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Pronounced effects on switching efficiency of diarylcycloalkenes upon cycloalkene ring contraction†

Dmytro Sysoiev,^a Tetyana Yushchenko,^a Elke Scheer,^b Ulrich Groth,^a Ulrich E. Steiner,^a Thomas E. Exner^{*a} and Thomas Huhn^{*a}

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Several difurylperfluorocyclobutenes showing reversible photochromism were synthesized. In comparison to their cyclopentene homologues they show enhanced quantum yields for ring opening but reduced quantum yields for ring closure. X-ray structure analysis and quantum chemical calculations provide a conclusive explanation for such a behaviour.

Successful design of photochromic molecular switches requires a detailed understanding of the switching mechanism and the factors controlling it.¹ For example, fatigue resistance, optical properties and kinetics of the switching process of diarylcycloethenes are governed by the types and positions of substituents.^{1,2} For Irie-type molecular switches³ (cf. Fig. 1) positions for functionalizations are mainly the bridging unit A,⁴ the heteroatom in the 5-membered-ring (X = CH₂, S, O, NH),⁵ the substituents Y at the reactive center,⁶ and the more peripheral substituents R.⁷ Whereas wide variations of R and X have been applied for rational design and tuning of photochemical properties, the substituent Y is usually restricted to the methyl group, and the structural element A to a 5- or 6-membered ring.

Most photochromic diarylcycloalkenes described so far are based on the dithienylperfluorocyclopentene core (A = (CF₂)₃, X = S, Y = CH₃).^{1a,3,8} Many of them show high quantum yields

for ring closure, high fatigue resistance under multiple switching and thermal irreversibility of the switching process. Only a limited number of studies dedicated to diarylcyclobutenes are known. They are mostly based on squaric acid and its derivatives as ring A building blocks.⁹ Recently, we synthesized a series of difurylperfluorocyclopentene (C5F₉)¹⁰ derived photochromic molecules, with X = O, so that unspecific bond formation of the thiophene sulphur to metal contacts in molecular electronics applications is avoided.¹¹ Structural variations were restricted to heteroatoms in R-group substituents extending the π -system.¹² Upon irradiation with UV-light, these systems showed high quantum yields for switching from the open to the closed form, while the reverse photoreaction, a cycloreversion under visible light, proceeded with very low quantum yields in the case of R-substituents with an extended π -system. This asymmetry of the quantum yield represents a major drawback for the application of these species in optoelectronic applications. Therefore, we became interested in exploring the effects of cyclobutene as a ring A building block which might facilitate the opening reaction due to an anticipated higher ring-tension of the closed form. Perfluorocyclobutene was chosen in order to decrease the possibility of (2 + 2)-cycloaddition of air oxygen at the double bond of the central ring compared with nonfluorinated ones and an anticipated higher thermal stability which becomes significant in continuous illumination experiments.¹³

Herein we report the synthesis and switching properties of hitherto unknown perfluorocyclobutene-derived bisfurylethenes. Based on combined synthetic, spectrokinetic, and theoretical studies we demonstrate a systematic enhancement of the photochemical quantum yield of ring opening by reducing the size of ring A from 5 to 4 atoms. Such a behaviour makes bisfurylcyclobutenes interesting candidates for further studies in molecular electronics.

Starting from 4-bromo-5-methyl-2-furaldehyde neopentyl acetal,¹⁴ lithiation and subsequent reaction with perfluorocyclobutene yielded neopentyl acetal C4F-NPA (**1**) (Scheme 1). Deprotection of **1** in a tetrahydrofuran–acetone mixture by slowly adding concentrated hydrochloric acid at 10–15 °C gave dialdehyde **2** in 90% yield. Synthesis of the π -conjugated methylthiosemicarbazone C4F-MTSC (**3**) and thiosemicarbazone C4F-TSC (**4**) was achieved in 94% and 91% yield, respectively, by azomethine formation with dialdehyde **2** and the respective hydrazine derivatives in boiling ethanol, catalyzed by acetic acid.¹⁵ As a reference compound for assessing the influence of the heteroatom on the

Fig. 1 Schematic representation of photochromic-switching of a diarylcycloalkene. Positions of possible structural variations are marked A, R, X, and Y.

^a Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany. E-mail: thomas.exner@uni-konstanz.de, thomas.huhn@uni-konstanz.de

^b Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany

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Scheme 1 Synthesis of photochromic diarylcyclobutenes with varying π -conjugated side chains. *Reagents and conditions:* (i) *t*-BuLi, -78°C , then PF-cyclobutene; (ii) H^+ , THF-Acet., 10 – 15°C ; (iii) $\text{MeS}(\text{C}=\text{NH})\text{N}_2\text{H}_3$, MeOH, room temp.; (iv) $\text{H}_2\text{N}(\text{C}=\text{S})\text{N}_2\text{H}_3$, MeOH, room temp.

optical and photokinetic properties, thiophene derivative **5** was also synthesized. Starting from 4-bromo-5-methylthiophene-2-carbaldehyde neopentyl acetal,¹⁶ **5** was prepared in 69% yield using the analogous procedure as for aldehyde **2**.

To analyze the effect of the perfluorocyclobutene ring on the structure of the newly synthesized diarylethenes, X-ray diffraction analysis of **1**, **2** and **5** was performed (*cf.* ESI†). Suitable crystals of C4F-NPA (**1**) were grown from a saturated solution of **1** in *n*-hexane at -20°C while **2** was crystallized from CHCl_3 by slow evaporation. Both, **1** and **2** crystallize as pairs of atropisomers and adopt a conformation of C_2 -symmetry in the solid state. With the reactive carbon centers C10/C19 (**1**) and C5/C15 (**2**) 6.00 – 6.10 Å apart (Fig. 2, left), **1** and **2** are incapable of switching in the solid state. The distance of the olefin α -atoms (C9, C16) in **1** (3.43 Å) and (C4, C11) in **2** (3.48 Å), as well as the dihedral angle C9–C12–C13–C16 (9.4 – 12.5°) for both atropisomers of **1** and **2**, compare very well with the data reported for the squaric acid derivatives.^{9b,c} While the torsion angle is quite similar in the C5F-homologue, the distance between the olefin α -atoms is distinctly shorter (3.25 Å) in the latter (*vide infra*).¹² Single-crystals of thiophene derived C4F-T-CHO (**5**) were grown by slow recrystallization from chloroform. This compound adopts the reactive conformation in the solid, with the aldehyde groups pointing away from the cyclobutene core and the reactive carbon atoms C5 and C5ⁱ in close proximity (Fig. 2, right). The dihedral angle C4–C7–C7ⁱ–C4ⁱ (9.19°) as well as the distance between the reactive carbon atoms C5 and C5ⁱ (3.90 Å) are larger than in the 5-ring homologue C5F-T-CHO (6.2° , 3.60 Å).¹⁷ This is a consequence of the smaller size of the alkene ring in **5** compared to its C5-homologue. The distance between olefin α -atoms C4–C4ⁱ amounts to 3.58 Å in **5** and is comparable

Fig. 2 Molecular structure of difurylperfluorocyclobutene **2** (left) and dithienyl perfluorocyclobutene **5** (right). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

with corresponding distances in **1** and **2** but it is much longer than in the hexafluorocyclopentene C5F-T-CHO (3.24 Å).

All difurylperfluorocyclobutenes showed reversible photochromism when irradiated in solution. The open forms have their first absorption bands around 300 nm. For the π -conjugated derivatives **3** and **4** this band is shifted by 30 nm to longer wavelengths. The closed forms absorb in the visible region and are deeply colored (for UV/Vis spectra, absorption spectra and spectrokinetic measurements *cf.* ESI†).

In Table 1, the quantum yields of the difurylperfluorocyclobutenes are compared with those of corresponding difurylperfluorocyclopentenenes. For the NPA substituted compounds with a saturated substituent of the base chromophore, the only effect is a moderate decrease of the quantum yield of ring closure on going from C5F to C4F. For the compounds with π -substituents, however, the changes are quite pronounced. In comparison to the C5F compounds the C4F-derived molecules show reduced quantum yields for ring closure, but enhanced quantum yields for ring opening, although the latter effects are less pronounced.

As generally observed,^{2a,3,12} in compounds of the C5F-type, the quantum yields of ring opening drop to quite low values when extending the π -system by unsaturated substituents. These observations have been assigned to a less reduced anti-bonding nature of the central photogenerated C–C bond in the excited singlet state³ and/or enhanced radiationless decay due to the higher degree of rotational flexibility in a more extended π -system.¹² The present results show the same trend for the quantum yield of ring opening in the C4F-compounds, although their absolute values are by a factor of 2–3 larger than for the corresponding C5F-compounds. On the other hand, extended π -conjugation has little effect on the quantum yields of ring closure in the C5F-compounds but causes a huge decrease in the quantum yields of ring closure in the C4F-compounds. Altogether, these findings reveal the important role of ring tension in the [4,6]-ring system, which supports the opening of the cyclohexadiene ring in the closed form but impedes its closing in the open form.

To address this point in more detail, quantum chemical calculations using the CASSCF method¹⁹ of the ground S_0 and excited S_1 states were performed for compounds C4F-CHO and C5F-CHO with the shortest extension of the π -system (Fig. 3). Details of these calculations can be found in the ESI.† From the S_1 closed state (H) up to the transition state (G) the picture is almost indistinguishable for both molecules. Energy uptake by the vertical excitation is sufficient to overcome the

Table 1 Photochemical quantum yields for ring-opening and closing reactions of C4F- vs. C5F-diarylcycloalkenes^a

π -Substituent	$\phi_{o \rightarrow c}$ (313 nm)		$\phi_{c \rightarrow o}$ (λ_2 [nm])	
	C4F-	C5F-	C4F-	C5F-
NPA	14	20	8.6 (438)	9.0 (438)
CHO	1.0 ^b	34 ^b	46 (576) ^b	14 (576) ^b
T-CHO	2.6 ^b	86 (351) ^c	8.8 (576) ^b	3.6 (514) ^c
TSC	0.024	28 ^d	2.4 (576)	0.49 (576) ^d
MTSC	0.039	38 ^d	1.0 (576)	0.32 (576) ^d

^a In %, given with a precision of two significant digits, solvent CHCl_3 , unless stated otherwise; for details of the photokinetics and UV/vis spectra see ESI; ^b Solvent CH_3CN . ^c Solvent toluene. ^d Solvent MeOH.¹²

Fig. 3 Energy profiles of the ground (S_0) and excited S_1 states of C4F-CHO (green) and C5F-CHO (red) obtained as relaxation paths following the steepest descent. The C5-C5' distance is used as a representative coordinate to specify the molecular conformations. Points marked A and B (B') represent the energy minima of the S_0 states of closed and open forms, respectively, of C5F-CHO (C4F-CHO), C represents the transition state on the S_0 surface. For both, C4F and C5F, the energy of the global minimum H, representing the relaxed closed S_1 state, was taken as the zero value of the energy scale. The encircled points marked X (X') represent conformations where relaxation mainly changed coordinates other than the C5-C5' distance. For further details, especially on the (meta)stable points C to H and X of the S_1 surface, cf. text.

barrier easily. Therefore, the higher quantum yield of ring opening for C4F cannot be explained by a smaller reaction barrier. In contrast, larger differences are seen on the side of the open form. While in C4F the S_1 energy landscape is almost flat for C5-C5' (atom numbering cf. Fig. 2 right) distances between 2.3 and 3.8 Å, a significant energy increase is seen for C5F when the two atoms are forced further away from each other. We therefore expect that all C4F molecules, which have overcome the activation barrier (G) starting from the closed Franck Condon state (D), move freely towards the open state on the S_1 landscape and can reach the S_0 state by radiationless deactivation. In C5F, most of the molecules will be reflected back to the closed form since they have to move uphill in energy if they follow the reaction coordinate further towards the conformation of the open form.

The steeper energy landscape of C5F may also account for the much better efficiency of ring closure in these compared to the C4F compounds. Upon vertical excitation (E), after an initial relaxation to an intermediate conformation X, in which the C5-C5' distance is still close to its value in the S_0 state of the open form, the open form of C5F will further relax to the local minimum (F) and can easily overcome the flat transition state maximum (G) to reach the global minimum (H) of the closed form (see animation in the ESI†). Differently from C5F, the open form of C4F relaxes to a significantly lower minimum (X). From there, the molecule has to explore the flat energy landscape until it finds the global minimum (H) of the closed form. This process resembles the diffusion of a particle through a medium. While this random search for the minimum is going on, there is a high chance of radiationless deactivation into the S_0 state with a subsequent relaxation to the open form.

It is important to note that according to the experimental results (cf. Table S1, ESI†), as well as the quantum chemical calculations, the size of the ring anellated to the central C-C bond has almost no influence on the vertical energy separation of S_0 and S_1 states in the open and in the closed form. Thus, different rates for the opening and closing reactions have to be fully attributed to the different

relaxation energies in the excited S_1 state of the open form impeding photocyclization but enhancing, photo-induced ring opening in C4F compared to C5F. These pronounced effects show that central-ring modification might provide a strategy towards rational design of molecular switches showing a more symmetric switching behaviour.

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