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Quantitative study of photochromic transformations of diarylethene derivatives with either perhydrocyclopentene or oxazolone or lactone units

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ABSTRACT

This work is devoted to the determination of ring-closure and ring-opening quantum yield values of 18 thermally irreversible photochromic diarylethene derivatives. Three classes have been systematically investigated. They have been obtained (i) by changing the bridging ring that stabilizes the central ethenic double bond in the *cis* configuration from perhydrocyclopentene, oxazolone and lactones, and (ii) by varying the lateral aryl moieties from thiophene, benzothiophene and thiazoles. Numerical modeling of UV/visible absorption *vs* time kinetic curves recorded under continuous monochromatic irradiation in combination with chemical actinometry was employed to determine the photo-cyclisation and cyclo-reversion quantum yields together with the molar absorption coefficient of the closed form. Structure-properties diagrams obtained by plotting λ_A *vs* λ_B, ε_A *vs* ε_B and Φ_{AB} *vs* Φ_{BA} visualize all the structural effects helping the evaluation of these compounds as possible photoswitches or high-density optical recording materials.

1. Introduction

Among all types of photochromic compounds [1], diarylethenes (DAE) are one of the most successful series [2]. Their photoisomerization results in large changes in their electronic and steric properties. Therefore there is an intense coloration after ring closure, while the reverse photoinduced ring-opening exhibits bleaching. Moreover, the photochemical properties of the diarylethenes can be modified through structural variations influencing the absorption spectra, fluorescence, quantum yields, and fatigue resistance. This makes the diarylethenes highly attractive for applications such as all-optical information processing and storage and photoswitches [3]. Diarylethenes photochromism is usually interpretated by the photoinduced 6 π electrons pericyclic interconversion between the central hexatriene in the open form (DAE open) and the cyclohexadiene of the closed one (DAE closed) (Scheme 1). As the hexatriene moiety is part of two aromatic rings, the dearomatization of the aryl rings substituents of the central double bond is the key feature of the DAE photocoloration [4]. Thus, in order to improve the thermal stability of the closed-ring isomer, moderately aromatic nuclei are chosen: aside the most popular thiophene, benzothiophene and thiazole [5] are usually employed. It is also worth mentioning that the incorporation of the cyclohexadiene moiety into a larger polyenic structure in the closed form is responsible of the coloration of this photosisomer. However when five membered aromatic heterocycles (*i.e.* thiophene, thiazole, etc) are used as lateral substituents the length of this conjugated part depends strongly on the position of the sulfur atom. Thus, when the double bond is sitting on the alpha position from the sulfur, the closed photoisomer displays opposite features to the beta substituted “normal DAE”. Having a fragmented polyenic structure, moderate changes in the spectroscopic properties are achieved hence their coined name of “inverse DAE” [6].

The efficiency of the photochemical processes has also been longuely explored and discussed. According to the Woodward–Hoffmann rules, the photocyclization occurs in a conrotatory mode, while the corresponding thermal back-reaction would be disrotatory. Since the conformer interconversion is slower than the excited-state lifetime, only the light, which has been absorbed by the antiparallel form, can stimulate cyclization. As a consequence, the open parallel conformer is inactive [7]. This discussion implicitly

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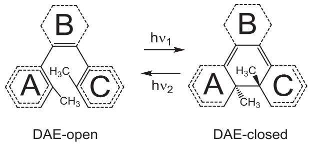

Scheme 1.

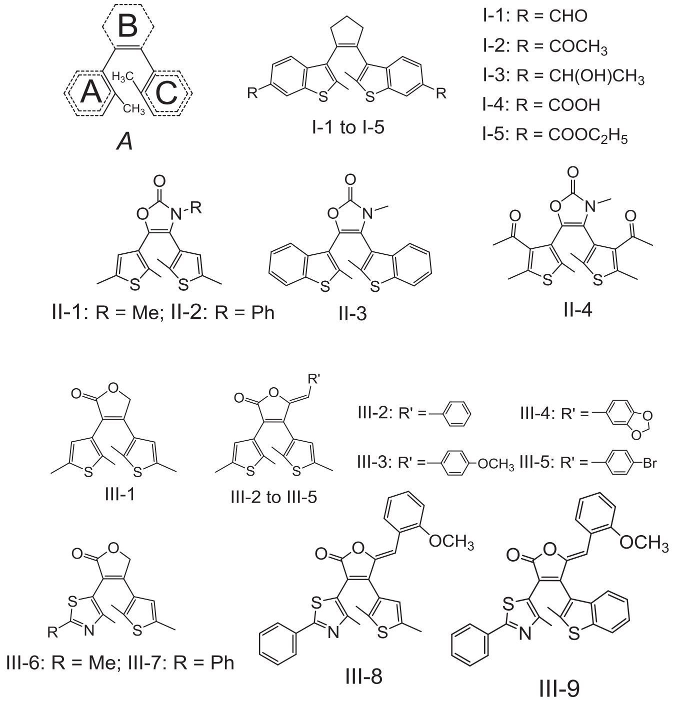

Fig. 1. Generic *A* and detailed (I-1 to III-9) structures of the 18 diarylethenes. Cycles A are variously substituted benzothiophenes, thiophenes or thiazoles. Cycle B are either cyclopentenic, oxazolinic or lactonic with or without exocyclic double bond. Cycle C are substituted benzothiophenes or thiophenes.

assumes that the excited state produced by the photon absorption leads to the photochemical reaction. Indeed, on small DAE's, calculations have shown a very efficient barrierless evolution of the excited state toward the ring closure [8]. This interpretation was also used for the ring opening reaction, usually quite inefficient compared to the ring closure [9]. However the presence of substituents or larger conjugated moieties can result in a complex arrangement of the molecule's various excited states resulting in overlap of several transitions [10].

Quantum yields measurement in diarylethene series has taken a rather long period to be performed extensively [11]. The majority were determined for the classical perfluorocyclopentene derivatives of diarylethenes. For instance, the 2000 Irie's review [2a] only mentions the quantitative values for 11 diarylethene compounds. Only very few supplementary values are provided in the next 2004 He Tian's review [2c]. As most of the measured photocyclization quantum yields were restricted at less than 50% [12], it was commonly considered that the two parallel and anti-parallel conformations of the open form were in equal concentrations. Nowadays, thanks to the very active Japanese and Chinese teams, a lot of new compounds have been quantified [13], photocyclization quantum yields higher than 50% were claimed for asymmetric derivatives [14] as well as for symmetric structures [15]. More recently, even higher photocyclization quantum yields have been reported thanks to some structural improvements. Two main ways have been explored either by keeping the perfluorocyclopentene center cycle and adding chlorine atoms on thiophenic terminal phenyl groups [16] or by exploiting hydrogen bonding when replacing thiophenes by thiazole derivatives [17] and central cyclopentene by various other cycles or heterocycles such as indenones [18], coumarine [19], phenylthiazole, azaindole and benzothiophene [20]. The result of such structural changes is a better accumulation of the photo-active anti-parallel conformation. Although no clearcut rules were established until now, it is suggested that these high yields could be the result of the influence of the nature and the position of the various substituents [21]. Other types of diarylethenes, in particularly perhydrocyclopentene [22] siloles and phospholes [23] and dithiolthiones and dithiolones [24] derivatives have been also synthesized in order to check the influence of a structural change on the quantum yields of photochromic transformations. High quantum yields (>50%) were also reported for the photobleaching reaction too.

By portraying a large panel of structural changes, this work tries to meet the recurrent challenge for new molecules with highly efficient photo-transformations. Therefore, this paper is devoted to the determination of quantum yields for photocoloration and photobleaching processes of 18 thermally irreversible diarylethenes derivatives obtained by changing the bridging ring that stabilizes the central ethenic double bond in the *cis* configuration: from perhydrocyclopentene [25], oxazolone [26] and lactones [27] and the lateral aryl moieties from thiophene to benzothiophene and thiazoles.

2. Experimental section

Solvents of the highest purity grade (toluene (Rectapur) and acetonitrile (H.P.L.C.) were used without further purification. They were not degassed. Synthesis of cyclopentenic compounds of the I–N series ($N = 1$ to 5) has been described in [25], oxazolones of the II-N series ($N = 1$ to 4) in [26a] and lactones of the III-N series ($N = 1$ to 9) in [27]. All experiments were carried out within the 1×10^{-5} to 5×10^{-5} M concentration range. Spectral and kinetic characteristics were measured on a diode array spectrophotometer 8452A (Hewlett Packard).

All of the experiments and manipulations were performed protecting the solutions against room light. 2.4 mL of solution was irradiated in a stirred and thermostated (25 °C) 1 cm × 1 cm quartz cuvette by filtered light from a 250 W high pressure mercury arc selecting lines at wavelengths 313, 365, 405, 436 and 546 nm. Two irradiation wavelengths are used successively, a shorter (λ_1) to obtain a photocoloration and a longer (λ_2) to bleach the obtained colored solution. Quantum yields of photo-cyclization and photocycloreversion and molar absorption coefficient of the closed forms were determined simultaneously from Absorbance *vs* time curves recorded under continuous monochromatic irradiation using a kinetic modeling method [28a,b]. In order to assure the quantum yield values, we used Parker's ferrioxalate as chemical actinometer in an identical geometry and a calibrated home-made silicon photodiode photometer to determine the intensity of the light used for photochromic reactions. The accuracy for the determination of the quantum yields and molar absorption coefficients was estimated at ±10%. (see Supplementary Information part for further details).

3. Results and discussion

The generic and detailed structures of the 18 diarylethenes are displayed on Fig. 1. The set has been divided into three main groups depending on the nature of the central ring B. Compounds I are cyclopentenic (I-1 to I-5), II oxazolinic (II-1 to II-4) and III lactonic (III-1 to III-9). Among them, 10 bring at less a thiophenic aryl group

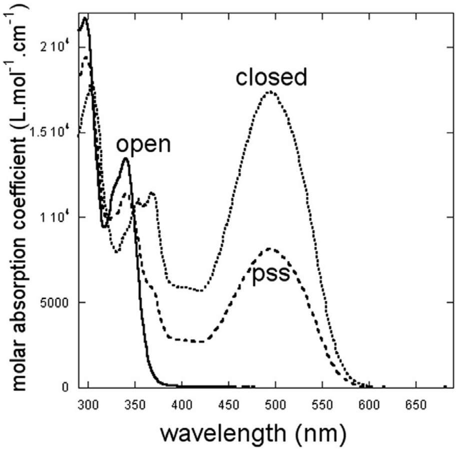

Fig. 2. Spectral changes of compound I-1 in toluene upon irradiation with 313 nm UV light at room temperature: pss: photosteady state reached after 600 s of irradiation; closed: recalculated spectrum of the closed form plotted in molar absorption coefficient units.

Table 1

Spectrocopic data of the open (o) and closed (c) forms of the various products in toluene (t) and acetonitrile (a) solution. sh: shoulder. The reported values refer to the lower energy absorption bands.

Product	λ(nm)o(t)	ε(cm^{-1} M^{-1}) o(t)	λ(nm)c(t)	λ(nm)o(a)	ε(cm^{-1} M^{-1}) o(a)	λ(nm)c(a)
I-1	340	13500	490			
I-2	334	17000	486	334	12000	486
I-3	sh (305)		446	sh (300)		440
I-4				312	5900	466
I-5	354	12300	516	354	14000	512
II-1				287	12400	452
II-2				284	11500	452
II-3				300	10000	444
II-4				sh (243)		447
III-1	305	9500	510			
III-2	358	25500	548			
III-3	386	25000	546			
III-4	394	26000	550			
III-5				352	27000	543
III-6	316	12000	460			
III-7	342	16000	465			
III-8	405	33000	504	396	27000	500
III-9	412	32000	506	400	38000	490

(II-1, II-2, III-1, III-2, III-3, III-4, III-5, III-6, III-7 and III-8), while there is a benzothiophene lateral ring in 7 compounds (I-1, I-2, I-3, I-4, I-5, II-3 and III-9). Substituted thiazole aryl groups are encountered in 4 molecules (III-6, III-7, III-8 and III-9).

To examine the substituent effect on photochromic reactivity we measured photo-cyclization and photo-cycloreversion quantum yields of the various diarylethenes compounds.

Upon irradiation with actinic light, in toluene and acetonitrile (depending on the compound and their solubilities) the color of the solution turned to blue and green. The electronic absorption spectra of both isomers of the 18 diarylethenes have been recorded before and after UV irradiation. Fig. 2 shows the absorption spectral changes of I-1 in toluene. The color formation is attributed to the production of the closed-ring isomer. Isosbestic point at 352 nm indicates a two-component photochromic reaction between the open and the closed form. This means that any secondary photoreaction cannot be practically observed during the course of the photo-cyclisation.

A simple kinetic analysis of the photokinetics will provide information for the determination of the quantum yields. The method for the simultaneous determination of ring-closure and ring-opening quantum yields and molar absorption coefficient of the closed-ring isomer is based on the numerical analysis of the kinetics under continuous monochromatic irradiation [28]. Assuming a two-isomer scheme without any photodegradation, the kinetics are described by Eqs. (1) and (2):

The color-forming kinetics is described by Eq. (1):

$$\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -\phi_{\mathrm{AB}}\varepsilon'_A I_0 F[\mathrm{A}] + \phi_{\mathrm{BA}}\varepsilon'_{\mathrm{B}} I_0 F[\mathrm{B}] \qquad (1)$$

and the mass-balance by Eq. (2):

$$[\mathrm{A}]_0 + [\mathrm{B}]_0 = [\mathrm{A}] + [\mathrm{B}] \qquad (2)$$

It is highly convenient to monitor the color evolution by UV/visible spectroscopy, therefore a third equation is given by the Beer's law:

$$\mathrm{Abs}^{\lambda} = \left(\varepsilon^{\lambda}_A[\mathrm{A}] + \varepsilon^{\lambda}_{\mathrm{B}}[\mathrm{B}]\right)^{*} l_{\mathrm{obs}} \qquad (3)$$

(See Supplementary Info Part for more details).

The significance of the various symbols is displayed in Table 2.

The photochemical behavior of the open-ring and closed-ring isomers can be studied quantitatively by following the changes in the absorption spectra. Typically, the determination of the ring-closure and ring-opening quantum yields needs the use of two different irradiation wavelengths. The first wavelength must be selected in order to promote the ring-closure, while the second, the ring-opening. However, due to spectral overlap especially in the UV region it is practically impossible to perform a photoisomerisation without making the reverse at the same time. This situation has been sometimes surmounted by separating the closed-ring isomer by HPLC [29], but it is now easily manageable using only UV/visible spectroscopy thanks to numerical techniques that could be used in photokinetic analysis [30]. Assuming that the spectrum of the open form has been measured independently (see Table 1), there are five unknown in the problem, namely ϕ_{AB}, ϕ_{BA}, $\varepsilon'_{\mathrm{B}}$, $\varepsilon''_{\mathrm{B}}$ (for the 2nd irradiation wavelength) and $\varepsilon^{\lambda}_{\mathrm{B}}$ at $\lambda_{\max}$. Fig. 3 shows that monitoring two wavelengths for each photoisomerisation run is sufficient to solve the problem. Each absorbance *vs* time kinetic curve exhibits two independent parameters: its apparent rate constant of

Table 2

List of symbols used in the photokinetic analysis of the diarylethene photochromism under continuous monochromatic irradiation. (a): when the used two wavelengths for ring-opening and ring-closure are close, the quantum yields are assumed to be wavelength independent. (b): must be determined by independent actinometry in the same geometry assuming that the solution perfectly stirred, (c): take into account the distribution of the light (absorbed by A, by B or not absorbed), (d): must be monitored continuously to follow the possible variation of F, (e): irradiation wavelength λ' and $\lambda_{\max}$ of the closed form are recommended.

Symbols	Significance	Comment or unit
t	Time	s
[A], [B]	Time dependent concentrations	mol L^{-1}
$[\mathrm{A}]_0$, $[\mathrm{B}]_0$	Initial concentrations	mol L^{-1}
ϕ_{AB}, ϕ_{BA}	Quantum yields of A → B, B → A	(a)
ε'_A, $\varepsilon'_{\mathrm{B}}$	Molar extinction coeff. of A, B at the irradiation wavelength	L mol^{-1} cm^{-1}
ε^{λ}_A, $\varepsilon^{\lambda}_{\mathrm{B}}$	Molar extinction coeff. of A, B at any wavelength λ	L mol^{-1} cm^{-1}
I_0	Rate of monochromatic irradiation	mol L^{-1} s^{-1} (b)
F	Photokinetic factor, $F = (1{-}10^{-\mathrm{Abs}'})/\mathrm{Abs}'$	(c)
Abs′	Absorbance of the solution at the irradiation wavelength	(d)
Abs^{λ}	Absorbance of the solution at any wavelength λ	(e)
l_{obs}	Optical path of the monitoring beam for observation	cm

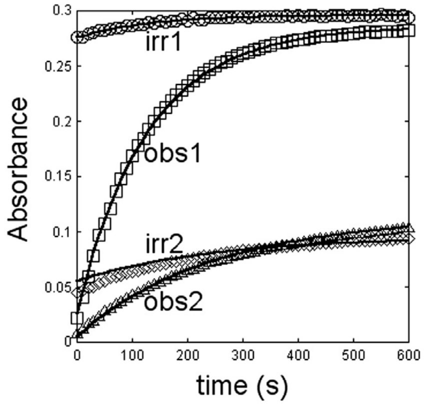

Fig. 3. Absorbance *vs* time photokinetic curves recorded under continuous monochromatic irradiation of compound I-1 in toluene solution (2.6×10^{-5} mol L^{-1}). irr1: evolution of the absorbance recorded at the first irradiation wavelength ($\lambda_1 = 313$ nm); obs1: evolution of the absorbance at the λ_{max} of the closed form during the irradiation at λ_1; irr2: evolution at the second irradiation wavelength ($\lambda_2 = 365$ nm); obs2: evolution at the λ_{max} during the irradiation at λ_2. Dots: experimental; solid lines: fitting by the model (Eqs (1)–(3)) with $\phi_{AB} = 0.80$, $\phi_{BA} = 0.40$, $\varepsilon_A^1 = 10600$ (fixed) $\varepsilon_A^2 = 1650$ (fixed), $\varepsilon_B^1 = 12300$, $\varepsilon_B^2 = 10400$, $\varepsilon_B^{max} = 17500$ L $mol^{-1}cm^{-1}$.

evolution which is roughly related to $(\phi_{AB}\varepsilon'_A + \phi_{BA}\varepsilon'_B)I_0$ and its amplitude at the photo-steady state which linked to $(\phi_{AB}\varepsilon'_A/\phi_{BA}\varepsilon'_B)\varepsilon_B^\lambda$. For a given irradiation wavelength, the two apparent rate constant are identical but the two amplitudes are different. Finally, six independent parameters are provided, they are sufficient to solve the photokinetic problem. The slight redundancy (six equations for five unknown) helps to overcome the deleterious effect of noisy data. Fig. 3 shows a representative example of such kinetic analysis.

The photocyclization (ϕ_{AB}) and cycloreversion (ϕ_{BA}) quantum yields and the molar absorption coefficients (ε_B) of the colored forms of the photoreactive molecules in toluene (t) and acetonitrile (a) are reported in Table 3.

Compounds I-2, I-3, I-5, III-8 and III-9 have been investigated both in toluene and acetonitrile solution. While cyclopentenic derivatives show only a negligible solvent effect, a slight hypsochromic shift is witnesed with lactonic compounds by increasing the solvent polarity. This effect is likely to be due to a higher stabilization of the ground-state of both open and closed forms by acetonitrile solvation. It appears that the highest energies (lower absorption wavelengths around 288 nm) are for the oxazolones open-ring compounds II-1 to II-4 while the lowest (higher wavelengths around 405 nm) are found in exocyclic lactone products III-4, III-8 and III-9. Lactonic III-1, III-2, III-6 and III-7 and cyclopentenic compounds (I-1, I-2, I-4 and I-5) lie in the intermediate range (from 300 to 370 nm). Compound I-3 deserves a special attention. Among the cyclopentenic compounds, this is the only one without a carbonyl subsituent on the benzothiophenic ring and its open-ring isomer spectrum displays only a shoulder (no maximum) around 305 nm (see supp. info part). Because, most of the compounds were not soluble in both solvent the evaluation was carried-out either in toluene or in acetonitrile. An easy way of comparison the various series is to consider the lower energy absorption bands of open and closed form and to plot in a diagram λ_{max} (closed) *vs* λ_{max} (open) (Fig. 4). Without any sophisticated statistical analysis, it is possible to discriminate five main domains showing that, as expected, molecules with similar structures behave similarly.

Looking upon the line “a”, it appears in the upper part (*i.e.* above line “a”) lie all the lactonic compounds bearing thiophenic side rings (III-1 to 4). On the other side, (*i.e.* under line “a”) are situated all the lactonic compounds bearing a thiazolinic side ring (III-6 to 9). The consideration of the parallel lines “b” or “c” helps to visualize on one side the lactonic exocyclic (III-2 to 4, III-8 and III-9) in the upper part and on the other side, the non-exocyclic (III-1, III-6 and III-7) in the lower part of the diagram. Finally, it is worth to mention the cyclopentenic group cluster in the central part of the plot. A similar chart-diagram has been drawn for compounds measured in acetonitrile solution (see supp. info. part).

In the same way, ε *vs* ε diagram (Fig. 5) provides also some interesting insight into this population of diarylethenes.

Considering line “b”, it appears clearly that the cyclopentenic diarylethenes are positioned in the upper part of the diagram. All the lactonic products lie on the other side. Line “a” discriminates these products: the lactonic exocyclic on the right and the non-exocyclic on the left. In both domain, the thiazolinic compounds: III-6 and 7, on the left and III-8 and 9, on the right are slightly departed. The closest data points (III-2, III-3 and III-4) correspond to the three lactonic exocyclic diaryethenes differing only by the remote phenyl substitution: H in III-2, OMe in III-3 and dioxalane in III-4. This cluster is remarkable because it must be borne in mind that the closed form epsilon values have been determined from the kinetic analysis without chemical isolation of the closed form. The lower epsilon for the open form is for the non-substituited lactonic compound III-1 bearing a methyl thiazole side-ring. It is amazing to

Table 3

Quantum yields of ring-closure and ring-opening and molar absortion coeffients of the lowest energy band of the closed-ring isomer of the various diaryethenes in toluene (t) and acetonitrile (a) solution. λ_1, λ_2: irradiation wavelengths; color: % maximum of the closed form at the end of the photocoloration under λ_1 continuous irradiation. In most cases the photosteady state (PSS) has not yet been reached.

n°	λ_1	ϕ_{AB}(t)	λ_2	ϕ_{BA}(t)	ε_B(t)	Color	λ_1	ϕ_{AB}(a)	λ_2	ϕ_{BA}(a)	ε_B(a)	Color
I-1	313	0.80	365	0.40	17500	54						
I-2	313	0.90	436	0.19	15000	83	313		405			
I-3	313	0.75	436	0.40	9500	48	313	0.19	436	0.50	12500	12
I-4							313	0.35	436	0.80	8500	43
I-5	313	0.70	546	0.20	18000	85	313	0.25	546	0.20	12000	43
II-1							313	0.50	405	0.65	6000	25
II-2							313	0.86	405	0.58	2300	
II-3							313	0.65	405	0.47	12400	27
II-4							313	0.79	405	0.51	11700	6
III-1	313	0.60	365	0.70	6500	62						
III-2	365	0.32	405	0.001	4750	75						
III-3	365	0.33	405	0.30	4350	64						
III-4	365	0.31	405	0.13	3700	77						
III-6	313	0.66	405	0.67	4300	41						
III-7	365	0.41	405	0.85	5400	62						
III-8	405	0.12	436	3e-4	4200	26	405	0.17	436	5e-4	3600	40
III-9	405	0.19	436	3e-6	1200	90	405	0.19	436	0.22	1000	67

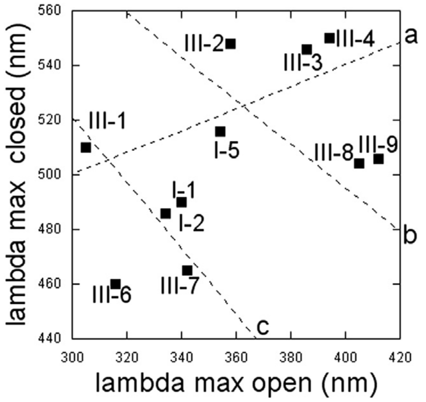

Fig. 4. λ_{max} (closed) *vs* λ_{max} (open) diagram of 11 compounds measured in toluene solution. The manually drawn eye-catching dashed straight lines discriminate five domains where similar compounds are gathered.

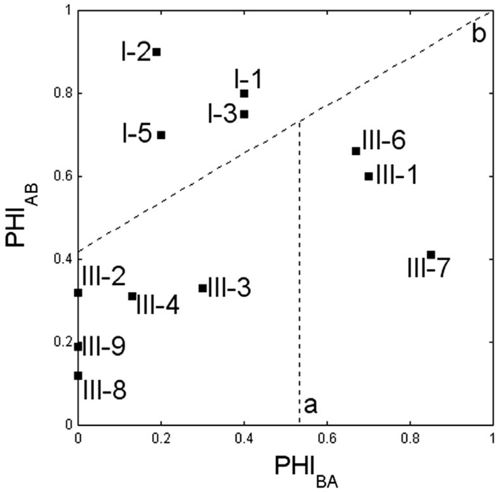

Fig. 6. Φ_{AB} *vs* Φ_{BA} diagram of the diarylethene compounds in toluene.

note that the lower epsilon for the closed form is for the compound III-9 which bears a benzothiophene side-ring while its homologue III-8, where a thiophene replaces the benzothiophene, is much more absorbing. A similar effect is noticed on Table 1: compound II-1 (with thiophenes) is more absorbing than II-3 (with benzothiophenes). Such diagram has been also plotted in acetonitrile where lactonic, oxazolinic and cyclopentenic compounds are easily discriminated. A special mention deserves to be pointed-out for the oxazolinic compound II-3 bearing benzothiophenic side rings: it is departed from its thiophenic homologues in both *λ vs λ* and *ε vs ε* diagrams (see Supp Info Part).

Table 3 summarizes the photochemical quantum yield of cyclization and cycloreversion reactions of the various compounds. The higher number of data points with $\Phi_{AB} > \Phi_{BA}$ can be interpreted by considering that the ring closure is almost barrierless, while there is an activation energy barrier in the ring opening [31]. However, the most interesting features are related to the extreme values (higher or lower quantum yields). About the photocyclisation quantum yields, the top value has been found at 0.90 for compound I-2 in toluene. Such a value is among the highest ever measured recently. For instance, only very few diarylethene photocyclisation quantum yields higher than 0.8 have been described [20a,b,c,7,18,30]. The high quantum yield of I-2 implies that this compound is almost completely present in toluene solution as its antiparallel conformer, whose photoreaction is very efficient. Relatively high values (*i.e.* ≥0.70) have been also found for homologous compounds I-1, I-3 and I-5. High photocyclisation quantum yield in acetonitrile has also been measured for II-2 and II-4. Effect of solvent polarity on the diarylethenes I-3 and I-5 photocyclisation quantum yields show a clear-cut decrease from toluene to acetonitrile solution. A reasonable interpretation of this solvent effect is the participation of a stongly solvated twisted intramolecular charge transfer state (TICT). In these conditions, the expected photoreactive antiparallel conformation is partly trapped into a photo-inactive twisted-twisted antiparallel conformation in the TICT leading to a decrease of the photocyclization quantum yields [32]. Other interesting characteristics can be found from the examination of the photocycloreversion quantum yields. Top values (>0.6) have been observed for the thiophene substituted lactonic compounds III-1 and III-7 in toluene solution. For these compounds, the photocycloreversion quantum yield is higher than the cyclization [33]. The same is true for I-3 and II-1 in acetonitrile. On the other side, low photo-cyclization and cycloreversion quantum yields have been found for lactone exocyclic compounds III-2, III-8 and III-9. For such compounds, it is likely that the presence of extra π-electrons in the central unit was responsible for some deactivation [34]. Low cycloreversion quantum yields have also been published in diarylethenes with methoxy substituent not conjugated with the π-system in the closed-ring isomer [35]. The Φ_{AB} *vs* Φ_{BA} diagram shown on Fig. 6 illustrates the presence of various clusters. The effect of an exocyclic moiety on the lactonic compound is striking if we compare the [III-2 to 4, III-8 and III-9] and [III-1, III-6 and III-7] groups (Fig. 6).

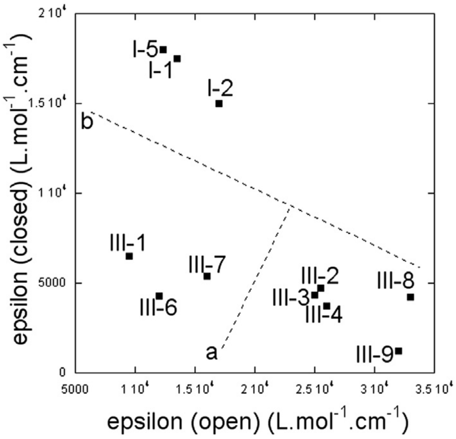

Fig. 5. ε_{max} (closed) *vs* ε_{max} (open) diagram of the diarylethene compounds in toluene solution.

However, beyond the clustering effect, it is also interesting to remark some compensation giving rise to close properties (for instance, very low photo-reversion quantum yield) for relatively different structures such as compounds III-2 and III-8 and III-9. However, comparing the three diagrams on Figs. 3–5, it appears that, on one side compounds I-2 and I-5 from the cyclopentenic series and, on the other side compounds III-3 and III-4 from the lactonic exocyclic groups are always together. In acetonitrile solution, closely related oxazolone compounds II-1 and II-2 come also together. This result is a brilliant confirmation of the accuracy of our investigations as it is expected that the photochromic behavior of the structurally closest compounds must be the same.

4. Conclusion

For the first time, the quantitative photochromic properties of a set of 18 diarylethenes have been investigated in parallel using a kinetic analysis based on classical UV/visible spectroscopic measurements. The photo-cyclisation and cycloreversion quantum yields together with the molar absorption coefficient of the non-isolated closed form have been determined simultaneously thanks to an original kinetic modeling approach. Depending on the nature of the central ring, the diarylethene set can be divided into three main groups: cyclopentenic, oxazolinic and lactonic. Diagrams obtained by plotting λ_A *vs* λ_B, ε_A *vs* ε_B or Φ_{AB} *vs* Φ_{BA} help to visualize in a striking manner all the structural effects. The three main groups are easily individualized. Compounds with similar structures such as III-2, III-3 and III-4 remain clustered on all of the three diagrams, thus introducing a non trivial correlation between the optical gaps, the extinction coefficients and the photochromic quantum yields. For cyclopentenic compounds I-3 and I-5, the quantum yield of photo-cyclisation decreases with solvent polarity. By providing a quantitative assessment of the spectroscopic and photochromic properties of a large set of diarylethenes compounds, these experimental results will be useful for a better understanding of the photochromism of diarylethenes both on the fundamental and more applied point of view.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.02.013.

References

[1] (a) In: Crano JC, Guglielmetti RJ, editors. Organic photochromic and thermochromic compounds. Photochromic families, vol. 1. Springer; 1999, ISBN: 978-1-441-93296-9; 1999. Vol 2: Physicochemical Studies, Biological Applications, and Thermochromism, ISBN: 978-0-306-45883-5;
(b) In: Dürr H, Bouas-Laurent H, editors. Photochromism: molecules and systems. Elsevier Science; 2003, 978-0-080-53883-9;
(c) In: Irie M, Yokoyama Y, Seki T, editors. New frontier in photochromism. Japan: Springer; 2013. ISBN 978-4-431-54250-2.

[2] (a) Irie M. Diarylethenes for memories and switches. Chem Rev 2000;100:1685–716;
(b) Kobatake S, Irie M. Photochromism. Ann Rep Prog Chem Sect 2003;199:277–313;
(c) Tian H, Yang S. Recent progresses on diarylethene based photochromic switches. Chem Soc Rev 2004;33:85–97;
(d) Matsuda K, Irie M. Diarylethene as a photoswitching unit. J Photochem Photobiol C Photochem Rev 2004;5:169–82;
(e) Tian H, Feng Y. Next step of photochromic switches? J Mater Chem 2008;18:1617–22;
(f) Shirinian VZ, Lonshakov DV, Lvov G, Krayushkin MM. Fluorescent photochromes of diarylethene series: synthesis and properties. Russ Chem Rev 2013;82:511–37.

[3] (a) Barachevsky VA, Kobeleva OI, Valova TM, Ait AO, Dunaev AA, Gorelik AM, Krayushkin MM, Levchenko KS, Yarovenko VN, Kiyko VV, Grebennikov EP. Photochromic and irreversible photo-fluorescent organic materials for 3D bitwise optical memory. Opt Mem Neural Networks (Information Opt 2010;19:187–95;
(b) Barachevsky VA, Krayushkin MM, Kyiko VV, Grebennikov EP. Light-sensitive organic recording media for 3D optical memory. Phys Status Solidi C 2011;8:2841–5.

[4] Nakamura S, Irie M. Thermally irreversible photochromic systems. A theoretical study. J Org Chem 1988;53:6136–8.

[5] Liu G, Pu S, Wang X. Photochromism of new 3,5-position hybrid diarylethene derivatives bearing both thiophene and thiazole moieties. Tetrahedron 2010;66:8862–71.

[6] (a) Iwata S, Ishihara Y, Qian CP, Tanaka K. Thermal stability of photochromic bis ((trifluoro-methy1) thiazoly1) ethene derivatives. J Org Chem 1992;57:3726–7;
(b) Uchida K, Ishikawa T, Takeshita M, Irie M. Thermally irreversible photochromic systems. Reversible photocyclization of 1,2-bis(thiazolyl) perfluorocyclopentenes. Tetrahedron 1998;54:6627–38;
(c) Uchida K, Matsuoka T, Kobatake S, Yamaguchi T, Irie M. Substituent effect on the photochromic reactivity of bis (2-thienyl) perfluorocyclopentenes. Tetrahedron 2001;57:4559–65;
(d) Norsten TB, Peters A, McDonald R, Wang M, Branda NR. Reversible [7]-thiahelicene formation using a 1,2-dithienyl-cyclopentene photochrome. J Am Chem Soc 2001;123:7447–8;
(e) Fukaminato T, Tanaka M, Kuroki L, Irie M. Invisible photochromism of diarylethene derivatives. Chem Commun; 2008:3924–6;
(f) Saitoh M, Fukaminato T, Irie M. Photochromism of a diarylethene derivative in aqueous solution capping with a water-soluble nano-cavitand. J Photochem Photobiol A Chem 2009;207:28–31;
(g) Tatsumi Y, Kitai J, Uchida W, Ogata K, Nakamura S, Uchida K. Photochromism of 1,2-bis(2-thienyl)perfluorocyclopentene derivatives: substituent effect on the reactive carbon atoms. J Phys Chem A 2012;116:10973–9;
(h) Yuan K, Boixel J, Le Bozec H, Boucekkine A, Doucet H, Guerchais V, Jacquemin D. Perfluorocyclohexene bridges in inverse diarylethenes: synthesis through Pd-catalysed C–H bond activation, experimental and theoretical studies on their photoreactivity. Chem Commun 2013;49:7896–8.

[7] Ribeiro Santos A, Ballardini R, Belser P, Gandolfi MT, Iyer V, Moggi L. Photochemical investigation of a photochromic diarylethene compound that can be used as a wide range actinometer. Photochem Photobiol Sci 2009;8:1734–42.

[8] Boggio-Pasqua M, Ravaglia M, Bearpark MJ, Garavelli M, Robb MA. Can diarylethene photochromism be explained by a reaction path alone? A CASSCF study with model MMVB dynamics. J Phys Chem A 2003;107:11139–52.

[9] Guillaumont D, Kobayashi T, Kanda K, Miyasaka H, Uchida K, Kobatake S, Shibata K, Nakamura S, Irie M. An ab initio MO study of the photochromic reaction of dithienylethenes. J Phys Chem A 2002;106:7222–7.

[10] Bens AT, Frewert D, Kodatis K, Kryschi C, Martin HD, Trommsdorff HP. Coupling of chromophores: carotenoids and photoactive diarylethenes-photoreactivity versus radiationless deactivation. Eur J Org Chem; 1998:2333–8.

[11] Barachevsky VA, Strokach YP, Puankov YA, Krayushkin MM. Thermally irreversible organic photochromic compounds for optical memory. J Phys Org Chem 2007;20:1007–20.

[12] (a) Irie M, Sakemura K, Okinaka M, Uchida K. Photochromism of dithienylethenes with electron-donating substituents. J Org Chem 1995;60:8305–9;
(b) Jeong YC, Yang SI, Kim E, Ahn KH. Development of highly fluorescent photochromic material with high fatigue resistance. Tetrahedron 2006;62:5855–61;
(c) Zheng C, Pu S, Xu J, Luo M, Huang D, Shen L. Synthesis and the effect of alkyl chain length on optoelectronic properties of diarylethene derivatives. Tetrahedron 2007;63:5437–49;
(d) Jeong YC, Yan JP, Kim Y, Kim E, Yang SI, Ahn KH. Characterization and photophysical properties of sulfur-oxidized diarylethenes. Tetrahedron 2007;63:3173–82;
(e) Pu S, Zheng C, Le Z, Liu G, Fan C. Substituent effects on the properties of photochromic diarylethenes. Tetrahedron 2008;64:2576–85;
(f) Jeong YC, Park DG, Lee IS, Yang SI, Ahn KH. Highly fluorescent photochromic diarylethene with an excellent fatigue property. J Mater Chem 2009;19:97–103;
(g) Pu S, Li M, Fan C, Liu G, Shen L. Synthesis and the optoelectronic properties of diarylethene derivatives having benzothiophene and n-alkyl thiophene units. J Mol Struct 2009;919:100–11;
(h) Pu S, Zhu C, Rao Y, Liu G, Wei H. Photochromism of 1,2-bis(2-n-alkyl-5-formyl-3-thienyl)perfluorocyclopentene derivatives. J Mol Struct 2009;921:89–100;
(i) Kuehn S, Friede S, Zastrow M, Gahl C, Rueck-Braun K, Elsaesser T. Photophysics of closed- and open-ring isomers of a diarylethene with a carboxylic anchor group. Chem Phys Lett 2012;542:94–8.

[13] (a) Pu S, Liu W, Liu G. The photochromism of unsymmetrical diarylethene isomers with an electron-withdrawing cyano substituent. Dye Pigm 2010;87:1–9;
(b) Taguchi M, Nakagawa T, Nakashima T, Kawai T. Photochromic and fluorescence switching properties of oxidized triangle terarylenes in solution and in amorphous solid states. J Mater Chem 2011;21:17425–32;
(c) Pu S, Wang R, Liu G, Liu W, Cui S, Yan P. Photochromism of new unsymmetrical diarylethene derivatives bearing both benzofuran and thiophene moieties. Dyes Pigm 2012;94:195–206;
(d) Zheng C, Pu S, Pang Z, Chen B, Liu G, Dai Y. Syntheses and photochromism of new isomeric diarylethenes bearing an indole moiety. Dyes Pigm 2013;98:565–74;
(e) Wang R, Pu S, Liu G, Chen B. Photochromic diarylethenes with a naphthalene moiety: synthesis, photochromism, and substitution effects. Tetrahedron 2013;69:5537–44;
(f) Shoji H, Kobatake S. Thermal bleaching reactions of photochromic diarylethenes with thiophene-S,S-dioxide for a light-starting irreversible thermosensor. Chem Commun 2013;49:2362–4;
(g) Liu H, Pu S, Liu G, Chen B. New photochromic diarylethenes with a pyrimidine moiety. Tetrahedron Lett 2013;54:646–50;
(h) Liu G, Pu S, Chen B. The effect of the fluorine atom position upon isomeric photochromic diarylethenes bearing a pyrrole unit. J Photochem Photobiol A Chem 2013;263:41–9;
(i) Liu HH, Chen Y. Synthesis and photophysical properties of thiolactone derivatives. Tetrahedron 2013;69:1872–6;
(j) Ishibashi Y, Umesato T, Kobatake S, Irie M, Miyasaka H. Femtosecond laser photolysis studies on temperature dependence of cyclization and cycloreversion reactions of a photochromic diarylethene derivative. J Phys Chem C 2012;116:4862–9.

[14] (a) Pu S, Yan L, Wen Z, Liu G, Shen L. Synthesis and chlorine atom position effect on the properties of unsymmetrical photochromic diarylethenes. J Photochem Photobiol A 2008;196:84–93;
(b) Pu S, Fan C, Miao W, Liu G. New photochromic diarylethenes with a six-membered aryl unit. Tetrahedron 2008;64:9464–70;

(c) Liu W, Pu S, Liu G. Synthesis and optoelectronic properties of unsymmetrical isomeric diarylethene derivatives having a fluorine atom. J Mol Struct 2009;936:29–36;
(d) Pu S, Fan C, Miao W, Liu G. The effect of substituent position upon unsymmetrical isomeric diarylethenes bearing a methoxy group. Dyes Pigm 2010;84:25–35;
(e) Liu G, Pu S, Wang R. Photochromism of asymmetrical diarylethenes with a pyrrole unit: effects of aromatic stabilization energies of aryl rings. Org Lett 2013;15:980–3;
(f) Pu S, Zheng C, Sun Q, Liu G, Fan C. Enhancement of cyclization quantum yields of perfluorodiarylethenes via weak intramolecular interactions. Chem Commun 2013;49:8036–8.

[15] (a) Morimitsu K, Kobatake S, Irie M. Large geometrical structure changes of photochromic diarylethenes upon photoirradiation. Tetrahedron 2004;45:1155–8;
(b) Takami S, Irie M. Photochromic properties of diarylethenes having 2,4-diphenylphenyl substituents in the amorphous and PMMA films. J Photochem Photobiol A 2007;187:202–8;
(c) Yamaguchi T, Takami S, Irie M. Photochromic properties of 1,2-bis (6-substitute-2-methyl-1-benzofuran-3-yl) ethene derivatives. J Photochem Photobiol A 2008;193:146–52.

[16] Fan C, Pu S, Liu G, Yang T. Substituent position effect on the properties of isomeric photochromic diarylethenes bearing chlorine atoms. J Photochem Photobiol A 2008;194:333–43.

[17] Giraud M, Leaustic A, Charlot MF, Yu P, Cesario M, Philouze C, Pansu R, Nakatani K, Ishow E. Synthesis and photochromism of two new 1,2-bis(thiazolyl) perfluorocyclopentenes with chelating sites. New J Chem 2005;29:439–46.

[18] Morinaka K, Ubukata T, Yokoyama Y. Structurally versatile novel photochromic bisarylindenone and its acetal: aAchievement of large cyclization quantum yield. Org Lett 2009;11:3890–3.

[19] Suzuki K, Ubukata T, Yokoyama Y. Dual-mode fluorescence switching of photochromic bisthiazolylcoumarin. Chem Commun 2012;48:765–7.

[20] (a) Nakashima T, Fujii R, Kawai T. Regulation of folding and photochromic reactivity of terarylenes through a host–guest interaction. Chem Eur J 2011;17:10951–7;
(b) Fukumoto S, Nakashima T, Kawai T. Intramolecular hydrogen bonding in a triangular dithiazolyl-azaindole for efficient photoreactivity in polar and nonpolar solvents. Eur J Org Chem; 2011:5047–53;
(c) Fukumoto S, Nakashima T, Kawai T. Photon-quantitative reaction of a dithiazolylarylene in solution. Angew Chem Int Ed 2011;50:1565–8.

[21] (a) Fan C, Pu S, Liu G, Yang T. Substituent position effect on the properties of new unsymmetrical isomeric diarylethenes having a chlorine atom. J Photochem Photobiol A 2008;197:415–25;
(b) Yin J, Lin Y, Cao X, Yui GA, Tu H, Liu SH. The synthesis and photochromic properties of two bis(phosphine) ligands based on dithienylethene backbone and their oxides, sulfures and selenides. Dyes Pigm 2009;81:152–5.

[22] (a) Hu H, Zhu M, Meng X, Zhang Z, Wie K, Guo Q. Optical switching and fluorescence modulation properties of photochromic dithienylethene derivatives. J Photochem Photobiol A 2007;189:307–13;
(b) Hania PR, Pugzlys A, Lucas LN, de Jong JJD, Feringa BL, van Esch JH, Jonkman HT, Duppen K. Ring closure dynamics of BTE-based photochromic switches: perfluoro- versus perhydro-cyclopentene derivatives. J Phys Chem A 2005;109:9437–42.

[23] Cipolloni M, Ortica F, El Yahyaoui A, Heynderickx A, Moustrou C, Favaro G. New photochromic symmetrical and unsymmetrical bis(heteroaryl)maleimides: a spectrokinetic study. Chem Phys 2009;358:258–64.

[24] (a) Favaro G, Mazzucato U, Ortica F, Smimmo P. Thermal reversibility and bistability in photochromic diarylethenes. Inorg Chim Acta 2007;360:995–9;
(b) Ortica F, Smimmo P, Zuccaccia C, Mazzucato U, Favaro G, Impagnatiello N, Heynderickx A, Moustrou C. Photobehaviour of diarylethenes with thiophenes as aryl groups and dithiole-2-thione and dithiole-2-one at the ethenic bond. J Photochem Photobiol A 2007;88:90–7.

[25] Krayushkin MM, Yarovenko VN, Khristoforova LV, Shashkov AS, Grebennikov EP, Devyatkov AG, Adamov GE, Levchenko KS, Shmelin PS, Barachevskii VA, Valova TM, Kobeleva OI. The synthesis and study of multilayer polymer structures based on 1,2-bis(2-methylbenzo[b]thiophen-3-yl) cyclopent-1-ene. Russ Chem Bull Intern Ed 2011;60:2536–43.

[26] (a) Krayushkin MM, Ivanov SN, Martynkin AY, Lichitsky BV, Dudinov AA, Vorontsova LG, Starikova ZA, Uzhinov BM. Photochromic dihetarylethenes 17. Synthesis and photochromic properties of dithienylethenes containing new heterocyclic bridging fragments. Russ Chem Bull 2002;51:1731–6;
(b) Krayushkin MM, Barachevsky VA, Irie M. Synthesis of thienyl-containing photochromes (dithienylethenes, fulgides, fulgimides, and spirocompounds). Heteroat Chem 2007;18:557–67;
(c) Barachevsky VA, Strokach YP, Valova MV, Puankov YA, Krayushkin MM. New bistable organic photochromic compounds for bitwise working optical memory. Opt Mem Neur Networks 2007;16:51–66.

[27] Strokach YP, Kobeleva OI, Valova TM, Barachevsky VA, Pashchenko DV, Lichitskii BV, Krayushkin MM. Spectral study of the properties of photochromic polysubstituted lactones. Opt Spectro 2007;103:936–42.

[28] (a) Pimienta V, Micheau JC. Kinetic analysis of photoreversible photochromic systems under continuous monochromatic irradiation from Abs vs time curves. Mol Cryst Liq Cryst 2000;144:157–62;
(b) Delbaere S, Vermeersch G, Micheau JC. Quantitative analysis of the dynamic behaviour of photochromic systems. J Photochem Photobiol C Photochem Rev 2011;12:74–105.

[29] Kobatake S, Irie M. Synthesis and photochromic reactivity of a diarylethene dimer linked by a phenyl group. Tetrahedron 2003;59:8359–64.

[30] Massaad J, Micheau JC, Coudret C, Sanchez R, Guirado G, Delbaere S. Gated photochromism and acidity photomodulation of a diacid dithienylethene dye. Chem Eur J 2012;18:6568–75.

[31] (a) Goldberg A, Murakami A, Kanda K, Kobayashi T, Nakamura S, Uchida K, Sekiya H, Fukaminato T, Kawai T, Kobatake S, Irie M. Rotational isomerization of dithienylethenes: a study on the mechanism determining quantum yield of cyclization reaction. J Phys Chem A 2003;107:4982–8;
(b) Nakamura S, Kobayashi T, Takata A, Uchida K, Asano Y, Murakami A, Goldberg A, Guillaumont D, Yokojima S, Kobatake S, Irie M. Quantum yields and potential energy surfaces: a theoretical study. J Phys Org Chem 2007;20:821–9;
(c) Nakamura S, Yokojima S, Uchida K, Tsujioka T, Goldberg A, Murakami A, Shinoda K, Mikami M, Kobayashi T, Kobatake S, Matsuda K, Irie M. Theoretical investigation on photochromic diarylethene: a short review. J Photochem Photobiol A 2008;200:10–8;
(d) Nakamura S, Uchida K, Hatakeyama M. Potential energy surfaces and quantum yields for photochromic diarylethene reactions. Molecules 2013;18:5091–103.

[32] Kobatake S, Terakawa Y, Imagawa H. Solvent effect on photochromism of a dithienylperfluoro-cyclopentene having diethylamino group. Tetrahedron 2009;65:6104–8.

[33] Pu S, Yang T, Xu J, Chen B. Syntheses and properties of new photochromic diarylethene derivatives having a pyrazole unit. Tetrahedron Lett 2006;47:6473–7.

[34] Ern J, Bens AT, Martin HD, Kuldova K, Trommsdorff HP, Kryschi C. Ring-opening and -closure reaction dynamics of a photochromic dithienylethene derivative. J Phys Chem A 2002;106:1654–60.

[35] Shibata K, Kobatake S, Irie M. Extraordinarily low cycloreversion quantum yields of photochromic diarylethenes with methoxy substituents. Chem Lett; 2001:618–9.