Towards multifold cycloswitching of biphotochromes: investigation on a bond-fused dihydroazulene/vinylheptafulvene and dithienylethene/dihydrothienobenzothiophene

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The concept of molecular switching within a *cyclic* four-stage process is introduced on the basis of two structurally fused photochromic systems (A–D). The synthesis of 1,8a-dihydro-2,3-bis(2,5-dimethyl-3-thienyl)azulene-1,1-dicarbonitrile (open/closed A) is described; irradiation with UV light leads to an equilibrium of open/open B, open/closed A and closed/closed C, whereas B is thermally rearranged to A by ring closure of the vinylheptafulvene substructure.

The photochromes dihydroazulene (**DHA**)/vinylheptafulvene (**VHF**)[1] and dithienylethene (**DTE**)/dihydrothienobenzothiophene (**DHB**)[2] are based on all-carbon cyclizations, which differ in the number of participating bonds. **DHA/VHF** uses a five-bond and **DTE/DHB** a three-bond cyclization. The light-induced reversible isomerization reactions between open and closed forms have been intensively studied,[3] both systems were also optimized for multimode switching, *e.g.* redox-switch,[1e,2b] fluorescent switch.[1d,2d] From a mechanistic point of view both systems differ in that **DHA/VHF** has a photochemical forward and a thermal back-reaction, whereas in **DTE/DHB** both isomerizations occur photochemically.

There are no reports of biphotochromic systems containing both systems structurally condensed and therefore strongly coupled as shown in Scheme 1.[4] Photochrome **A**, for example, which contains **DTE** and **DHA** substructures fused by a common double bond, represents an energy minimum on a closed circuit established by the four photochromes **A**–**D**. A manifold of independent switching arises, which is likely to be controlled by substituents or functional units. Multimode switches, as shown in Scheme 1, are of interest for information handling at the molecular level.[2c,3,5] Here we report on the synthesis of the open/closed **A** (R[1] = R[2] = CH$_3$) and demonstrate the reversible interconversion of **A** into isomers **B** and **C**.

The synthesis[6] of **A** is shown in Scheme 2; the synthetic and analytical details will be published elsewhere.

(*Z*)-1,2-Bis(3-thienyl)ethenes[2a] are known to form stable atropisomers with perpendicular arrangement of ethene and thiophene substructures thus leading to three stereoisomers (a *meso* form with mirror symmetry and two enantiomeric forms with C_2 symmetry). Isomer **A** may give rise to eight stereoisomers consisting of four enantiomeric pairs of diastereomers due to the additional chiral center at C-8a.[1a,f] The ^{1}H-NMR at −50 °C (Fig. 1, top) reveals a 2:1 mixture of two atropisomers indicated by four pairs of singlets due to the thiophene's methyl groups: δ (stereoisomer 1) = 1.68, 1.80, 2.38, 2.46; δ (stereoisomer 2) = 1.77, 2.00, 2.34, 2.45. At room temperature the ^{1}H-NMR displays broadening of the methyl signals which is in agreement with fast equilibrating rotational isomers. We assume that the π–π repulsion of the neighbouring thiophenes favors the two stereoforms with pseudo-C_2 symmetry leading to two diastereomeric forms due to the chiral center at C-8a.

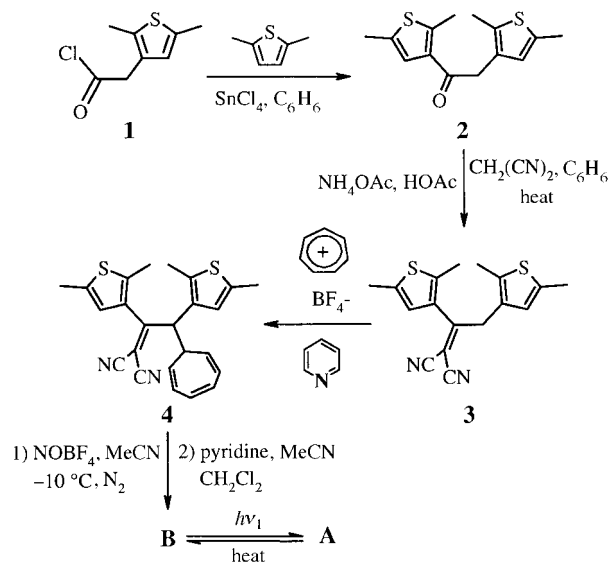UV/Vis spectroscopy gives a detailed insight into the photochromic behaviour; the photochemically induced re-arrangement was also monitored by IR (not shown) and ^{1}H-NMR. Irradiation of **A** in THF-d_8 at room temperature (quartz NMR tube, 254 nm[7a]) leads to a new compound, the structure of which is assigned to **C**. The methyl singlets at δ 1.90, 2.02, 2.20 and the doublet at δ 2.25 prove that only one isomer is formed (Fig. 1, bottom). Since the photochemical electrocyclization occurs in a conrotatory mode,[2] only one of the two pseudo-C_2 symmetric conformers will lead to the final product.

Irradiation of **C** with light $\lambda \geqslant 450$ nm[7b] restores the original spectrum of **A** completely. This clearly demonstrates the retroelectrocyclization of the 1,2-dihydrobenzene moiety of dihydrothienobenzothiophene **C**. Under the conditions of the ^{1}H-NMR experiment we could find no evidence for the formation of photochrome **B** under irradiation. This is due to the fast thermal back-reaction of the **VHF** substructure in **B** to the **DHA** form in **A**.

Irradiation with UV light, either steady-state (254, 313 or 366 nm) or pulsed (248, 308 or 354 nm),[1c] of **A** in non-polar solvents, *e.g.* cyclohexane (Fig. 2) and methylcyclohexane (MCH), leads to new strong absorption bands with maxima at
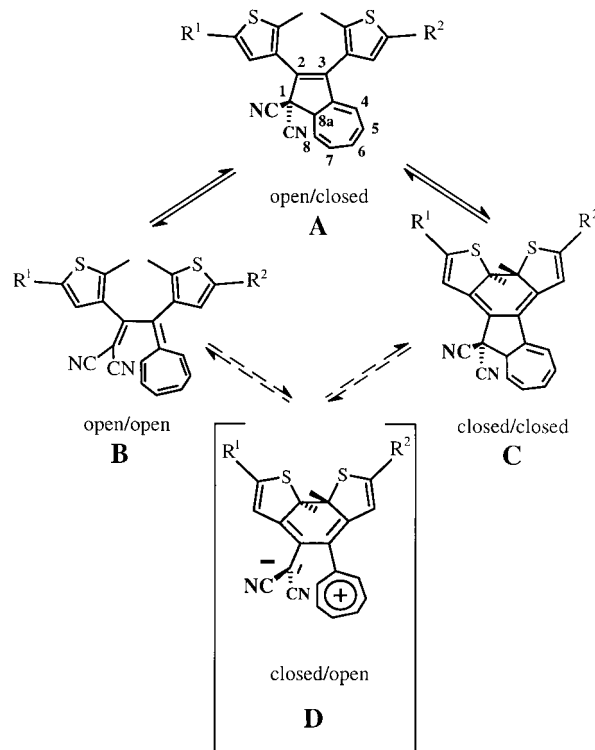
Scheme 1 Concept of a four-step cyclic process of biphotochromic compounds. The notation 'open/closed' for isomer **A** refers to the dithienyl moiety being in its 'open' state and the dihydroazulene moiety in a 'closed' one. This nomenclature is equally applied to forms **B**, **C** and **D**.

Scheme 2 Synthesis of open/closed A.

Fig. 2 Reversible irradiation of A in cyclohexane (4.4×10^{-5} mol dm^{-3}) at room temperature: A prior to (—) and after irradiation at 254 nm (----), after thermal relaxation (■) and after subsequent irradiation with visible light ($\geqslant 450$ nm), where A is restored (▲).

Table 1 Pre-exponential factor A, activation energy E_a and relaxation time $\tau_{B \rightarrow A}$ for the thermal ring-closure reaction[a]

Solvent	$A/10^{10}$ s^{-1}	E_a/kJ mol^{-1}	$\tau_{B \rightarrow A}$ s[b]	Temperature range/°C
MCH	20	82	1100	25–95
PhMe	1	70	130	25–110
DMF	100	78	30	25–130
MeCN	1	66	30	25–70
EtOH	0.5	64	25	0–70

[a] Obtained from Arrhenius plots, detection wavelength 475 nm and excitation wavelength $\lambda_{exc} = 308$ nm. [b] At 25 °C.

300, 360 and 480 nm within 10 ns. When the UV light is removed, the 300 nm peak slowly disappears and the visible band becomes less intense and is red-shifted to 510 nm. The latter findings are characteristic for VHF chromophores, which thermally revert back, reaction $\mathbf{B} \rightarrow \mathbf{A}$.[1c] For comparison and reference, typical long wavelength absorption bands of chromophores DHA, VHF, DTE and DHB in various solvents are as follows: DHA:[1] 320–380 nm; VHF:[1] 410–470 nm; DTE:[2] 250–450 nm; DHB:[2] 420–820 nm.

Similar changes within 10 ns were observed for A in PhMe and polar solvents, e.g. DMF, MeCN, MeOH or EtOH, at room temperature, where after a few seconds or some minutes only the intense 360 nm band, in addition to the broader band centered at ca. 500 nm, were observed and no further spectral changes occur on heating. This is in agreement with the formation of C in the photochemical forward step. Note that the photochemical $\mathbf{A} \rightarrow \mathbf{B}$ forward and thermal $\mathbf{B} \rightarrow \mathbf{A}$ backward steps take place in all solvents. By irradiation with visible light ($\lambda \geqslant 450$ nm), A is completely restored.

Kinetic measurements quantify the solvent effects of the thermal ring closure. They follow a first order rate process. The corresponding pre-exponential factor (A), the activation energy (E_a) and the relaxation time ($\tau_{B \rightarrow A}$) at room temperature are given in Table 1. The activation parameters are similar, but they clearly demonstrate the trend that the more polar the solvent is, the faster the thermal rearrangement proceeds.
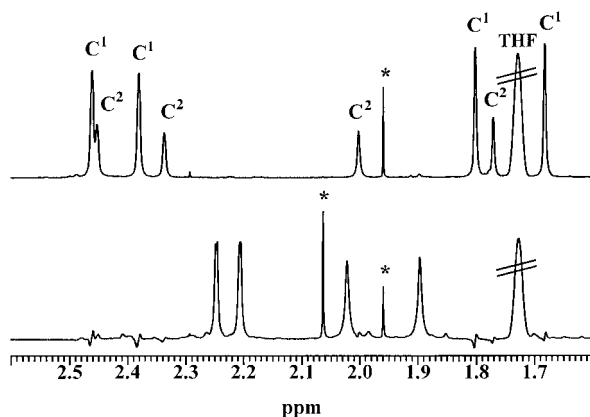
To summarize, both open/open B and closed/closed C are rapidly formed on irradiating open/closed A. B is thermally rearranged to A, and C can photochemically be reverted into A. Closed/open D has not yet been observed in the system with the substitution pattern $R^1 = R^2 = CH_3$. Appropriate donor and acceptor groups at the DTE/DHB moiety (R^1: acceptor subtituent; R^2: donor substituent) would make its formation likely.

Notes and references

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7 (a) UV-lamp (K. Benda, Laborgeräte und Ultraviolettstrahler); (b) High pressure Hg/Xe-cathode tip lamp with cut-off filter GG 455 (Schott).

Fig. 1 Irradiation experiments of A in THF-d_8 (3.8×10^{-3} mol dm^{-3}) monitored by ^{1}H-NMR spectroscopy (−50 °C), representing the methyl signals. Top: precursor isomer A before irradiation; C^1,C^2 = methyl groups of the two conformers. Bottom: A after irradiation at room temperature (254 nm) for 5 h (photoconversion: ca. 50%) and subtraction of the upper spectrum (subtraction spectr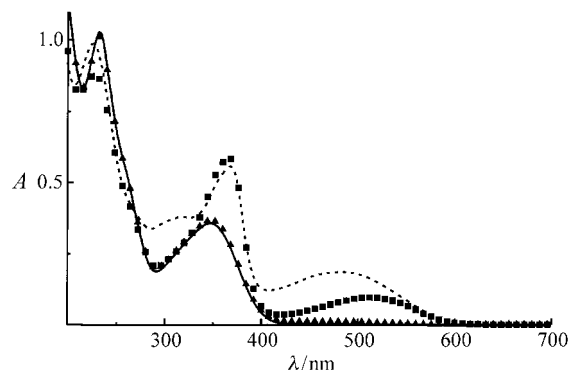um is shown). * = Unidentified signals.