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Molecular photoswitches based on spiro-acridans†

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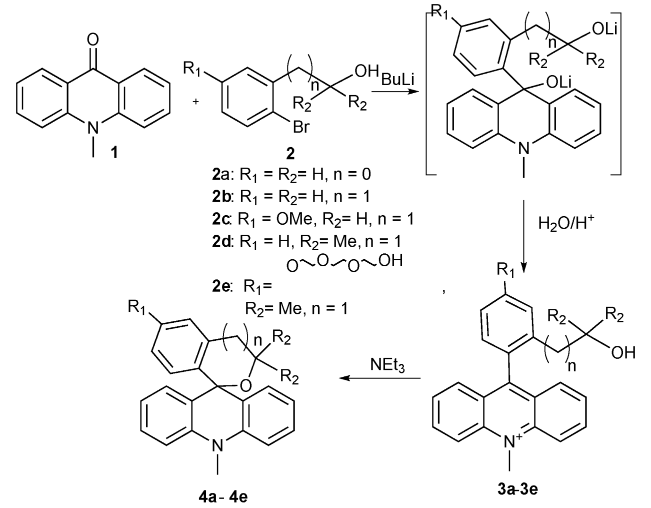
Thermally reversible photochromic spiro-acridans have been synthesized for the first time. They exhibit high ring opening efficiencies. As the formed zwitterions do not possess a merocyanine structure their lifetime is in the range of milliseconds to seconds. An observed side reaction can be avoided by suitable substitution of hydrogen atoms.

Photochromic molecules can reversibly switch between two states having different absorption spectra. A starting material is converted to a product by means of UV or visible light. The back reaction can occur thermally or photochemically.[1]

The reversible reactions performed by photoswitches are accompanied by drastic changes in properties of the compound such as the shape or the dipole moment. Electrocyclic reactions and *trans–cis* isomerization induce such changes in the molecular structure and, as a consequence, the physical properties of the species are altered. To induce mechanical movement at the molecular level is just as important.[2] Spiropyrans have been one of the most highly investigated classes of photochromic compounds. In the closed form, the two halves of the molecules are located in two perpendicular planes. The photoreaction produces a more planar zwitterionic merocyanine.[3] Rhodamine spiroamides have been used for switching fluorescent nanoscopy.[4]

We have recently introduced the 9-alkoxy-9-arylacridan (9-alkoxy-9-aryl-9,10-dihydroacridine)/9-aryl-acridinium-photoswitch for controlling the ring movement of rotaxanes.[5] The photoreaction of acridans results in the formation of an acridinium salt with an alkoxide as the counterion. The present study describes a new class of photoactive heterocyclic spiro-acridans **4** (Scheme 1) that undergo ring-opening, which results not in a salt, but in a zwitterion.

The routes employed for the synthesis of spiro-acridans are outlined in Schemes 1 and 2. *N*-Methyl-acridone **1** is reacted with organolithium precursors obtained from alcohols **2a–2e** (see Scheme 1). After acidification, the acridinium compounds are the primary products.



Scheme 1 Synthesis of spiro-acridans.

Compounds **3a–3d** were not isolated, but were transformed into spiro-acridans under basic conditions because these spiro-acridans are more easily purified using column chromatography (for details see ESI†). The corresponding acridinium salts were prepared from the spiro-acridans by reacting with an acid.

Alcohol **6** containing an amino substituent was introduced into acridinium iodide **5** according to the method developed by Chupakhin *et al.*[6] (Scheme 2).

Upon irradiation of the spiro-acridans, the furan- or pyran-ring was opened with high efficiency to form a zwitterionic acridinium compound 3_Z which does not possess a merocyanine structure (Scheme 3). The quantum yield obtained from the ring opening in MeCN–MeOH solution is relatively high (Table 1).

Because of the spiro-structure (see the crystal structure of **4a**, Fig. 1) the UV-spectra of compounds **4** were dominated by the acridan-absorption and were independent of R^1 (see Fig. 2 and Scheme 3). As 3_Z has a more planar structure, the UV-Vis spectra of the zwitterions were very similar to those of the

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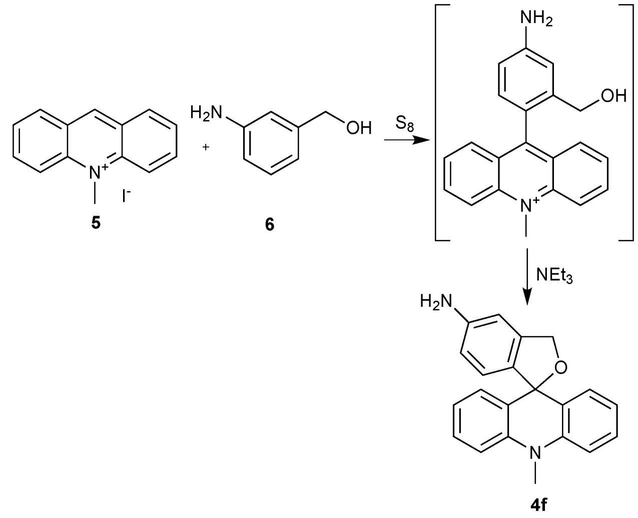
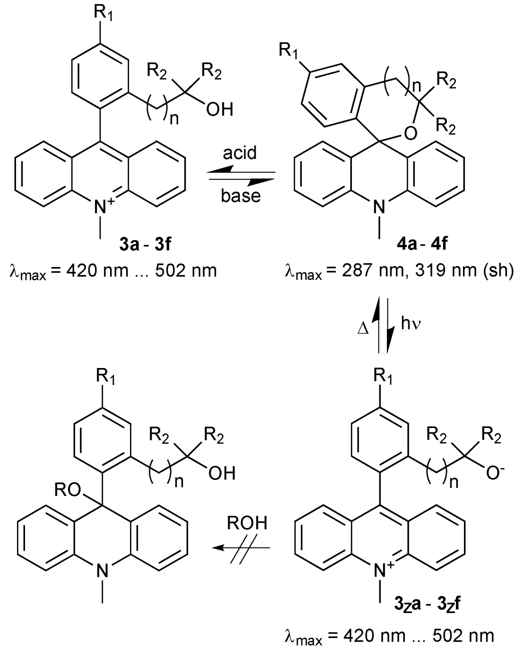
† Electronic supplementary information (ESI) available: Full synthetic details pertaining to the preparation of new compounds, crystallographic information file (CIF) for compound **4a**; and analysis of thermal back reactions (transient decay curves and absorption spectra). CCDC 919797. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41135d



Scheme 2 Synthesis of an amino-substituted spiro-acridan.



Scheme 3 Ring opening of spiro-acridans **4**.

acridinium salts **3** (Table 1). The absorption maxima of acridinium ions are dependent on the donor property of R^1.[7]

Since the stabilization by a merocyanine structure was absent, the zwitterions $\mathbf{3_Z}$ rapidly converted back to **4**, as acridinium alkoxides do.[5] The lifetime depended both on the ring size and on the solvent (see Table 1 and Fig. S1–S4, ESI†).

The presence of alcohol in the solution was necessary to obtain the reaction cycle. Obviously, the ionic path is already preformed by the solvent and the solvent plays an active role in the early stage of the ring opening process.[8] Accordingly, the question arises as to whether the reaction of the alcohol with $\mathbf{3_Z}$ is able to compete with the ring closure reaction.

NMR-spectroscopic investigations after irradiation of **4** in ethanol or methanol solution showed that the alkoxy group had not been introduced into the acridan moiety (see Scheme 3).

Table 1 Spectroscopic and kinetic data of **4** and $\mathbf{3_Z}$

	Quantum yield Φ_r MeCN–MeOH	Lifetime of $\mathbf{3_Z}$/s (solvent)	Absorption maximum $\mathbf{3_Z}$/nm	Absorption maximum **3**/nm
4a	—	0.007 (MeOH)	420	423
4b	0.5	13 (MeOH) 23 (MeCN–EtOH 1 : 1)	423	423
4c	0.4	9 (MeOH)	426	428
4d	0.3	30 (EtOH)	423	426
4e	0.5	36 (MeOH) 54 (MeCN–MeOH 4 : 1)	431	432
4f	—	0.003 (MeOH)	502	503

— Not determined.

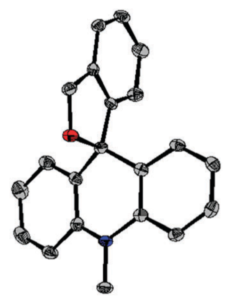


Fig. 1 Single crystal X-ray structure of compound **4a** (the hydrogen atoms have been omitted for clarity).

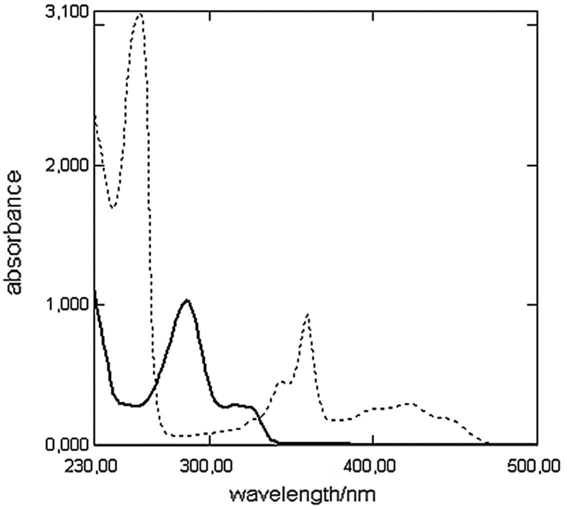
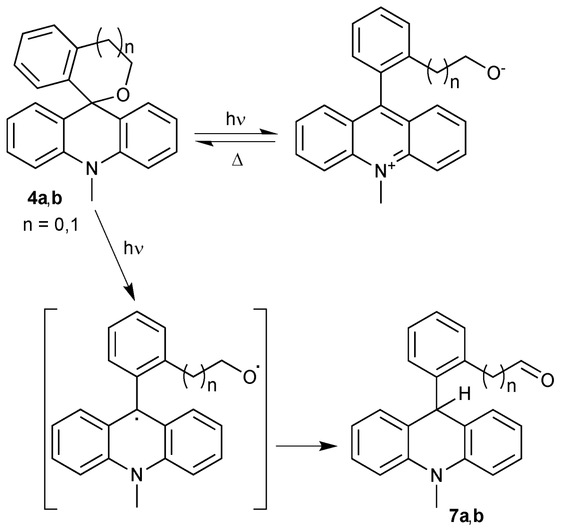


Fig. 2 UV-Vis spectra of compounds **4b** (—) and **3b** (-----) in acetonitrile solution (6×10^{-5} M).

In contrast to the 9-alkoxy-9-arylacridans studied previously,[5] the spiro-acridans were not transformed to the corresponding acridinium ions in alcoholic solution. This finding emphasized the increased thermodynamic stability of the cyclic acridans.

By repeating the switching cycle, we observed that the acridinium chromophore was recovered in diminishing amounts. By irradiation of **4a,b** in aerated methanol solution on a preparative scale, the photo-inactive 9-*H*-acridans **7a,b** could be isolated (Scheme 4).

In general, homolysis may compete with the heterolytic bond fission of the C–O-bond such as was found for xanthenol.[9] However, a recent mechanistic study of the photolysis of



Scheme 4 Proposed radical ring opening process resulting in 9-*H*-acridans **7**.

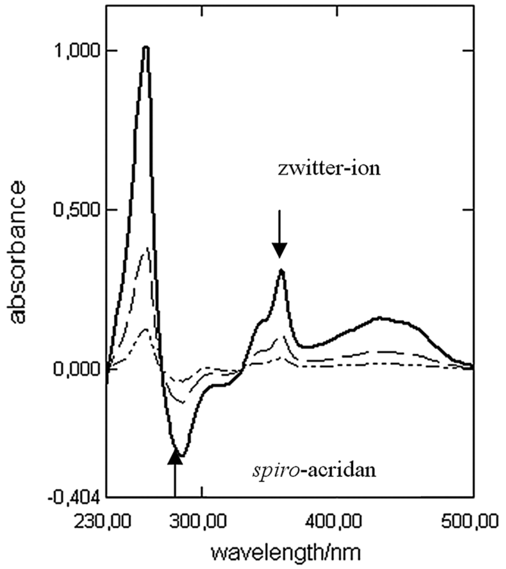


Fig. 3 Time evolution (20 s, 1 min, 3 min) of the transient UV-Vis absorption spectra of a solution of **4e** in MeCN–MeOH 4 : 1 after irradiation for 5 s (>300 nm).

9-hydroxy/9-methoxy-9-phenyl-acridan demonstrated that in methanol solution only the heterolytic bond fission occurred while in acetonitrile solution, an intersystem crossing process dominated.[10] In our system we think that homolytic and, mainly, heterolytic ring opening occurs after photoexcitation of **4a,b**. The formed biradical then undergoes hydrogen abstraction to yield **7**. Actually ESR spectra recorded after irradiation of **4a** in methanol or ethanol solution at 77 K exhibit signals of radicals formed from the solvent[11] as well as the typical ESR fine structure of a biradical. The signals disappear when the temperature is increased (see Fig. S5, ESI†).

An alternative hydride transfer from the zwitterion in the ground state[12] is unlikely, because the corresponding acridinium ions are stable in methanol solution without any decomposition. Such hydride transfer was also not found with a fluoren-9-yl cation.[13]

To avoid an irreversible hydrogen abstraction, compounds **4d** and **4e** were synthesized. With these structures, the decomposition of the dimethyl-substituted derivatives was stopped and the switching cycle could be repeated at least ten-times in solvents such as methanol and ethanol or their mixtures with acetonitrile (see Fig. S6–S8, ESI†).

For example, the transient UV-Vis absorption spectra recorded at different times after the irradiation of **4e** displayed isosbestic points which indicated the presence of only two components (see Fig. 3). Compound **4e** was synthesized in order to offer the possibility of elongating the chain for use as the molecular thread of rotaxanes.

Work is in progress to prepare rotaxanes which include the spiro-acridan unit within the molecular axle.

In conclusion, we have synthesised compounds of a novel class of photochromic molecules which show high ring opening efficiencies under UV-irradiation and rapid thermal ring closure back reactions. With a suitable substitution mode, at least ten switching cycles can be performed. The two parts of the photochromic system differ strongly not only in the absorption spectra, but also in the molecular shape.

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