{1,2} = \text{S}$ structure, the reference data maximum UV/visible wavelength may be

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

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, that 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.

The topology of the frontier orbitals of both closed and open forms (Figure 2, with $X_{1,2} = \text{CH}_2$ and $R_{1,2} = \text{CH}_3$), demonstrates that the related electronic density (e.d.) is not similarly located for the two forms. For the HOMOs, the e.d. is centered 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 doesn't modify the absorption spectra of DA (λ_{max} value). In this paper we only discuss the absorption spectra of the closed forms. Nor the modifications of cyclopentadienyl nor chemical substitution on the reactive carbons will strongly influence the absorption spectra of the open form. Therefore, we only discuss the results of the closed form in the following and for the records, the theoretical values of λ_{max} for open DA are given as *Supplementary Materials*.

Figure 2. HOMO (bottom) and LUMO (top) of the closed (left) and open (right) forms for $X_{1,2} = \text{CH}_2$ and $R_{1,2} = \text{CH}_3$. See Figure 1

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 $X_1 = \text{CH}_2$ series the same evolution as Yamaguchi and Irie [27]: going from $X_2 = \text{O}$ and to $X_2 = \text{S}$ 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 ($X_1 = \text{CH}_2$ and $X_2 = \text{S}$) are respectively +24 nm, +48 nm, +77 nm [27–29], which values are adequately reproduced by our PCM-TD-DFT calculations: +24 nm, +64 nm and +76 nm.

Table 1. λ_{max} (in nm) of closed form of DA (Figure ??) with $R_1=R_2 = \text{CH}_3$ featuring heteroatoms X_1 and X_2 . All values are 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

X_2	CH_2	NH	O	X_1 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

As can be deduced from the Table 1, the largest λ_{max} are reached for compounds containing at least one pyrrol, 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 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 pyrrol and a selenophene cycle absorbs at 549 nm, that is very close to the average of 527 nm ($X_{1,2} = \text{N-H}$) and 575 nm ($X_{1,2} = \text{Se}$). 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 ($X_1 = \text{PH}$ and $X_2 = \text{SiH}_2$), the computed values are always higher or very close (agreement is within few nm) 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 ($X_1 = X_2 = \text{S}$) with various functional groups (R_1 and R_2) attached to the reactive carbon atoms (see Figure 1 and Table 2). For the typical structure ($R_1 = R_2 = \text{CH}_3$), we notice that the theoretical λ_{max} (551 nm) correctly produces Irie's reference of 551 nm (in hexane) [25]. For $R_1 = R_2 = \text{CN}$, CH_3 , OCH_3 series, the trend is similar to the bathochromic effect experimentally observed [30]. Starting from $R_1 = R_2 = \text{CN}$ and going to CH_3 and OCH_3 , a +23 nm and a +105 nm red shift is obtained theoretically; whereas +30 nm and +80 nm displacements are measured for similar (perfluoro) DA.

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 to that observed with different heteroatoms (see above), as this case several computed values ($R_1 = \text{CH}_3$, CN , CF_3 with $R_2 = \text{F}$ and $R_1 = \text{CH}_3$ with $R_2 = \text{Cl}$) for asymmetric units are 15 to 20 nm lower than the average.

Figure 3. Comparison between the average $\lambda_{\max}$ (calculated with the two $\lambda_{\max}$ of symmetric unit) and the computed $\lambda_{\max}$ 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 2. $\lambda_{\max}$ (in nm) of closed forms of DA (Figure 1), with $X_1=X_2= S$ and substitution of the reactive carbons (R_1 and R_2). All values are 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.

R_2	CH_3	OCH_3	OH	R_1 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

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 effects on $\lambda_{\max}$ follow a dual substituent parameter 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 diarylethene derivatives have been investigated, with an approach combining both time-dependent density functional theory and bulk solvent effect. The

Figure 4. Comparison between the average $\lambda_{\max}$ (calculated with the two $\lambda_{\max}$ of symmetric unit) and the computed $\lambda_{\max}$ 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 ($\lambda_{\max}$) and Mulliken charges, or σ_R , corresponding to substitutions of R_2 of maleic anhydre DA when R_1 is fixed (CH_3)

main electronic transition presents a systematic HOMO $\rightarrow$ LUMO character, and is associated with an oscillator strength ≥ 0.09 . Preliminary, we have shown that different heterocycles do not influence significantly the open form transition because the electronic density 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 $\lambda_{\max}$ 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 for each case, 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 $\lambda_{\max}$ 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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RESEARCH ARTICLE

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

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Table 1. λ_{max} (in nm) of open DA (Fig. 1) with $R_1=R_2=\text{CH}_3$ featuring heteroatoms X_1 and X_2 . All values 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

X_2	CH_2	NH	O	X_1 SiH_2	PH	S	Se
CH_2	456						
NH	445	441					
O	448	436	427				
SiH_2	454	431	429	444			
PH	455	431	426	439	432		
S	450	431	420	430	424	410	
Se	453	435	424	434	428	414	418

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Table 2. $\lambda_{\max}$ (in nm) of open DA (Fig. 1), with $X_1=X_2=S$ and substitution of the reactive carbons (R_1 and R_2). All values are 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

R_2	Me	OMe	OH	R_1 CN	CF ₃	Cl	F
Me	410						
OMe	432	445					
OH	426	438	438				
CN	443/389	463/374	457/376	362			
CF ₃	421/368	442/370	439/355	392	372/345		
Cl	414	438	432	382	417/432	412/354	
F	417	440	434	422/376	402/356	411	408