

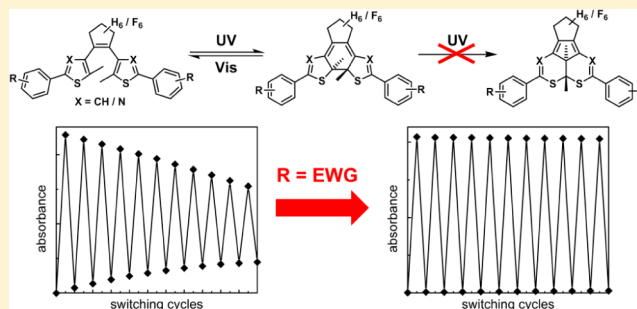
# Improving the Fatigue Resistance of Diarylethene Switches

Martin Herder, Bernd M. Schmidt, Lutz Grubert, Michael Pätzelt, Jutta Schwarz, and Stefan Hecht\*

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

**S** Supporting Information

**ABSTRACT:** When applying photochromic switches as functional units in light-responsive materials or devices, an often disregarded yet crucial property is their resistance to fatigue during photoisomerization. In the large family of diarylethene photoswitches, formation of an annulated isomer as a byproduct of the photochromic reaction turns out to prevent the desired high reversibility for many different derivatives. To overcome this general problem, we have synthesized and thoroughly investigated the fatigue behavior of a series of diarylethenes, varying the nature of the hetaryl moieties, the bridging units, and the substituents. By analysis of photokinetic data, a quantification of the tendency for byproduct formation in terms of quantum yields could be achieved, and a strong dependency on the electronic properties of the substituents was observed. In particular, substitution with 3,5-bis(trifluoromethyl)phenyl or 3,5-bis(pentafluorosulfanyl)-phenyl groups strongly suppresses the byproduct formation and opens up a general strategy to construct highly fatigue-resistant diarylethene photochromic systems with a large structural flexibility.

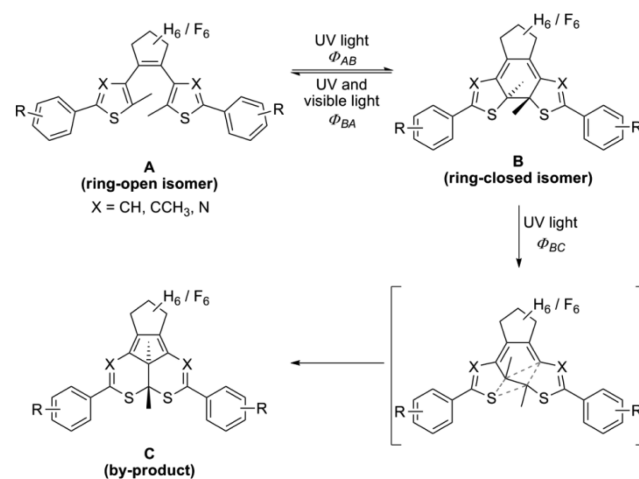


## INTRODUCTION

Photochromic molecules, which interconvert reversibly between two states by irradiation with light, increasingly receive attention as photoswitches that allow control over complex functions on the molecular scale, e.g., reactivity and catalysis,<sup>1</sup> single-molecule fluorescence,<sup>2</sup> or supramolecular binding,<sup>3</sup> as well as functions of large molecular ensembles, e.g., photoactuation and optomechanics<sup>4</sup> or charge transport in organic electronic devices.<sup>5</sup> Nevertheless, in order to eventually render such functional systems technologically relevant, it is mandatory to use switches, which in addition to undergoing a highly efficient photoisomerization reaction in both directions show no or at least extremely low fatigue over a large number of switching cycles. Even the occurrence of a slight side reaction that is hardly observed when the photoisomerization is performed only once will lead to a significant loss of photochromic material after tens or hundreds of switching cycles. In this regard diarylethene switches, interconverting between the ring-open isomer **A** and the ring-closed isomer **B** by irradiation with UV light and visible light (Scheme 1), are generally regarded to possess outstanding properties. These are manifested in the fact that they typically show fast and nearly quantitative interconversion between thermally stable isomers, with some derivatives being reported to last more than 10<sup>4</sup> switching cycles without any sign of degradation.<sup>6</sup> In particular for structural motifs possessing either benzothiophene<sup>7</sup> or  $\beta$ -methyl-substituted thiophenes<sup>8</sup> as hetaryl moieties in conjunction with a central hexafluorocyclopentene bridge (Scheme 2), no byproduct formation has been observed.

However, it has been noted by several groups that distinct diarylethene derivatives show different types of photochemical side reactions, e.g., oxidation or elimination reactions of the ring-

## Scheme 1. Isomerization Behavior and Byproduct Formation of Diarylethenes

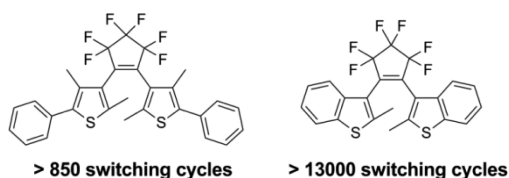


closed isomer.<sup>9</sup> In particular, the formation of an annulated ring system **C** (Scheme 1) has been reported for perfluorocyclopentene and perhydrocyclopentene derivatives.<sup>8,10</sup> The structure of the byproduct has been proven by X-ray crystallography.<sup>8,10g</sup> It is formed upon excitation of the ring-closed isomer with UV light by a formal 1,2-dyotropic rearrangement, which may proceed via a concerted mechanism as shown in Scheme 1 or via radical or ionic intermediates.<sup>10g,11</sup> A

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Scheme 2. Rare Examples of Highly Fatigue-Resistant Diarylperfluorocyclopentenes



recent theoretical work identified the cleavage of the C–S bond of one of the thiophene rings as the excited-state reaction coordinate leading to the byproduct.<sup>12</sup> Although there are no systematic investigations on the influence of diarylethene structure on byproduct formation, it has been noted in earlier work that dithienylperhydrocyclopentenes suffer more pronounced fatigue as compared to the respective perfluorocyclopentene derivatives.<sup>13</sup> For the latter, the presence of an additional methyl group in the 4-position ( $\beta$ -position) of the thiophene ring or the use of benzothiophenes as hetaryl moieties is essential to fully shut off the reaction pathway to the annulated ring system.<sup>8,14</sup> Additionally, oxidation of one thiophene or benzothiophene unit to the *S,S*-dioxide or substitution with acetyl groups may lead to an improved photochemical stability.<sup>15</sup> Note that, for the photoconversion of diarylethenes in the single-crystalline state, the formation of the annulated byproduct has not been observed.<sup>8</sup>

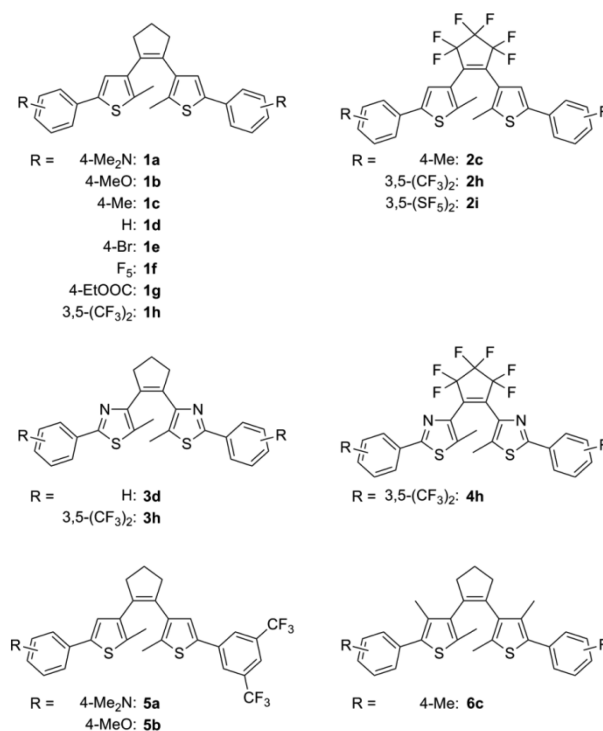
Recently, large structural variations of the parent diarylethene motif have been made in order to implement distinct properties or functions, e.g., functionalization of the bridging ethylene unit with reactive or catalytically active moieties,<sup>16</sup> incorporation of the central double bond into heteroaromatic rings in terarylenes giving rise to a highly efficient isomerization behavior,<sup>17</sup> or use of double-bond-containing structures different from the parent thiophene or benzothiophene units.<sup>18</sup> In this context, it is highly important to find a general concept of implementing fatigue resistance to diarylethenes while maintaining a maximum degree of structural and synthetic flexibility and hence not being restricted to the parent motifs shown in Scheme 2.

In our ongoing work on diarylethene switches, we noticed a ubiquitous appearance of the condensed ring system **C** for quite different structures. Nevertheless, we noticed as well that there is a strong dependency of the amount of byproduct formed on the substitution pattern of the adjacent phenyl rings. In order to gain a systematic insight into this structure-switch relationship, we prepared a series of diarylethene derivatives and investigated their fatigue behavior in detail. Starting with the parent dithienylperhydrocyclopentene structure **1** (Scheme 3), substituents on the phenyl ring were varied from strongly donating (4-Me<sub>2</sub>N, **1a**) to strongly accepting (3,5-(CF<sub>3</sub>)<sub>2</sub>, **1h**) moieties. To study the effect of the perfluorocyclopentene bridge, derivatives **2c**, **2h**, and **2i** were prepared. In addition, thiazole analogues **3** and **4** as well as two non-symmetrically substituted dithienylcyclopentenes **5** were investigated. Last but not least, dithienylcyclopentene **6c** was synthesized to determine the effect of the additional  $\beta$ -methyl group in the case of a bridge other than perfluorocyclopentene.

## RESULTS AND DISCUSSION

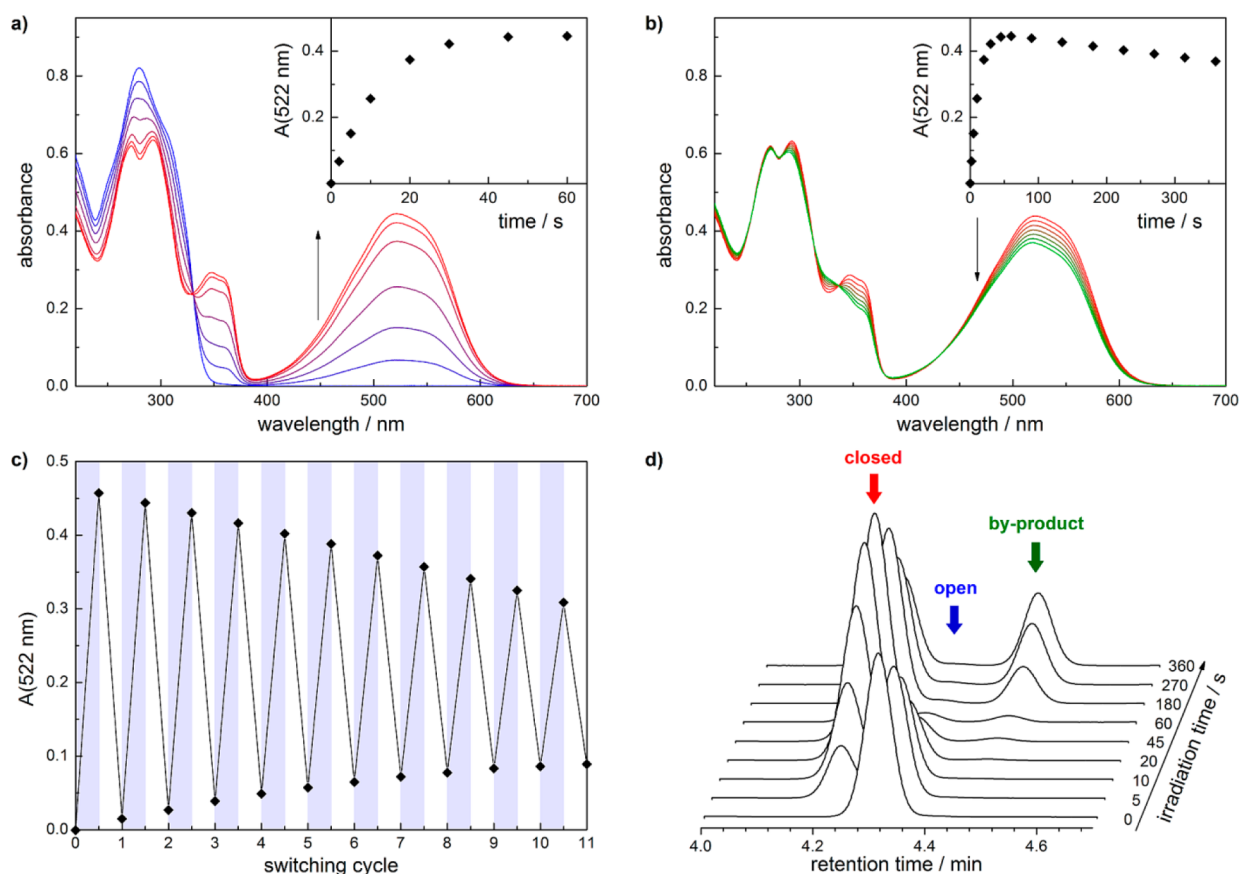
**Synthesis.** The investigated diarylethenes were synthesized following established procedures.<sup>19</sup> Perhydrocyclopentene derivatives **1a–h** and **5a,b** were easily obtained by borylation and subsequent Suzuki cross-coupling of 1,2-(2-chloro-5-methyl-

Scheme 3. Diarylethene Derivatives Investigated in This Work



thien-4-yl)cyclopentene with the corresponding aryl halides.<sup>13</sup> Perhydrocyclopentene derivatives bearing thiazole units (**3d,h**) were synthesized by cross-coupling of substituted thiazolylboronic acids or stannanes and 1,2-dibromocyclopentene.<sup>20</sup> Analogous compounds bearing the perfluorocyclopentene bridge were obtained by borylation and subsequent Suzuki cross-coupling of 1,2-(2-chloro-5-methylthien-4-yl)perfluorocyclopentene<sup>13</sup> or by cross-coupling of corresponding thienyl and thiazolyl boronic esters with 1,2-dichlorohexafluorocyclopentene.<sup>21</sup> Compounds **1b**,<sup>13</sup> **1c**,<sup>22</sup> **1d**,<sup>23</sup> **1e**,<sup>13</sup> **2c**,<sup>24</sup> **2h**,<sup>25</sup> and **6c**<sup>26</sup> have been reported earlier. Details on the synthesis and characterization are given in the Supporting Information (SI).

**Fatigue Behavior.** An example of the typical spectral response of diarylethene switches upon irradiation with UV light is shown in Figure 1 for the methyl-substituted compound **1c**. While the ring-open isomer possesses a strong absorbance in the UV range, upon irradiation with 313 nm light, a new broad band centered at 522 nm builds up that is characteristic for the ring-closed isomer with its extended  $\pi$ -conjugation (Figure 1a). The fast growth of the visible band is completed after 60 s when a plateau is reached; i.e., the absorbance does not increase upon further UV illumination. This is the expected behavior for a photochemical equilibrium between the ring-open and ring-closed isomers, leading to a photostationary state (PSS). Importantly, when the sample after reaching the PSS is further subjected to UV illumination, a slow decrease of the visible absorbance can be observed, accompanied by a small hypsochromic shift of the band maximum (Figure 1b). Analysis of the irradiation solution by ultraperformance liquid chromatography (UPLC) reveals the emergence of a second photoproduct upon longer irradiation times (Figure 1d). In contrast to the formation of the ring-closed isomer, this process is not reversible; i.e., upon visible light irradiation to induce the ring-opening reaction, a weak absorbance in the visible range is



**Figure 1.** UV/vis spectroscopy of an acetonitrile solution of **1c** ( $2.38 \times 10^{-5}$  M, 25 °C). (a) Irradiation with UV light (310 nm) until reaching maximum absorbance in the visible range. (b) Prolonged UV irradiation (310 nm) after reaching maximum absorbance. (c) Evolution of absorbance in the visible range during repetitive switching cycles consisting of alternating UV (310 nm, 90 s) and visible irradiation (>500 nm, 600 s). (d) Evolution of UPLC traces (absorbance monitoring by diode array detector integrated between 250 and 800 nm) upon continuous UV irradiation (310 nm).

retained and corresponds to the formed byproduct. Although the observed byproduct formation seems to be very slow, it leads to a significant loss of photochromic material already after a few switching cycles, which consist of short UV irradiation until reaching the (pseudo)PSS and subsequent visible light irradiation until no further spectral change can be observed (Figure 1c).

The identity of the formed byproduct with the condensed ring system **C** shown in Scheme 1, which was reported earlier by the group of Irie,<sup>8</sup> was proven by its preparative isolation and subsequent NMR spectroscopic examination. While <sup>1</sup>H NMR spectra of the ring-open and ring-closed isomers of **1c** show only one signal for the methyl groups attached to the reactive carbons, two separate singlets, each integrating for three protons, appear in the spectrum of the isolated byproduct (see Figure S30). 2D NMR spectroscopy proves the structure by unambiguous assignment of the observed signals and analysis of the coupling paths (see Figures S32 and S33). Notably, the downfield-shifted part of the <sup>1</sup>H NMR spectrum of the byproduct is nearly identical to that of the ring-closed isomer, which is an indication for their similar  $\pi$ -electronic structure.

From inspection of the irradiation spectra of *all* other diarylethene derivatives discussed here (collected in section 2.1 of the SI), it can be deduced that the fatigue exemplified in Figure 1 for compound **1c** is a general feature of diarylethenes, independent of the nature of their aryl moieties or their bridging unit. While, as discussed above, the formation of the annulated ring system has been noted earlier for some dithienylethene

derivatives, for diarylethenes bearing thiazoles as aryl moieties, the formation of a byproduct has not been reported yet. In contrast, they were originally characterized as highly fatigue resistant.<sup>27</sup>

To prove that the photochemical byproduct formed from dithiazolylolethene **3d** is structurally analogous to the thiophene counterpart, it has been isolated by irradiation and subsequent chromatography on a preparative scale. Again, <sup>1</sup>H NMR spectroscopy shows signals for two magnetically inequivalent methyl groups (Figure S31), while <sup>13</sup>C NMR shows two signals for quaternary carbon atoms at high field. Long-range couplings observed in 2D NMR spectra are similar to those observed for the byproduct of **1c** (Figures S34 and S35). Note that for *all* compounds reported in this study, UPLC/MS analysis of irradiated samples verifies that the emerging byproduct is an additional isomer of the parent, possessing an  $m/z$  ratio identical to that of the respective ring-open and ring-closed forms. Given the close similarities between all compounds in the observed UV/vis spectra and corresponding UPLC/MS traces, we can assume that, in any case, the fatigue of the photochrome is based on the formation of the same condensed ring system as a byproduct. Only in the case of electron-rich dithienylcyclopentenes **1a–f** and **5a,b** some additional unspecific byproduct formation, in the form of oxidation reactions, can be detected by UPLC/MS (peaks corresponding to  $(M+16)^+$  and  $(M+32)^+$ ). However, in argon-saturated solutions, the emergence of the rearranged isomer is much faster than photooxidation.

Table 1. Photochemical Properties of Investigated Diarylethenes in Acetonitrile

compd	$\lambda_{\max}/\text{nm}$ ( $\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )			yield/% (310 nm)					
	ring-open isomer	ring-closed isomer	byproduct	PSS <sup>a</sup>	byproduct <sup>b</sup>	$\Phi_{\text{AB}}$ (313 nm) <sup>c</sup>	$\Phi_{\text{BA}}$ (313 nm) <sup>c</sup>	$\Phi_{\text{BC}}$ (313 nm) <sup>c</sup>	$\Phi_{\text{BA}}$ (546 nm) <sup>d</sup>
1a	331 (4.33)	537 (2.66)	530 (1.44)	99	71	0.74 ± 0.09	0.03 ± 0.06	0.008 ± 0.003	0.0029 ± 0.0002
1b	283 (3.19)	520 (1.90)	509 (0.84)	89	86	0.47 ± 0.05	0.03 ± 0.03	0.007 ± 0.002	0.0072 ± 0.0006
1c	279 (3.45)	522 (1.97)	508 (1.13)	94	79	0.43 ± 0.05	0.01 ± 0.03	0.009 ± 0.003	0.008 ± 0.0006
1d	278 (3.25)	520 (1.78)	510 (0.94)	98	73	0.47 ± 0.05	0.02 ± 0.05	0.013 ± 0.003	0.0093 ± 0.0007
1e	284 (3.71)	532 (2.16)	514 (1.17)	96	66	0.42 ± 0.05	0.02 ± 0.03	0.006 ± 0.002	0.0055 ± 0.0004
1f	273 (2.83)	512 (1.18)	476 (0.51)	96	37	0.41 ± 0.04	0.01 ± 0.05	0.006 ± 0.001	0.020 ± 0.002
1g	334 (3.58)	556 (2.32)	532 (1.18)	98	25	0.65 ± 0.07	0.06 ± 0.05	0.0013 ± 0.0003	0.0021 ± 0.0002
1h	284 (3.16)	548 (1.96)	524 (0.95)	97	6	0.44 ± 0.04	0.02 ± 0.06	0.0004 ± 0.0001	0.0046 ± 0.0004
2c	289 (3.87)	588 (1.79)	550 (0.85)	94	13	0.62 ± 0.08	0.03 ± 0.03	0.0006 ± 0.0002	0.015 ± 0.001
2h	300 (3.45)	590 (1.54)	549 (0.72)	96	8	0.58 ± 0.06	0.05 ± 0.05	0.0004 ± 0.0001	0.017 ± 0.001
2i	302 (3.43)	590 (1.58)	545 (0.76)	96	3	0.50 ± 0.05	0.04 ± 0.05	0.00019 ± 0.00004	0.018 ± 0.001
3d	316 (2.13)	500 (1.55)	521 (0.80)	94	65	0.53 ± 0.05	0.03 ± 0.05	0.007 ± 0.001	0.021 ± 0.002
3h	332 (1.80)	522 (1.34)	540 (0.77)	95	22	0.56 ± 0.06	0.03 ± 0.05	0.002 ± 0.0005	0.015 ± 0.001
4h	307 (3.11)	538 (1.13)	538 (0.64)	89	13	0.45 ± 0.05	0.06 ± 0.04	0.0008 ± 0.0002	0.039 ± 0.003
5a	326 (3.37)	570 (2.54)	539 (1.22)	97	6	0.051 ± 0.005	0.005 ± 0.008	0.0009 ± 0.0002	0.0022 ± 0.0002
5b	282 (3.04)	546 (1.82)	515 (0.82)	99	19	0.56 ± 0.06	0.02 ± 0.04	0.0013 ± 0.0002	0.0058 ± 0.0005
6c	271 (2.75)	483 (1.29)	459 (0.35)	91	26	0.47 ± 0.05	0.04 ± 0.03	0.004 ± 0.001	0.043 ± 0.003

<sup>a</sup>Amount of ring-closed isomer in the (pseudo)PSS reached after UV irradiation (310 nm), obtained by UPLC. <sup>b</sup>Amount of byproduct after 30 min of UV irradiation (310 nm), obtained by UPLC. <sup>c</sup>Quantum yields obtained by nonlinear regression of photokinetic data under UV irradiation (313 nm). <sup>d</sup>Ring-opening quantum yields under visible light irradiation (546 nm) obtained from the initial slope of photoconversion.

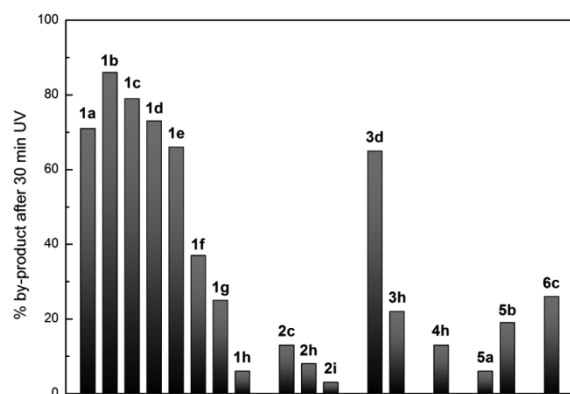
Interestingly, close inspection of the UV/vis spectra (section 2.1 of the SI) and spectroscopic data given in Table 1 reveals subtle differences in the spectroscopic characteristics of the byproduct when comparing dithienylethenes **1c**, **1h**, and **2h** with their thiazole analogues **3d**, **3h**, and **4h**. For all compounds, both the ring-closed isomer and the byproduct possess very similar absorbances in the visible region, due to analogous  $\pi$ -conjugation pathways throughout their molecular backbone. Nevertheless, the molar absorptivity of the byproduct is significantly lower, leading to the typical decrease of the absorption band upon prolonged UV irradiation. For thiophene derivatives, the decrease is accompanied by a hypsochromic shift, which is more pronounced for electron-deficient derivatives ( $\Delta\lambda_{\max} = 14$  nm for **1d**,  $\Delta\lambda_{\max} = 41$  nm for **2h**). However, thiazole derivatives show a bathochromic shift of 21 and 18 nm for **3d** and **3h**, respectively; in the case of **4h**, the  $\lambda_{\max}$  values of the ring-closed form and the byproduct are identical.

To gain further insight into the spectroscopic characteristics, some calculations were performed on the prototype thiophene- and thiazole-containing structures **1c** and **3d**. Following procedures outlined by Jacquemin et al.,<sup>28</sup> ground-state geometries were optimized using density functional theory (DFT) at the B3LYP/6-311G(d,p) level of theory, and vertical transition energies were computed by time-dependent DFT using the CAM-B3LYP as well as PBE0 functionals together with the 6-311+G(2d,p) basis set (for details, see section 6 of the SI). It has been shown that CAM-B3LYP and PBE0 give a good agreement between experimental spectra and calculated vertical transition energies of diarylethenes.<sup>29</sup> In the cases of **1c** and **3d**, CAM-B3LYP reproduces the experimentally observed  $\lambda_{\max}$  for all three isomers very accurately (Figures S55 and S57), while the PBE0 functional significantly underestimates the transition energies (Figures S56 and S58). Nevertheless, both methods confirm a hypsochromic shift of  $\lambda_{\max}$  for **1c** (11 nm with CAM-B3LYP/15 nm with PBE0) and a bathochromic shift of  $\lambda_{\max}$  for **3d** (24 nm with CAM-B3LYP/21 nm with PBE0) when going from the ring-closed isomer to the byproduct. The reduced oscillator strength

of the lowest energy transition of the byproducts is demonstrated as well. Inspecting the optimized geometries, one finds that the major difference between isomers of **1c** and **3d** lies in the twisting of the adjacent phenyl groups, while deviations in the central hexatriene/cyclohexadiene core are small (see Table S4 for structural parameters). In general, the dihedral angle  $\theta$  between thiophenes and phenyl rings in **1c** is larger for all isomers than that between thiazoles and phenyl rings in **3d**. Importantly,  $\theta$  increases on going from the ring-closed isomer to the byproduct due to increased steric repulsion by expanding the former thiophene/thiazole 5-membered ring to a 6-membered ring. While for **3d** the increase is moderate ( $\theta = 4^\circ$  for the ring-closed isomer/ $\theta = 20^\circ$  for the byproduct), it is larger for **1c** ( $\theta = 13^\circ$  for the ring-closed isomer/ $\theta = 40^\circ$  for the byproduct). Thus, a smaller increase of the dihedral angle of **3d** due to less steric repulsion by the nitrogen atom may lead to a better delocalization of  $\pi$ -electron density, resulting in the experimentally observed bathochromic shift, while a stronger twisting of the phenyl group shifts the absorbance maximum of the byproduct of **1c** to shorter wavelengths (Figure S59).

**Quantification of Byproduct Formation.** Along the whole series of diarylethene derivatives possessing electronically different substitution patterns, significant differences in the rate of byproduct formation have been observed. At first glance, a good indication for the performance of a switch is the amount of byproduct formed after a certain time of UV irradiation under comparable conditions, which can readily be determined by UPLC. Although this can only serve as a crude estimate since the exact amount of byproduct depends on the sample concentration, molar absorptivities at the irradiation wavelength, and quantum yields for all photochemical reactions, the obtained conversions clearly show a strong correlation of the fatigue behavior with the substitution pattern (Figure 2, Table 1). After 30 min of high-intensity UV irradiation using a 1000 W Xe arc lamp together with a 310 nm interference filter, the most electron-rich dithienylethenes **1a–d**, bearing perhydrocyclopentene bridges and electron-donating or electron-neutral sub-





**Figure 2.** Amount of byproduct formed after 30 min of UV irradiation (1000 W Xe arc lamp, 310 nm interference filter,  $I_0 = 5.67 \times 10^{-9} \text{ E s}^{-1} \text{ cm}^{-3}$  determined by ferrioxalate actinometry) of acetonitrile solutions ( $c = 2.5 \times 10^{-5} \text{ M}$ ) of diarylethenes **1a–6c**.

stituents on the adjacent phenyl rings, are almost quantitatively converted to the byproduct. For analogous compounds possessing substituents with increasing acceptor strength, e.g., bromine (**1e**), fluorine (**1f**), ester (**1g**), or trifluoromethyl (**1h**) groups, the yield of byproduct is more and more suppressed, down to a minimum amount of ca. 6% for compound **1h**. Notably, structurally analogous diarylethenes of the thiophene and thiazole series possess a comparable fatigue resistance. Introduction of the perfluorocyclopentene bridge strongly reduces byproduct formation for donor- or electron-neutral-substituted compounds, while no further suppression is observed for trifluoromethyl-substituted compound **2h** when compared to the respective perhydrocyclopentene **1h**.

In order to obtain more precise information on the dependency of fatigue behavior on the substitution pattern, a precise quantification of the rate of byproduct formation is needed. Therefore, quantum yields for all photochemical steps involved in the isomerization and fatigue of diarylethenes have been determined by means of measurement of absorbance–time profiles under continuous UV irradiation and their evaluation by numerical nonlinear regression.<sup>30</sup> For this purpose, the molar absorptivities of the ring-closed isomer and byproduct have to be known. However, as their UV/vis spectra overlap with that of the ring-open isomer, a calculation from pure photokinetic data without simplifying assumptions or the use of special irradiation conditions is impossible.<sup>31</sup> A preparative isolation of the isomers is laborious and in some cases very difficult due to their similar structures and susceptibility to oxidation. Thus, a careful analysis of irradiated samples at different stages of the irradiation was conducted by UPLC, and spectra of the pure isomers were calculated by determination of conversions to the ring-closed isomer and byproduct (for details, see section 1.2 of the SI). A comparison of the spectra obtained by this method with spectra of isolated isomers of compound **3d** shows an excellent agreement (Figure S3).

As a kinetic model for the nonlinear regression, a photochromic ABC(3 $\Phi$ ) system according to the reaction scheme shown in Scheme 1 was assumed, consisting of a photochemical equilibrium between species A and B and a subsequent irreversible photochemical reaction from species B to C. Since the corresponding rate equations cannot be integrated in a closed form, they were treated numerically. By fitting the theoretical model to the experimental data, quantum yields  $\Phi_{AB}$  for ring closure,  $\Phi_{BA}$  for ring opening, and  $\Phi_{BC}$  for byproduct formation

were obtained (Table 1). Note that assuming a different model with the byproduct being formed parallel to the ring-closed isomer by excitation of the ring-open isomer does not lead to a satisfying fit of the experimental data, in accordance to previous findings.<sup>10g</sup> A detailed discussion of the photokinetic model, the fitting procedure, and experimental errors can be found in section 1.4 of the SI.

#### Quantum Yields for Ring Closure and Ring Opening.

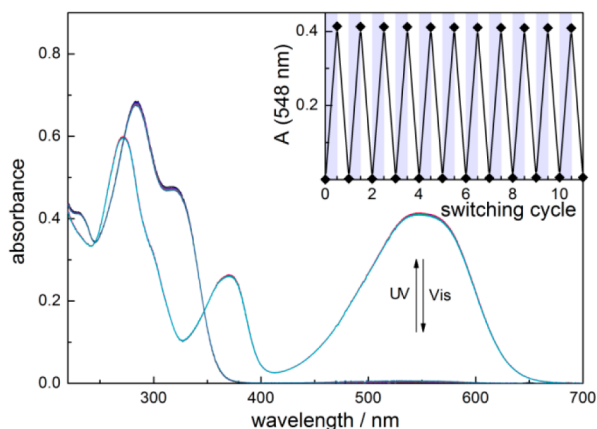
The data in Table 1 show that the majority of the investigated compounds possess the expected photochemical behavior of diarylethenes substituted with methyl groups and phenyl rings at the inner and outer  $\alpha$ -positions of the hetaryl groups, respectively.<sup>13,32</sup> Quantum yields for ring closure are in the range of 0.4–0.6, reflecting the thermal equilibrium between the parallel and antiparallel conformers of the ring-open isomer, with only the latter being photoactive.<sup>6b</sup> Quantum yields for ring opening are more than 1 order of magnitude smaller and strongly wavelength-dependent; i.e., the ring-opening reaction performed upon irradiation with visible light proceeds much more slowly than the reaction with UV light.<sup>33</sup> Due to the ratio of  $\Phi_{AB}:\Phi_{BA}$ , the amount of ring-closed isomer in the PSS generally exceeds 90%, although both isomers absorb UV light. Only compounds **1a** and **5a** deviate from the described behavior, with the former possessing a slightly larger quantum yield for ring closure of 0.74, and the latter showing a significantly reduced photoreactivity, with  $\Phi_{AB}$  being only 0.05. Whereas a differing population of the antiparallel and parallel conformers in the electronic ground state may serve as explanation for these deviations, for compound **5a** an electronic reason, i.e., the pronounced donor–acceptor character of the  $\pi$ -electronic system, seems plausible as well. This is manifested in the fact that quantum yields for both ring closure and ring opening are reduced by approximately 1 order of magnitude. In addition, compound **5a** shows a strong bathochromic shift of the absorption bands of all three isomers, pointing to a charge-transfer character of the excitation.

#### Quantum Yields for Byproduct Formation.

The measured quantum yields for byproduct formation confirm the qualitatively observed trends. The largest values for  $\Phi_{BC}$  are found for donor-substituted and unsubstituted dithienylethenes possessing the perhydrocyclopentene bridge (**1a–d**), between 0.007 and 0.013. Thus, for these structures, the rate of byproduct formation is in the same order of magnitude as the rate of the ring-opening reaction, leading to the observed fast depletion of the photochromic material under continuous UV irradiation and high irreversibility during full switching cycles (Figure 1c, Figure S25). A comparison between structures **1d** and **3d** shows that employing less electron-rich thiazoles instead of thiophenes increases the fatigue resistance only marginally. In contrast, the perfluorination of the cyclopentene bridge has a much larger effect. Compared to perhydrocyclopentene **1c**,  $\Phi_{BC}$  is reduced by a factor of 15 to a value of 0.0006 for perfluorocyclopentene **2c**.

Importantly, in the perhydrocyclopentene series, byproduct formation is suppressed to the same degree by introduction of acceptor groups on the adjacent phenyl rings. While a small effect is observed for substitution with *p*-bromophenyl groups (**1e**) and pentafluorophenyl groups (**1f**), substitution with an ester group in the *para* position of the phenyl ring (**1g**), exerting a  $-M$  effect, reduces  $\Phi_{BC}$  to a value of 0.001. An exceptional improvement of the fatigue behavior is found when chemically inert trifluoromethyl groups, exerting a strong  $-I$  effect, are attached at the *meta* positions of the phenyl rings. With  $\Phi_{BC} = 0.0004$  for compound **1h**, byproduct formation is suppressed by a factor of 20–30 when compared to the unsubstituted or donor-

substituted analogues **1a–d**. Importantly, the  $\text{CF}_3$  substitution does not alter the rates of the desired photochemical isomerization reactions between the ring-open and ring-closed isomers and has only a minor influence on the electronic spectra (Figure 3). The positive effect of the 3,5-bis(trifluoromethyl)-



**Figure 3.** UV/vis absorbance spectra of an acetonitrile solution of **1h** ( $2.09 \times 10^{-5}$  M,  $25^\circ\text{C}$ ) during repetitive switching cycles consisting of alternating UV (310 nm, 60 s) and visible irradiation (>500 nm, 600 s). Inset: Evolution of absorbance in the visible range.

phenyl groups can be observed in the dithiazolylolethene series as well. However, compared to the parent structure **3d**, the quantum yield of byproduct formation of compound **3h** is reduced by only a factor of 3. The combination of the 3,5-bis(trifluoromethyl)phenyl substituents with the perfluorocyclopentene bridge in diarylethene structures **2h** and **4h** gives a further reduction of  $\Phi_{\text{BC}}$  only in the case of the thiazole-containing compound. In the thiophene series, the performances of the perhydro- and perfluorocyclopentene switches **1h** and **2h** are very similar. The large improvement of fatigue resistance for structures **1h**, **2h**, **3h**, and **4h** is manifested as well in the excellent reversibility during full switching cycles (Figure 3, Figure S25).

In an attempt to further suppress byproduct formation by substitution with strong acceptor groups, compound **2i** was synthesized, possessing pentafluorosulfanyl groups. Compared to  $\text{CF}_3$ , the  $\text{SF}_5$  group is an even stronger electron acceptor while being structurally related and chemically inert.<sup>34</sup> In fact, comparing structures **2h** and **2i** upon introduction of  $\text{SF}_5$  groups,  $\Phi_{\text{BC}}$  is further reduced by a factor of 2. Thus far, compound **2i** shows the highest fatigue resistance of all diarylethene structures in our hands. Note that, similar to  $\text{CF}_3$  groups,  $\text{SF}_5$  substitution only marginally alters the photochromic properties of the parent unsubstituted compound.

Given the outstanding performance of  $\text{CF}_3$ - and  $\text{SF}_5$ -substituted diarylethenes in terms of fatigue resistance, we speculated that it could be sufficient to functionalize only one heteraryl terminus of the structure with this motif while still suppressing byproduct formation. This would enable a flexible choice of the structure of the second terminus, thus allowing for implementing any desired chemical functionality to be modulated by the photochromic reaction. To answer this question, non-symmetrically substituted dithienylethenes **5a** and **5b** were synthesized, possessing the 3,5-bis(trifluoromethyl)phenyl group on one thiophene ring and a 4-*N,N*-dimethylamino- or 4-methoxy-substituted phenyl group on the other. In terms of fatigue, this substitution pattern combines one of the best-performing acceptors with poor-performing donor

substituents. Besides modulation of the rates of ring closure and ring-opening in the case of compound **5a** (*vide supra*), it was found that for both structures byproduct formation is strongly suppressed compared to the symmetrically donor-substituted compounds. This strategy of using a non-symmetrical substitution pattern to implement fatigue resistance via the 3,5-bis(trifluoromethyl)phenyl group on one side and a functional moiety on the other side of the diarylethene recently allowed us to remote-control the reactivity of a furan in a Diels–Alder reaction.<sup>18a</sup> Importantly, in this particular case, a perfluorinated bridge could not be used to provide improved fatigue resistance for electronic reasons, as it would significantly reduce the Diels–Alder reactivity of the attached furan. This nicely demonstrates the power of imparting fatigue resistance via the diarylethene termini and not the bridge.

The second previously known strategy to impart fatigue resistance to diarylethenes making use of  $\beta$ -methyl-substituted thiophenes was reported only for compounds possessing the perfluorocyclopentene bridge.<sup>8</sup> To test if the  $\beta$ -methyl substituent has an effect on the fatigue behavior when other bridges are used, the photochemistry of compound **6c**, possessing  $\beta$ -methyl-substituted thiophenes and the perhydrocyclopentene bridge, was investigated. In fact, **6c** shows significant byproduct formation with a quantum yield only slightly lower than that of compound **1c** without  $\beta$ -methyl substituents. This finding supports theoretical investigations,<sup>14</sup> which attribute the lack of fatigue of  $\beta$ -methyl-substituted dithienylperfluorocyclopentenenes to steric hindrance between the  $\beta$ -methyl group and the fluorine atoms, which are not present in compound **6c**.

**Solvent and Wavelength Dependence of  $\Phi_{\text{BC}}$ .** The photochemistry of dithiazolylolethene **3d** was investigated in different solvents and under different irradiation conditions (Table 2, Figures S23 and S24). Using solvents with lower

**Table 2.** Solvent and Wavelength Dependence of Quantum Yields of Compound **3d**

solvent	$\lambda_{\text{irr}}$ /nm	PSS yield/% <sup>a</sup>	$\Phi_{\text{AB}}^b$	$\Phi_{\text{BA}}^b$	$\Phi_{\text{BC}}^b$
MeCN	313	94	$0.53 \pm 0.05$	$0.03 \pm 0.05$	$0.007 \pm 0.001$
$\text{CH}_2\text{Cl}_2$	313	94	$0.59 \pm 0.06$	$0.03 \pm 0.04$	$0.007 \pm 0.001$
$\text{C}_6\text{H}_{12}$	313	96	$0.73 \pm 0.07$	$0.02 \pm 0.06$	$0.008 \pm 0.002$
MeCN	297	88	$0.51 \pm 0.05$	$0.04 \pm 0.03$	$0.007 \pm 0.001$
MeCN	334	96	$0.60 \pm 0.06$	$0.04 \pm 0.08$	$0.008 \pm 0.001$

<sup>a</sup>Amount of ring-closed isomer in the (pseudo)PSS. <sup>b</sup>Quantum yields obtained by nonlinear regression of photokinetic data under UV irradiation (313 nm).

polarity than acetonitrile causes a small increase of the quantum yield for ring closure, while quantum yields for ring opening as well as byproduct formation are not altered. Interestingly, quantum yields for all three isomerization reactions are not affected within the error of measurement by the choice of the irradiation wavelength in the UV range. For photochemical ring closure of diarylethenes, the insensitivity to the irradiation wavelength was expected.<sup>33a</sup> The previously observed wavelength dependence of the quantum yield for the ring-opening process<sup>33</sup> is manifested in the much lower values for excitation with visible light (Table 1), yet probably could not be resolved in our experiments within the UV range due to the high statistical error of this parameter.

In accordance with previous reports,<sup>8,10g</sup> we find that byproduct formation is not induced by irradiation of the ring-closed isomer using visible light (see section 1.6 of the SI). This may be ascribed to a thermal barrier in the  $S_1$  excited state, making excitation to a higher excited state by UV light necessary to deliver sufficient kinetic energy upon internal conversion to the  $S_1$  state to overcome the barrier.<sup>12</sup> Thus, one would also expect a dependence of the quantum yield for byproduct formation on the wavelength within the UV range. However, we find that  $\Phi_{BC}$  is essentially wavelength independent between 297 and 334 nm.

**Electronic Effects of the Substituents.** To estimate the effects of the substituents on the diarylethenes' electronic structure, cyclic voltammetry measurements were performed (see section 5 of the SI). Perhydrocyclopentene-substituted dithienylethenes **1a–e**, **5a**, **5b**, and **6c** show the expected electrochemical behavior, consisting of an irreversible oxidation of the ring-open isomer followed by the appearance of cathodic waves at potentials similar to those of the two reversible oxidations of the respective ring-closed isomers, which indicates a thermal cyclization reaction in the dicationic state.<sup>35</sup> Interestingly, in the case of the non-symmetrically substituted derivative **5a**, two separated oxidation waves can be observed for the ring-open isomer, the first being fully reversible and only the second leading to the cyclization reaction. For the acceptor-substituted analogues **1f**, **1g**, and **1h**, the oxidative cyclization cannot be observed. The same holds for thiazole-substituted compounds **3d** and **3h**. For the perfluorocyclopentene derivatives, an oxidative cyclization takes place only for the most electron-rich derivative **2c**. Reductions, which are generally observed within the accessible potential range for all ring-closed isomers and only for acceptor-substituted ring-open isomers, do not induce isomerization reactions.

Peak potentials (against Fc/Fc<sup>+</sup>) reported in Table 3 show that, by changing the substitution pattern, the electron density within the  $\pi$ -electronic system is varied over a broad range. Thus, ring-open isomers become oxidized between 0.13 V in the case of

strong donor substitution (**1a**) and >2.00 V in the case when the perfluorocyclopentene bridge is used (**2h**, **2i**, and **4h**). The same trend is observed for ring-closed isomers, with their first oxidation potential  $E_p^{a1}$  between  $-0.37$  V (**1a**) and 1.35 V (**4h**). In particular, oxidation potentials of ring-closed isomers may be related to the observed trends in the fatigue behavior of the photochromes. In fact, starting from the parent dithienylcyclopentene **1c**, the largest effect on oxidation potentials has the perfluorination of the cyclopentene bridge shifting  $E_p^{a1}$  of the ring-closed isomer by 520 mV (**1c** vs **2c**) to more positive values, accompanied by a massive improvement of the fatigue resistance. Introduction of CF<sub>3</sub> groups in **1h**, exerting the same effect on the fatigue, gives a potential shift of 260 mV. Comparing **1h** and **2h**, one finds again a shift of 520 mV arising from the perfluorination of the bridge; nevertheless, there is no difference in the rate of byproduct formation between these two structures. The replacement of CF<sub>3</sub> with SF<sub>5</sub> groups, giving rise to the structure with the lowest rate of byproduct formation, is accompanied by a further increase of the oxidation potential by 110 mV.

In contrast to this general trend, the thiazole-containing structure **3d** becomes oxidized at slightly higher potentials than **1h**, despite showing a much higher rate of byproduct formation. Again, introduction of CF<sub>3</sub> groups in **3h** shifts the potential by 210 mV.

Another example showing that there is no straightforward correlation between electrochemical oxidation potentials and photochemical fatigue is the pentafluorophenyl-substituted compound **1f**. It was synthesized with the expectation that the pentafluorophenyl group would have an effect similar to that of the 3,5-bis(trifluoromethyl)phenyl group in **1h**. Indeed, both structures become oxidized at very similar potentials in the ring-open and ring-closed states. However, for **1f** the quantum yield for byproduct formation is larger by more than 1 order of magnitude. Possibly the +M effect of fluorine atoms directly attached to a  $\pi$  system stabilizes the transition state or intermediate during formation of the annulated isomer.

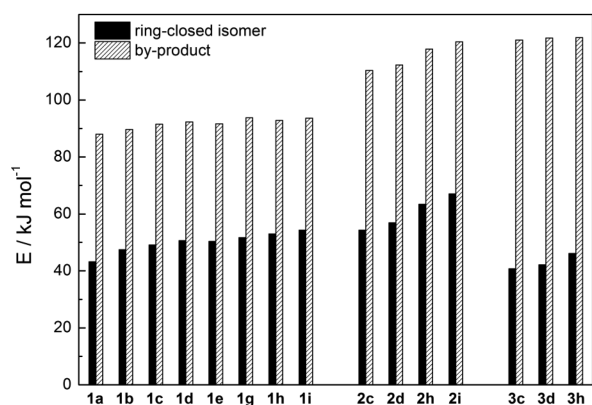
DFT calculations at the B3LYP/6-31G(d) level of theory were performed to estimate the influence of the substituents on the geometry and relative ground-state stability of the three isomers (see section 6.2 of the SI). Therefore, the hypothetical derivatives **1i** (R = 3,5-(SF<sub>5</sub>)<sub>2</sub>), **2d** (R = H), and **3c** (R = Me) (see Scheme S2) were also included. Remarkably, in all cases the geometry optimization led to very similar structures of the diarylethene cores, independent of the substituents on the phenyl rings, with only small, non-systematic variations in geometric parameters such as dihedral angles, the distance between the ring-closing carbons, or the length of the C–S bonds (Table S6). Computed NICS values<sup>36</sup> of the thiophene or thiazole rings in the ring-open isomers also show only minimal variation upon exchange of substituents (Table S6). However, ground-state energies of the ring-closed isomers and byproducts, relative to the respective ring-open isomers, slightly rise within a series of similar structures on going from donor to acceptor substitution (Figure 4, Table S6). While the byproducts are generally much less stable than the ring-closed isomers, their further destabilization by acceptor substitution may lead to an increased fatigue resistance. Nevertheless, comparing the different series (cyclopentene vs perfluorocyclopentene and thiophene vs thiazole switches), it is obvious that, for compounds experimentally possessing similar fatigue behavior (e.g., **1h** and **2h**), the stabilities of the byproducts are very different. Thus, more advanced quantum mechanical calculations concerning

**Table 3. Anodic and Cathodic Peak Potentials Determined by Cyclic Voltammetry in Acetonitrile<sup>a</sup>**

compd	open isomer		closed isomer		
	$E_p^{a1}/V$	$E_p^{c1}/V$	$E_p^{a1}/V$	$E_p^{a2}/V$	$E_p^{c1}/V$
<b>1a</b>	0.13	<−2.80	−0.37		−2.40
<b>1b</b>	0.62	<−2.80	−0.07	0.06	−2.30
<b>1c</b>	0.79	<−2.80	−0.02	0.20	−2.25
<b>1d</b>	0.79	<−2.80	0.03	0.27	−2.17
<b>1e</b>	0.81	−2.86	0.07	0.31	−2.18
<b>1f</b>	1.08	−2.79	0.29	0.55	−1.90
<b>1g</b>	0.87	−2.48	0.13	0.39	−1.87
<b>1h</b>	1.08	<−2.80	0.24	0.53	−1.84
<b>2c</b>	1.08	−2.53	0.50		−1.56
<b>2h</b>	>2.00	−2.56	0.76		−1.27
<b>2i</b>	>2.00	−2.63	0.87	1.02	−1.20
<b>3d</b>	0.84	−2.85	0.40	0.61	−1.99
<b>3h</b>	1.06	−2.38	0.61	0.88	−1.61
<b>4h</b>	>2.00	−2.11	1.35		−1.08
<b>5a</b>	0.22 <sup>b</sup>	−2.71	−0.13	0.09	−2.02
<b>5b</b>	0.74	<−2.80	0.05	0.28	−2.02
<b>6c</b>	0.77	<−2.80	−0.02	0.22	−2.45

<sup>a</sup>All values are reported against the ferrocene/ferrocenium redox couple as external standard. <sup>b</sup> $E_p^{a2} = 0.64$  V.





**Figure 4.** Energies (including zero-point corrections) of ring-closed isomers and byproducts, relative to the corresponding ring-open isomers, as obtained from DFT calculations at the B3LYP/6-31G(d) level of theory. Calculations were also performed on the hypothetical derivatives **1i**, **2d**, and **3c**.

stabilities in the excited state and reaction barriers will be needed to rationalize the experimental trends.

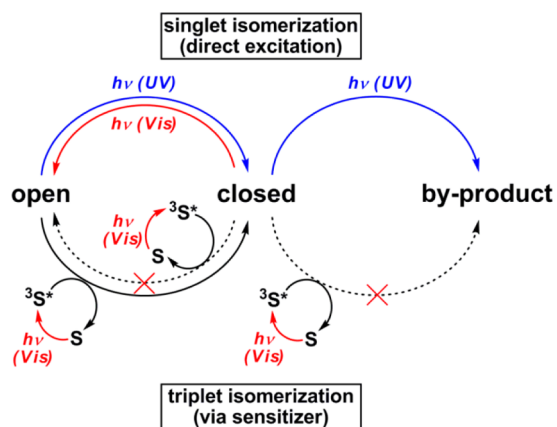
**Byproduct Formation via Triplet Excited States?** From the theoretical standpoint,<sup>12</sup> it seems possible that byproduct formation is induced by intersystem crossing of the excited state, facilitated by the presence of sulfur atoms, and subsequent relaxation of the triplet species to a different conical intersection than that leading to ring opening. To address this question, the fatigue behavior of compound **1c** in the presence of triplet sensitizers was investigated. It is well known in the literature that diarylethenes covalently bound to diverse transition metal complexes undergo efficient ring closure via metal-to-ligand charge-transfer (MLCT) excitation, subsequent intersystem crossing, and transfer of the triplet energy to the photochromic core.<sup>37</sup> In an intermolecular fashion, cyclization of a diarylethene via its triplet state has been achieved using xanthone as an organic sensitizer.<sup>38</sup> In our work, we chose butane-2,3-dione (biacetyl, **BA**) as an intermolecular sensitizer undergoing quantitative intersystem crossing ( $\Phi_{\text{ISC}} = 1$ <sup>39</sup>). It can be selectively excited at 405 nm in the presence of the ring-open or ring-closed isomers of **1c**. Although its absorption is red-shifted relative to that of the ring-open isomer of **1c**, the triplet energy of **BA** is within the range of the triplet energy of **1c**<sub>open</sub>, which was estimated by TD-DFT calculation (Table S3). Thus, effective triplet energy transfer from **BA** to the ring-open isomer of **1c** can be expected.

In fact, irradiation of a thoroughly degassed mixture of **1c**<sub>open</sub> and excess **BA** in acetonitrile with 405 nm light results in efficient formation of the ring-closed isomer (Figure S26). Importantly, when irradiating **1c** alone or the mixture of **1c** and **BA** in the presence of oxygen, no changes in the absorption spectra can be observed. A significant difference in the rate of conversion can be observed comparing a sample that was thoroughly degassed by freeze–pump–thaw cycles and one that was only treated with a stream of argon for 10 min (Figure S28a). The observed impact of traces of oxygen and the fact that, in the presence of the ring-open isomer of **1c**, the phosphorescence of **BA** is quenched (Figure S27) prove the involvement of triplet species and the efficient energy transfer from the **BA** moiety to the diarylethene. Due to the low absorbance of **BA**, the absolute rate of conversion to the ring-closed isomer via the triplet pathway is relatively low compared to that of the isomerization of **1c** alone with 313 nm light (Figure S28a). However, determination of an effective quantum yield for the cyclization

at 405 nm with the initial slope method gave a surprisingly high value of  $\Phi_{\text{AB,eff}} = 0.40$ . Of course, this value is highly dependent on concentrations, light intensity, and triplet lifetimes due to the bimolecular triplet energy-transfer process. Nevertheless, the fact that the effective quantum yield of the sensitized ring closure in this experiment is as high as the quantum yield for ring closure by direct excitation with 313 nm light ( $\Phi_{\text{AB}} = 0.43$ , see Table 1) shows that the cyclization reaction of **1c** within the triplet state is highly efficient. Kinetic traces recorded during irradiation of **1c** alone with 313 nm light, and of the mixture of **1c** and **BA** with 405 nm light, both show the emergence of a (pseudo)PSS with a subsequent decrease of the absorbance in the visible range. However, UPLC analysis of the irradiated samples reveals that the byproduct is exclusively formed upon excitation with 313 nm light (Figure S28b). Note that the decrease in absorbance during the sensitized cyclization can be attributed to residual traces of oxygen in the degassed solution, being transformed into singlet oxygen by the sensitizer and thus unspecifically degrading the diarylethene.

In a second experiment, methylene blue (**MB**,  $\Phi_{\text{ISC}} = 0.52$ <sup>39</sup>) was used to sensitize the formation of the triplet selectively for the ring-closed isomer of **1c**, whose triplet energy was calculated to lie far below that of **MB** (Table S3). Importantly, **MB** can be selectively excited at longer wavelengths than **1c**<sub>closed</sub>, thus preventing (singlet) resonance energy transfer. As expected, during irradiation of a mixture of **1c**<sub>open</sub> and **MB** or a mixture of **1c**<sub>closed</sub> and **MB** with 654 nm light, no changes in the absorbance spectra could be observed (Figure S29). While triplet energy transfer from **MB** to **1c**<sub>open</sub> is not possible, and thus no reaction can take place, the latter result points to the inability of the triplet excited state of the ring-closed isomer either to undergo ring opening or to form the byproduct. For the ring-opening reaction, this has been attributed earlier to the presence of a barrier on the triplet reaction pathway.<sup>37b</sup> From the photochemistry of the singlet excited state of the ring-closed isomer, it can be deduced that the barrier for byproduct formation is even higher than the barrier for ring opening,<sup>12</sup> as excess energy in terms of excitation with UV light is needed. In analogy to ring opening, byproduct formation in the triplet excited state following the same pathway would not be expected. The singlet and triplet pathways for the isomerization and byproduct formation of diarylethenes are summarized in Scheme 4.

**Scheme 4.** Singlet and Triplet Pathways for the Isomerization and Byproduct Formation of Diarylethenes (S = Triplet Sensitizer)





These results show that the sensitized cyclization of a diarylethene via its triplet state, in combination with low-energy excitation of the ring-closed isomer for the reverse ring-opening reaction, may represent an alternative way to guarantee high fatigue resistance while efficiently operating the switch, given that strict oxygen-free conditions are applied.

## CONCLUSION

A detailed investigation of the photochemistry of a series of diarylethenes, systematically varying the nature of the hetaryl moieties, the substituents on the adjacent phenyl rings, and the bridging moiety, allowed for the identification of the previously known annulated byproduct as the major source of fatigue appearing ubiquitously over the broad range of structures. Photokinetic measurements and evaluation of quantum yields for the elementary photochemical processes revealed a strong dependency of the rate of byproduct formation on the electronic properties of the substituents. It appears that when more and stronger electron-accepting units are introduced to the parent structure, less fatigue due to formation of the annulated isomer is observed. While the stabilizing effect of the perfluorocyclopentene compared to perhydrocyclopentene bridge was recognized earlier, we found that, in the latter structures, an equally high fatigue resistance can be imparted by substitution with 3,5-bis(trifluoromethyl)phenyl groups. By exchanging  $\text{CF}_3$  with  $\text{SF}_3$  groups, a further improvement can be observed, making compound **2i** the diarylethene structure with the highest fatigue resistance in our hands thus far. Importantly,  $\text{CF}_3$  or  $\text{SF}_3$  groups are chemically inert, and their introduction into diarylethenes does not alter their efficient isomerization between the ring-open and ring-closed isomers.

While our results show a clear correlation between the electronic nature of the substituents and the fatigue behavior of diarylethene photochromes, they are only phenomenological at the current point. From a mechanistic standpoint, substitution of the diarylethene core with donor or acceptor groups may alternate the relative stability of intermediates or transition-state structures on pathways leading to either ring-opening or byproduct formation after excitation of the ring-closed isomer.<sup>12</sup> However, for obtaining a deeper understanding, the observation of byproduct formation using time-resolved spectroscopic techniques together with a theoretical rationalization supported by high-level quantum mechanical calculations of the excited-state potential energy surface will be needed.

On the basis of our experimental results, we propose a strategy for imparting excellent fatigue resistance to diarylethenes while allowing a high flexibility in the choice of the components out of which the photochromic system may be assembled. Non-symmetrically substituted derivatives **5a** and **5b** show that it is sufficient to substitute one hetaryl ring with a 3,5-bis(trifluoromethyl)phenyl group, leaving the other aryl ring and the bridging moiety of the diarylethene structure open to modifications. Notably, the reported compounds demonstrate that the performance of dithienylperhydrocyclopentenones, which typically show a low reversibility in their switching behavior, can be massively improved. Experiments using an organic sensitizer to induce the cyclization reaction of the ring-open isomer via its triplet state revealed that the byproduct is not formed at all under these conditions, rendering triplet-sensitized isomerization an attractive alternative for the operation of diarylethenes.

## ASSOCIATED CONTENT

### Supporting Information

Details on synthesis and characterization; photochemical and electrochemical procedures; NMR spectra, UV/vis spectra, and cyclic voltammograms of all compounds; and details on quantum mechanical calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*sh@chemie.hu-berlin.de

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) (a) Göstl, R.; Senf, A.; Hecht, S. *Chem. Soc. Rev.* **2014**, *43*, 1982–1996. (b) Neilson, B. M.; Bielawski, C. W. *ACS Catal.* **2013**, *3*, 1874–1885. (c) Stoll, R. S.; Hecht, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 5054–5075.
- (2) (a) Raymo, F. M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14840–14850. (b) Fukaminato, T. *J. Photochem. Photobiol., C* **2011**, *12*, 177–208. (c) Cusido, J.; Deniz, E.; Raymo, F. M. *Eur. J. Org. Chem.* **2009**, *2009*, 2031–2045. (d) Heilemann, M.; Dedecker, P.; Hofkens, J.; Sauer, M. *Laser Photon. Rev.* **2009**, *3*, 180–202.
- (3) (a) Szymański, W.; Beierle, J. M.; Kistemaker, H. A. V.; Velema, W. A.; Feringa, B. L. *Chem. Rev.* **2013**, *113*, 6114–6178. (b) Natali, M.; Giordani, S. *Chem. Soc. Rev.* **2012**, *41*, 4010–4029. (c) Yagai, S.; Kitamura, A. *Chem. Soc. Rev.* **2008**, *37*, 1520–1529.
- (4) (a) Kim, T.; Zhu, L.; Al-Kaysi, R. O.; Bardeen, C. J. *ChemPhysChem* **2014**, *15*, 400–414. (b) Bleger, D.; Yu, Z.; Hecht, S. *Chem. Commun.* **2011**, *47*, 12260–12266.
- (5) (a) Orgiu, E.; Samorì, P. *Adv. Mater.* **2014**, *26*, 1827–1845. (b) Shallcross, R. C.; Zacharias, P.; Köhnen, A.; Körner, P. O.; Maibach, E.; Meerholz, K. *Adv. Mater.* **2013**, *25*, 469–476. (c) Tsuboi, T.; Irie, M. *J. Photochem. Photobiol., C* **2010**, *11*, 1–14.
- (6) (a) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. *Chem. Rev.* **2014**, *114*, 12174–12277. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
- (7) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206–207.
- (8) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. *Chem. Commun.* **1999**, 747–750.
- (9) (a) Shoji, H.; Kobatake, S. *Chem. Commun.* **2013**, *49*, 2362–2364. (b) Liu, H.-h.; Chen, Y. *New J. Chem.* **2012**, *36*, 2223–2227. (c) Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, *29*, 1358–1359.
- (10) (a) Hirose, T.; Inoue, Y.; Hasegawa, J.-y.; Higashiguchi, K.; Matsuda, K. *J. Phys. Chem. A* **2014**, *118*, 1084–1093. (b) Harvey, E. C.; Areephong, J.; Cafolla, A. A.; Long, C.; Browne, W. R.; Feringa, B. L.; Pryce, M. T. *Organometallics* **2014**, *33*, 447–456. (c) Sakano, T.; Imaizumi, Y.; Hirose, T.; Matsuda, K. *Chem. Lett.* **2013**, *42*, 1537–1539. (d) Ikeda, H.; Sakai, A.; Kawabe, A.; Namai, H.; Mizuno, K. *Tetrahedron Lett.* **2008**, *49*, 4972–4976. (e) Sevez, G.; Gan, J.; Pan, J.; Sallenave, X.; Colin, A.; Saadoui, H.; Saleh, A.; Vögtle, F.; Pozzo, J.-L. *J. Phys. Org.*

- Chem.* **2007**, *20*, 888–893. (f) Peters, A.; Branda, N. R. *Adv. Mater. Opt. Electron.* **2000**, *10*, 245–249. (g) Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2389–2394.
- (11) Ikeda, H.; Kawabe, A.; Sakai, A.; Namai, H.; Mizuno, K. *Res. Chem. Intermed.* **2009**, *35*, 893–908.
- (12) Mendive-Tapia, D.; Perrier, A.; Bearpark, M. J.; Robb, M. A.; Lasorne, B.; Jacquemin, D. *Phys. Chem. Chem. Phys.* **2014**, *16*, 18463–18471.
- (13) de Jong, J. J. D.; Lucas, L. N.; Hania, R.; Pugzlys, A.; Kellogg, R. M.; Feringa, B. L.; Duppen, K.; van Esch, J. H. *Eur. J. Org. Chem.* **2003**, *2003*, 1887–1893.
- (14) Patel, P. D.; Mikhailov, I. A.; Belfield, K. D.; Masunov, A. E. *Int. J. Quantum Chem.* **2009**, *109*, 3711–3722.
- (15) (a) Jeong, Y.-C.; Park, D. G.; Kim, E.; Ahn, K.-H.; Yang, S. I. *Chem. Commun.* **2006**, 1881–1883. (b) Jeong, Y.-C.; Yang, S. I.; Kim, E.; Ahn, K.-H. *Tetrahedron* **2006**, *62*, 5855–5861.
- (16) (a) Asadirad, A. M.; Boutault, S.; Erno, Z.; Branda, N. R. *J. Am. Chem. Soc.* **2014**, *136*, 3024–3027. (b) Neilson, B. M.; Bielawski, C. W. *Chem. Commun.* **2013**, *49*, 5453–5455. (c) Neilson, B. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2012**, *134*, 12693–12699. (d) Lemieux, V.; Spantulescu, M.; Baldrige, K.; Branda, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 5034–5037.
- (17) (a) Nakashima, T.; Kajiki, Y.; Fukumoto, S.; Taguchi, M.; Nagao, S.; Hirota, S.; Kawai, T. *J. Am. Chem. Soc.* **2012**, *134*, 19877–19883. (b) Fukumoto, S.; Nakashima, T.; Kawai, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 1565–1568.
- (18) (a) Göstl, R.; Hecht, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 8784–8787. (b) Cahová, H.; Jäschke, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 3186–3190.
- (19) Szalóki, G.; Pozzo, J.-L. *Chem.—Eur. J.* **2013**, *19*, 11124–11132.
- (20) Herder, M.; Utecht, M.; Manicke, N.; Grubert, L.; Pätzl, M.; Saalfrank, P.; Hecht, S. *Chem. Sci.* **2013**, *4*, 1028–1040.
- (21) Hiroto, S.; Suzuki, K.; Kamiya, H.; Shinokubo, H. *Chem. Commun.* **2011**, *47*, 7149–7151.
- (22) Orgiu, E.; Crivillers, N.; Herder, M.; Grubert, L.; Pätzl, M.; Frisch, J.; Pavlica, E.; Duong, D. T.; Bratina, G.; Salleo, A.; Koch, N.; Hecht, S.; Samori, P. *Nat. Chem.* **2012**, *4*, 675–679.
- (23) Lucas, L. N.; de Jong, J. J. D.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Org. Chem.* **2003**, *2003*, 155–166.
- (24) Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
- (25) Chung, J. W.; Yoon, S.-J.; Lim, S.-J.; An, B.-K.; Park, S. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 7030–7034.
- (26) Göstl, R.; Kobin, B.; Grubert, L.; Pätzl, M.; Hecht, S. *Chem.—Eur. J.* **2012**, *18*, 14282–14285.
- (27) Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. *Tetrahedron* **1998**, *54*, 6627–6638.
- (28) (a) Maurel, F.; Perrier, A.; Jacquemin, D. *Int. J. Quantum Chem.* **2012**, *112*, 1122–1133. (b) Jacquemin, D.; Perpète, E. A.; Maurel, F. o.; Perrier, A. I. *J. Phys. Chem. C* **2010**, *114*, 9489–9497. (c) Jacquemin, D.; Perpète, E. A.; Ciofini, I.; Adamo, C. *Acc. Chem. Res.* **2008**, *42*, 326–334.
- (29) Jacquemin, D.; Perpète, E. A.; Scuseria, G. E.; Ciofini, I.; Adamo, C. *J. Chem. Theory Comput.* **2007**, *4*, 123–135.
- (30) (a) Delbaere, S.; Vermeersch, G.; Micheau, J.-C. *J. Photochem. Photobiol., C* **2011**, *12*, 74–105. (b) Higashiguchi, K.; Matsuda, K.; Irie, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3537–3540. (c) Deniel, M. H.; Lavabre, D.; Micheau, J. C. In *Organic Photochromic and Thermochromic Compounds*; Crano, J., Guglielmetti, R., Eds.; Kluwer Academic: New York, 1999; Vol. 2, pp 167–209.
- (31) Maafi, M.; Brown, R. G. *Photochem. Photobiol. Sci.* **2008**, *7*, 1360–1372.
- (32) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309.
- (33) (a) Santos, A. R.; Ballardini, R.; Belser, P.; Gandolfi, M. T.; Iyer, V. M.; Moggi, L. *Photochem. Photobiol. Sci.* **2009**, *8*, 1734–1742. (b) Sumi, T.; Takagi, Y.; Yagi, A.; Morimoto, M.; Irie, M. *Chem. Commun.* **2014**, *50*, 3928–3930.
- (34) Sheppard, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3072–3076.
- (35) (a) Staykov, A.; Areephong, J.; R. Browne, W.; L. Feringa, B.; Yoshizawa, K. *ACS Nano* **2011**, *5*, 1165–1178. (b) Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6414–6429. (c) Guirado, G.; Coudret, C.; Hliwa, M.; Launay, J.-P. *J. Phys. Chem. B* **2005**, *109*, 17445–17459.
- (36) (a) Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; van Eikema Hommes, N. J. R. *Org. Lett.* **2001**, *3*, 2465–2468. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- (37) (a) Monaco, S.; Semeraro, M.; Tan, W.; Tian, H.; Ceroni, P.; Credi, A. *Chem. Commun.* **2012**, *48*, 8652–8654. (b) Indelli, M. T.; Carli, S.; Ghirelli, M.; Chiorboli, C.; Ravaglia, M.; Garavelli, M.; Scandola, F. *J. Am. Chem. Soc.* **2008**, *130*, 7286–7299. (c) Ko, C.-C.; Kwok, W.-M.; Yam, V. W.-W.; Phillips, D. L. *Chem.—Eur. J.* **2006**, *12*, 5840–5848. (d) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779–2792.
- (38) Murata, R.; Yago, T.; Wakasa, M. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1336–1338.
- (39) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2006; pp 83–351.