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The reversible [4 + 4] photocycloaddition of acridizinium derivatives

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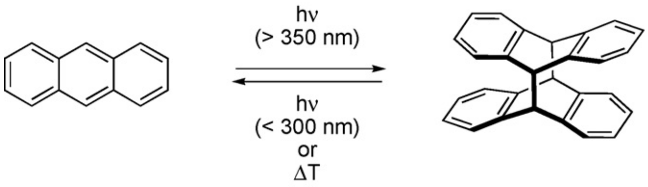
ABSTRACT

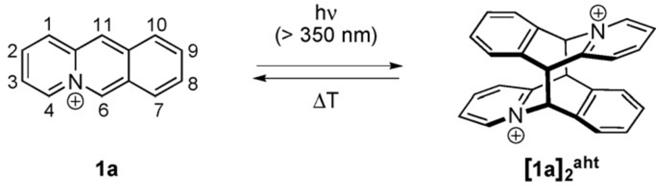
Several aspects of the photoinduced dimerization of acridizinium ions, also known as benzo[*b*]quinolizinium ions or 4a-azoniaanthracenes, are reviewed. In particular, the photochemical and photophysical studies of the [4 + 4] photocycloaddition and the cycloreversion of the corresponding acridizinium dimers in solution, in the solid state and in other organized media are presented and discussed. Examples are given for the possible application of this photochromic system for data storage or for photoinduced switching of material properties.

Anthracene derivatives are well known for their propensity to dimerize in a [4 + 4] photocycloaddition (Scheme 1) [1–6]. Notably, the anthracene photodimer may be reverted back to the monomers either thermally or by irradiation, thus establishing an efficient photochromic system. Considering the fact that the extent of the π system, especially the spectroscopic properties, change significantly upon the transformation of the monomer to the dimer, this photochromic system offers a high potential to be applied in optical switches or sensors [7–17]. Along these lines, the photochemical and photophysical behavior of anthracene derivatives was investigated in detail and is documented in several excellent review articles [1–6].



Scheme 1. Reversible photodimerization of anthracene.

The exchange of the quaternary carbon atom of anthracene with a quaternary nitrogen atom establishes the isoelectronic 4a-azoniaanthracene (**1a**), the so-called benzo[*b*]quinolizinium or acridizinium ion [18–21], which exhibits similar photochemical and photophysical behavior as anthracene. In particular, it was observed early that acridizinium ions readily undergo a reversible [4 + 4] photocycloaddition (Scheme 2) [22]. In this short review, several aspects of the photodimerization of acridizinium ions will be highlighted, and it shall be demonstrated that this class of compounds may be used complementary to anthracene derivatives to establish interesting photochromic systems based on the reversible photocycloaddition–cycloreversion sequence.



Scheme 2. Reversible photodimerization of the acridizinium ion (**1a**).

It should be noted that within this review the counter anion of the acridizinium cation is usually omitted for clarity, although identical acridizinium ions with different counter ions are treated as different compounds. In those cases, when it was demonstrated that that counter ion has a significant influence on the properties of the acridizinium, it is mentioned explicitly; and the identity of the anion is given in brackets after the corresponding compound number.

1. Photodimerization of acridizinium derivatives in solutions

The first example of the photodimerization of the acridizinium ion was reported by Bradsher et al. [22], i.e., shortly after the first acridizinium derivatives had been synthesized by the same

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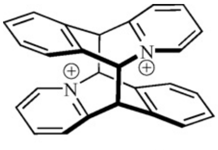
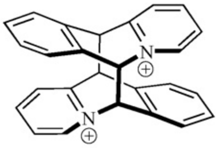
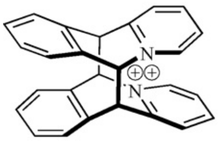
group [23]. Upon exposure to sunlight in the crystalline state, the fluorescent acridizinium bromide **1a** was converted to a non-fluorescent compound, which has the same composition as the starting material. Considering the analogy between the acridizinium ion and anthracene, it was proposed that a photodimer was formed upon irradiation (Scheme 2). Supporting evidence for this assumption was provided by the observation that the monomer **1a** was regained in 82% yield upon heating the dimer in refluxing ethanol. Interestingly, it was proposed in this early report that only one product is formed upon irradiation of the acridizinium ion (**1a**), namely the *anti*-head-to-tail dimer $[\mathbf{1a}]_2^{\mathbf{aht}}$ (the superscript in the dimer number indicates the orientation of two acridizinium moieties relative towards each other: aht = *anti*-head-to-tail; ahh = *anti*-head-to-head; sht = *syn*-head-to-tail; shh = *syn*-head-to-head). Nevertheless, to be stressed is the fact that the structure assignment was not based on spectroscopic data. It was only assumed that the product is formed with a "maximum separation between the like charges" of the two positively charged nitrogen atoms. The exclusive formation of this *anti*-head-to-tail dimer was not questioned for a long time, and even highlighted in several reviews. Nevertheless, Wolff et al. reinvestigated the regioselectivity of this reaction in detail [24]. It was demonstrated that *all* of the four possible isomeric photodimers are formed, two of which exist as pairs of enantiomers. Thus, irradiation of an aqueous solution of **1a** (c = 20 mM) with $\lambda > 300$ nm for 80 min gave the dimers $[\mathbf{1a}]_2^{\mathbf{aht}}$, $[\mathbf{1a}]_2^{\mathbf{ahh}}$, $[\mathbf{1a}]_2^{\mathbf{sht}}$, and $[\mathbf{1a}]_2^{\mathbf{shh}}$ in a ratio of 41:18:30:11 according to ^{1}H NMR-spectroscopic analysis of the reaction mixture. In particular, the shifts and the multiplicities of the signals of the bridgehead protons, as well as the ones of the aromatic protons next to the quaternary nitrogen atoms were utilized to assign the structures of the photoproducts. Especially characteristic is the multiplicity of signals of the bridgehead protons to distinguish between head-to-tail and head-to-head isomers: whereas the head-to-head isomer is expected to give a singlet in the ^{1}H NMR spectrum, the corresponding protons of the head-to-tail dimers give doublets at lower field with coupling constants of ^3J = 10–11 Hz. Although not all of the photoproducts could be separated, the photodimer $[\mathbf{1a}]_2^{\mathbf{aht}}$ was isolated by *30-fold* (!) crystallization with 93% purity (overall yield not given).



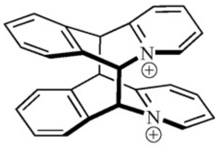
$[\mathbf{1a}]_2^{\mathrm{aht}}$



$[\mathbf{1a}]_2^{\mathrm{ahh}}$

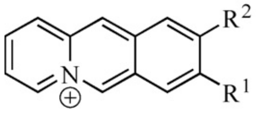


$[\mathbf{1a}]_2^{\mathrm{sht}}$



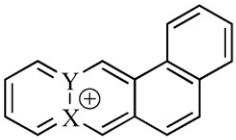
$[\mathbf{1a}]_2^{\mathrm{shh}}$

Considering the large number of available acridizinium derivatives, only a few selected derivatives have been investigated with respect to their photodimerization. Probably, the lack of regioselectivity in this photodimerization leads research teams to refrain from such studies. Indeed, the irradiation of the 9-substituted acridizinium derivatives **1b**–**d** [25] or the benzo-annelated derivatives **2a** and **2b** [26] was shown to yield all possible regioisomeric dimers, whose separation is difficult, time-consuming, and almost impossible in most cases. Moreover, sometimes the reaction cannot be completed as it reaches a photostationary state due to the photoinduced cycloreversion of the dimers under the employed conditions [26].



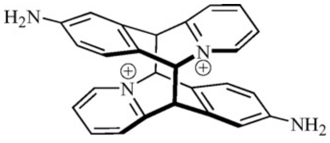
1b–f

1b : $R^1 = H, R^2 = Cl$
1c : $R^1 = H, R^2 = Br$
1d : $R^1 = H, R^2 = OMe$
1e : $R^1 = H, R^2 = NH_2$
1f : $R^1 = NH_2, R^2 = H$

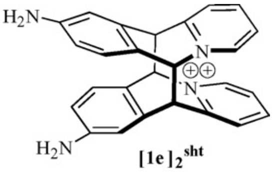


2a : X = C, Y = N
2b : X = N, Y = C

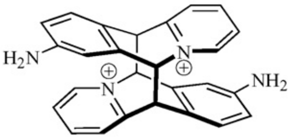
The amino-substituted acridizinium derivatives **1e** and **1f** represent exceptional cases, as the photodimerization of these compounds proceeds with improved regioselectivity [27,28]. Thus, the irradiation of a solution of 9-aminoacridizinium (**1e**) in acetonitrile gave the head-to-tail dimers $[\mathbf{1e}]_2^{\mathbf{aht}}$ and $[\mathbf{1e}]_2^{\mathbf{sht}}$ in a 1:1 ratio exclusively, as indicated by ^{1}H NMR-spectroscopic analysis, i.e., the formation of head-to-head dimers was excluded because from the product mixture only two sets of two doublets for the bridgehead protons could be detected. The *anti*-head-to-tail dimer $[\mathbf{1e}]_2^{\mathbf{aht}}$ was isolated in low yield (10%) by crystallization. The reason for this regioselectivity, which resembles the one observed for the photodimerization of 1,3-diazaanthracenes [29], is not clear so far; however, it was proposed that the photoreaction proceeds via a conical intersection with an energy minimum for a head-to-tail arrangement of two acridizinium molecules [28]. The photodimerization of 8-aminoacridizinium tetrafluoroborate (**1f**) in acetonitrile gave the head-to-tail dimer $[\mathbf{1f}]_2^{\mathbf{aht}}$ as the major product, along with smaller amounts of the corresponding two head-to-head dimers [28]. Nevertheless, the latter were found to be not persistent, i.e., the cycloreversion to the monomers takes place rapidly even at room temperature. Thus, under thermodynamic control the exclusive formation of $[\mathbf{1f}]_2^{\mathbf{aht}}$ may be achieved.



$[\mathbf{1e}]_2^{\mathrm{aht}}$

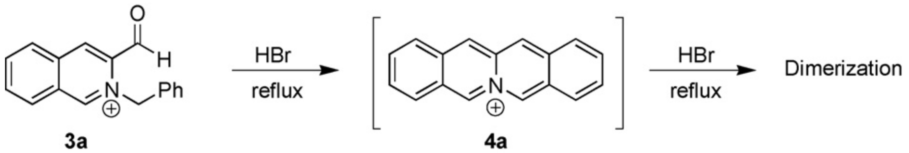


$[\mathbf{1e}]_2^{\mathrm{sht}}$



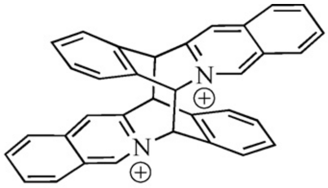
$[\mathbf{1f}]_2^{\mathrm{aht}}$

The benzo[*b*]acridizinium (**4a**), also named as 5a-azoniatetracene, represents an interesting example for an acridizinium derivative that may dimerize upon photolysis or induced by thermal reaction. The parent compound **4a** was synthesized by Bradsher and Solomons [30], and it was observed that during the acid-induced cyclodehydration of the isoquinolinium **3a**, a dimerization takes place even without the involvement of light (Scheme 3). Nevertheless, with reduced reaction times and

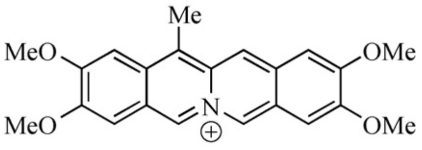


Scheme 3. Dimerization of benzo[*b*]acridizinium (**4a**) in the presence of hydrobromic acid.

isoquinolinium-3-carbaldimine as precursor, the monomer **4a** could be isolated in 23% yield, along with 35% of the dimer. Control experiments showed that either refluxing the monomer in aqueous conc. HBr or irradiation in the solid state yields identical products, as shown by mixed melting points and IR-spectroscopic analysis. Further photophysical studies on **4a** revealed that the dimers and the corresponding monomer may be reversibly interconverted upon irradiation [31]. Nevertheless, considering the four possible isomers that may be formed, it was pointed out that a structure assignment could not be made on the basis of the available physical data (no NMR) [30]. Later it was demonstrated by detailed NMR-spectroscopic analysis that the *syn*-head-to-tail dimer is formed in the thermal dimerization of compound **4a** [32]. Although there was no explanation offered so far on the mechanism of this reaction, the experiments show that the dimerization of **4a** is induced by the hydrobromic acid. This assumption is supported by the observation that the monomer **4a** may be obtained in good yields with the isoquinolinium tetrafluoroborate salt as precursor and polyphosphoric acid as the cyclization reagent [32]. Also, the benzo[*b*]acridizinium derivative **4b** was reported to be persistent, however, a detailed analysis uncovered the formation of impurities due to dimerization [33].



$[\mathbf{4a}]_2^{\mathrm{sht}}$

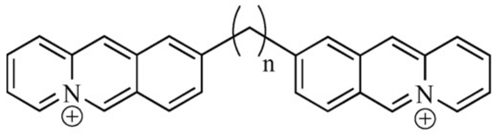


4b

2. Photophysical studies of the photodimerization of acridizinium derivatives

Bendig et al. examined the photophysical aspects of the reversible photodimerization of acridizinium ions in detail. The quantum yield of the dimerization depends on the concentration and was extrapolated to $\phi_{\mathrm{Dim}} = 0.23$ at $c \to \infty$ (in MeOH) [34,35]. In addition, it was observed by detailed kinetic analysis that fluorescence quenchers such as heavy atoms, electron donors or highly polar anions decrease the quantum yield of the photodimerization of **1a** significantly by quenching the excited state of the monomer as well as by deactivating the corresponding excimer [34]. The proposed kinetic scheme for the photodimerization involves the formation of an excimer that may deactivate by relaxation to the acridizinium ground state or by dimerization, thus resembling the reversible photodimerization of anthracene derivatives [1,2]. Further experimental support for the formation of an exciplex as reactive intermediate during the photocycloaddition of acridizinium derivatives was provided by detailed kinetic and thermodynamic analyses [36]. The acridizinium excimers are too short-lived in solution at room temperature to be detected. However, in polymer matrices at low temperature the lifetimes of the excimers increase significantly. Thus, acridizinium monomers were generated by photoinduced cycloreversion of the corresponding dimers in an ethanol matrix at low temperatures, such that the monomers remain preorganized for excimer formation in the constrained medium. Excitation of these monomers indeed leads to the formation of detectable excimers.

The quantum yield of the cycloreversion of $[\mathbf{1a}]_2$ was shown to be independent from the concentration and determined to be $\phi_{\mathrm{Cyclorev}} = 0.49$ [34]. Considering the emission lifetime of the parent acridizinium **1a** ($\tau_{\mathrm{em}} = 4.4$ ns), the quantum yield of the radiationless photophysical deactivation of the excited dimer was estimated to be $\phi_{\mathrm{Dim,relax}} = 0.36$. In a separate work, it was demonstrated that the parameters of the excitation wavelength need to be considered for the determination of the quantum yield of the cycloreversion reaction. With an improved method the quantum yields were determined for the cycloreversion of the dimers of **1a** ($\phi_{\mathrm{Cyclorev}} = 0.\ 74$ in MeOH), **1g** ($\phi_{\mathrm{Cyclorev}} = 0.76$ in MeOH) and the benzo[*b*]acridizinium (**4a**) ($\phi_{\mathrm{Cyclorev}} = 0.95$ in CH_2Cl_2) [35]. However, it should be noted that – although determined with high accuracy – these data may be used with great care; as they may be a combined data set from all possible acridizinium dimers (see discussion above).



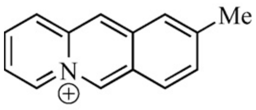
5a–g

5a : n = 1
5b : n = 2
5c : n = 3
5d : n = 4
5e : n = 5
5f : n = 6
5g : n = 8

The *intramolecular* photodimerization of two acridinizium moieties in α,ω-bis-(9-acridiziniumyl)-alkanes **5a**–**g** was investigated by absorption and emission spectroscopy (steady state and time-resolved) as well as by chemical quantum yield determination [37,38]. It was suggested that the intramolecular interaction occurs between one excited chromophore and one molecule in the ground state, and that the excimer collapses to the dimer through a pericyclic transition state, which may lead to dimerization or relaxation to the ground state of the starting materials. A systematic analysis of the absorption spectra of compounds **5a**–**g** revealed no intramolecular interaction, such as association, between the two chromophores. Upon irradiation, however, an intramolecular photocycloaddition takes place, as indicated by photometric monitoring of the reaction. Detailed photophysical studies showed that the photodimerization proceeds via intermediate intermolecular excimer formation. The quantum yields of the photoreaction are significantly lower (e.g. **5a**: $\phi_{\mathrm{Dim}} = 0.001$; **5e**: $\phi_{\mathrm{Dim}} = 0.10$, both in MeOH) than the one of the intermolecular dimerization of acridizinium derivatives [34,35]. Moreover, the quantum yields depend on the solvent, i.e., they are slightly larger in acetonitrile. On the basis of the absorption spectra of the product mixtures, it was proposed that with a chain length of $n \leq 3$, the *syn*-head-to-head dimer is formed, whereas with a chain length of $n \geq 4$, the *syn*-head-to-tail isomer is formed. However, further spectroscopic evidence for the product assignment is not provided. It was shown that depending on the chain length, the quantum yields of the photodimerization are significantly governed by the persistence of the photodimer. Thus, in relatively strained systems such as **5a**–**c**, the cycloreversion, either photochemically or thermally induced, is significantly more efficient than the photodimerization. In compounds with chain length $n \geq 6$, the photodimerization requires a preorganization of the two monomers after excitation ("transport phase") during which deactivation by fluorescence may take place, as indicated by increasing fluorescence lifetimes. This effect leads to a decrease of the dimerization quantum yield.

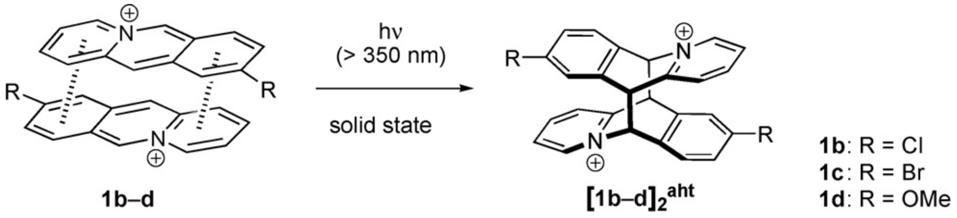
3. Photodimerization of acridizinium derivatives in the solid state

Because of the constraints in a crystal lattice, solid-state reactions proceed with a minimum of molecular motion [39–41]. The investigation of structures of the photoactive compounds in the crystalline state and the comparison with their reactivities provided fundamental insight in the geometric requirements of several photoreactions [42–46]. Along these lines, the photodimerization of many crystalline anthracene derivatives was examined, and notably some anthracene derivatives were identified that react in exceptional non-topochemical solid-state photoreactions, i.e., the formation of the product cannot be correlated with the solid-state structure [47–49]. Since *one* of the factors that lead to a non-topochemical behavior may be the *relatively* high degree of mobility of the molecules within the crystal lattice, the introduction of attractive ionic interactions by salt formation [45,50] may be useful to establish a topochemical reaction. Thus, a positively or negatively charged molecule remains in the close proximity of its counter ion and also tends to be well separated from another molecule with the same charge, which should significantly restrict its mobility. Moreover, salts are usually high-melting, crystalline compounds, and the risk of melting during the solid-state reaction is rather low. Thus, it may be proposed that ionic acridizinium salt derivatives are ideal compounds to perform reactions in the solid state. The photoreactivity of single crystals of the parent compound **1a** was first investigated in detail by Kearsley [51] and Wang and Jones [52]. Most notably, the formation of the photodimer $\mathbf{[1a]_2^{aht}}$ proceeds in a single-crystal to single-crystal transformation, thus representating a topochemical photoreaction. A series of salts of the parent compound **1a** and the 9-methylacridizinium (**1g**) with different counter ions was examined, and it was demonstrated that water molecules in the crystal lattice are essential to maintain the crystal integrity during the course of reaction. Moreover, the geometric requirements for the photodimerization of the ions **1a** and **1g** were investigated by X-ray diffraction analysis. It was shown that an ideal arrangement of the molecules in the ground state, in particular a distance between the CC-bond forming carbon atoms C6 and C11 smaller than ca. 420 pm, is essential for a photodimerization to proceed; however, it is not the only factor that determines whether or not an acridizinium ion dimerizes upon irradiation in the solid state [53]. Indeed, the crucial step for an efficient photodimerization is the excimer formation between the two molecules, which requires a significant movement of at least one of the molecules within the crystal lattice. As such a mobility of the acridizinium ions was shown to be influenced significantly by the nature of the counter ion, it was proposed that an efficient solid-state dimerization of acridizinium ions in the crystal requires the choice of an appropriate counter anion. The movement of the acridizinium monomers in the solid state was also found to be affected by the rigidity of the surrounding lattice, and is hence dependent on the temperature. Thus, at liquid-nitrogen temperature, the ions **1a** and **1g** are photoinert due to the severe limitation of the thermally assisted molecular movement required for the dimerization. It should be noted, however, that these results strictly apply to reactions of single crystals, as it was demonstrated later that amorphous or polycrystalline samples of **1a** yield a mixture of all four regioisomers upon irradiation, presumably due to the less ordered arrangement of the acridizinium molecules in these media [24]. This drawback may be overcome by the introduction of a π donor substituent in the 9-position of acridizinium ion, which leads to directional π stacking [54–56], even in the polymorphous state [25]. Thus, the irradiations of crystalline acridizinium salts **1b**, **1c**, and **1d** afforded the *anti*-head-to-tail dimers exclusively even in the polycrystalline state (Scheme 4) [57]. X-ray diffraction analyses of the representative example revealed that the crystal lattices of the photoreactive derivatives consist of pairs of chromophores which are arranged in a slightly distorted *anti*-head-to-tail orientation (Fig. 1). For a quantitative analysis, the distances between the opposite reactive *meso* positions (i.e., C6 and C11), that form the new C—C bonds in the photodimerization, as well as the deviation from an ideal superposed position of two molecules, as quantified by the shift of one molecule along the long and the short molecule axis, Δx and Δy, were taken as structural parameters to discuss the reactivity of the acridizinium derivatives in the solid state. The observed structural features of compounds **1b** (Br) and **1c** (Br) are comparable to the ones observed for the parent acridizinium ion **1a** [51,52]. Although the distance between the reaction centers is suitable for the photoreactive acridizinium salts **1b** and **1c** (378–389 pm), the solid-state arrangements of these compounds deviate from an ideal superposed *anti*-head-to-tail arrangement as indicated by the data for Δx and Δy (Δx: 18–24 pm; Δy: 112–124 pm). Apparently, the two acridizinium molecules need to shift slightly along the short and long molecular axis in the course of the dimerization process. In contrast, with tetrafluoroborate as counter ion, the chloroacridizinium tetrafluoroborate (**1b**) (BF_4) crystallizes such that the two closest acridizinium molecules face each other in a distorted *syn*-head-to-head arrangement (Fig. 1). Consequently this salt is photoinert in the solid state as there is no possibility for both molecules to arrange for a [4+4] photocycloaddition within the constrained crystal lattice. Additional solid-state emission spectroscopy revealed excimer emission in the solid state for the photoreactive acridizinium derivatives, which provides further evidence for a close overlap of the π systems of a pair of acridizinium molecules in the solid state. In contrast, the solid-state photodimerization of 8-bromoacridizinium bromide led to all four regioisomeric dimers [58].



1g

The naphthoquinolizinium salts **2a** and **2b** are converted exclusively into the corresponding *anti*-head-to-tail regioisomers $\mathbf{[2a]_2^{aht}}$ and $\mathbf{[2b]_2^{aht}}$ upon irradiation in the solid state as shown for **2b** as representative example in Scheme 5 [26,58]. It was shown by X-ray diffraction analyses that the regioselective photodimer-



Scheme 4. Regioselective photodimerizations of 9-substituted acridizinium ions in the solid state.

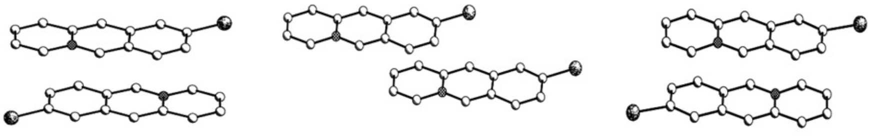
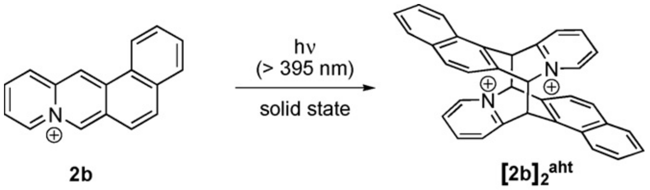


Fig. 1. Packing diagram of acridizinium derivatives **1b** (Br), **1b** (BF_4), and **1c** (BF_4); a pair of the two closest molecules is shown and hydrogen atoms and counter anions are omitted for clarity; the respective counter ions are given in the brackets. Reprinted with permission from J. Org. Chem. 64 (1999) 5715–5718. Copyright (1999) American Chemical Society.



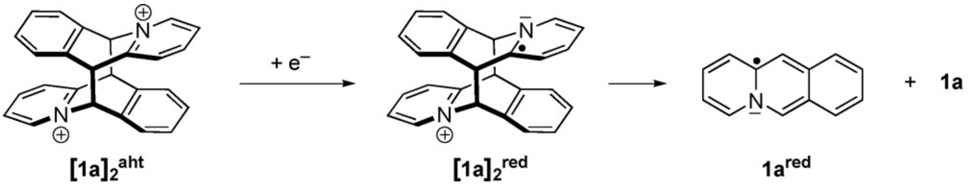
Scheme 5. Regioselective photodimerization of benzo-annelated acridizinium ion **2b** in the solid state.

ization of **2b** in the solid state is the result of an appropriate arrangement of two molecules in the crystalline state, which differs slightly depending on the solvent from which the compound has been crystallized.

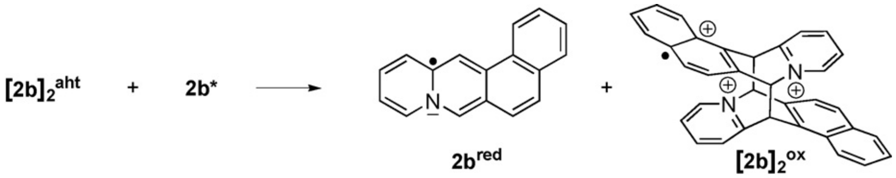
4. Cycloreversion of acridizinium photodimers induced by electron-transfer reactions

Although the thermally induced and the photoinduced cycloreversion reactions of anthracene dimers are well established and represent efficient tools to regain the monomer [59], these methods have a few drawbacks that may be considered. Firstly, the thermally induced cyloreversion cannot be applied in biological systems or in organized or constrained media whose structure will be reorganized or decomposed at elevated temperatures (polymers, micelles, crystals). On the other hand, the photoinduced cycloreversion requires the choice of an appropriate excitation wavelength to avoid the establishment of a photostationary state. This task is quite challenging as usually the absorption bands of the dimer overlap significantly with the ones of the monomers [59]. Therefore, it would be helpful to have the opportunity to induce the cycloreversion with additional, complementary stimuli. In the case of anthracene it was demonstrated that a rapid cycloreversion may be induced by irradiation of the anthracene dimer in the presence of an appropriate electron acceptor (chloranil, 9,10-dicyanoanthracene, or cadmium sulfide) [60,61]. The reaction was shown to be initiated by a photoinduced electron transfer (PET) between the anthracene dimer and the electron donor, and the intermediate radical cation of the dimer cleaves to the monomers with subsequent electron back transfer.

It may be proposed that acridizinium dimers may also be cleaved by electron-transfer processes. Especially the inherent pyridinium substructure of these dimers may act as appropriate electron acceptor in a PET reaction. First evidence for such a reaction was provided by Bendig and co-workers [62]. Thus, electrochemical reduction of the acridizinium dimer **[1a]$_2$^{aht}** to the “radical cation” **[1a]$_2$^{red}** leads to a cycloreversion of the dimer (Scheme 6). Alternatively, radical anions of e.g. anthraquinone were employed as electron donor. The initially formed charge-neutral radical **1a^{red}** may act as an efficient electron donor that establishes a chain reaction by inducing another cycloreversion by an ET reaction with a dimer **[1a]$_2$**; however, at the same time two radicals, which are also formed by reduction of **1a** at the cathode, may react in a radical combination to give the corresponding coupling product. Indeed the latter reaction is an efficient chain termination and interferes significantly with the formation of the acridizinium (**1a**). In contrast, a PET reaction between the dimer **[1a]$_2$^{aht}** and erythrosine was shown to lead to an efficient cycloreversion to give the monomer **1a**. At early stages of the reaction, the quantum yields of the photoreaction are larger than 30, indicating a chain reaction as described above. The electron transfer between the dimer and the excited dye was confirmed by the detection of the one-electron oxidized erythrosine by time-resolved absorption spectroscopy. The authors point out that the reduced dimer **[1a]$_2$^{red}** is a very short-lived intermediate which – after its formation –



Scheme 6. Cycloreversion of the acridizinium dimer **[1a]$_2$^{aht}** initiated by an electron-transfer reaction.



Scheme 7. Cycloreversion of the benzo-annelated acridizinium dimer $[\mathbf{2b}]_2^{\mathbf{aht}}$.

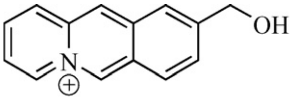
immediately cleaves to $\mathbf{1a}^{\mathbf{red}}$ and **1a** due to the highly exothermic cycloreversion.

The cycloreversion of the dimers $[\mathbf{2a}]_2^{\mathbf{aht}}$ and $[\mathbf{2b}]_2^{\mathbf{aht}}$ by a PET was assumed to be responsible for the establishment of a photostationary state between monomer and dimer even at excitation wavelengths at which the dimer does not absorb [26]. It was demonstrated that the irradiation of the dimer $[\mathbf{2b}]_2^{\mathbf{aht}}$ at $\lambda > 395$ nm in the presence of the corresponding monomer leads to a photocleavage. A PET was assumed to take place between the excited benzo-annelated acridizinium $\mathbf{2b}^*$ and the corresponding dimer. In this case, however, the dimer acts as the electron donor, i.e., the naphthalene residue is the oxidized unit, whereas the acridizinium is reduced in the course of the electron-transfer reaction (Scheme 7). Such as proposed for the reduced dimer $[\mathbf{1a}]_2^{\mathbf{red}}$ [62] the oxidized dimer $[\mathbf{2b}]_2^{\mathbf{ox}}$ is likely to dissociate immediately to the monomers.

5. The application of acridizinium derivatives as photochromic materials

The reversible photodimerization of acridizinium ions has received attention as a photochromic system which might be facilitated in a rigid matrix and thus be used in such media for data storage or data processing. The stable photodimers may be cleaved within the polymer matrix thermally, or by irradiation with suitable wavelength. With the reduced mobility of the monomers within the polymer matrix they may remain in an arrangement which allows efficient photodimerization. Indeed, in a *proof of principle* the toluenesulfonate salt of the parent acridizinium (**1a**) was employed along these lines [63]. The acridizinium dimer was incorporated within a copolymer of methyl methacrylate and acrylic acid and irradiated at $\lambda = 313$ nm such that the dimer dissociates. Irradiation of this sample at $\lambda = 365$ nm regained the dimer. At the applied concentrations, this photochromic reaction has a significant influence on the refractive index of the doped polymer because of the differences between the electronic and optical properties of the dimer and the monomer. It was shown that the determination of the refractive index may be employed to successfully write and erase diffraction gratings in this material, repeatedly. Nevertheless, this system appeared to exhibit fatigue after several cycles. Interestingly, the cycloreversion of the dimer of the benz[*b*]acridizinium **4a**, which was also investigated along these lines, is very slow within the methyl methacrylate–arcylic acid copolymer matrix. Moreover, in this case the redimerization of the monomers **4a** could not be achieved with full conversion [64].

In another application, the 9-(hydroxymethyl)acridizinium (**1h**) was connected covalently by ester formation with the copolymer of *N*-isopropyl acrylamide and acrylic acid to establish a hydrophilic photo-responsive polymer. Notably, this material exhibits promising polymer properties to be applied as hydrogel films in aqueous media. The high chromophore content in the polymer results in a reversible photodimerization of the acridizinium chromophore, which was utilized to enable an almost complete photocrosslinking of the polymer. As this process is reversed upon irradiation with appropriate wavelengths, it may be used for an isothermal switching of the polymer properties, in particular a reversible change of the lower critical solution temperature (LCST) of the hydrogel film properties in aqueous media [65].



1h

The photodimerization of the acridizinium (**1a**) in the presence of surfactants or micelles was reported to alter the regioselectivity as compared to the reaction in isotropic solution [24]. Thus, the formation of dimers with larger dipole moments increases significantly, presumably due to the preorientation of the monomers at the micellar surface. This effect is mainly determined by the type of solubilization (electrostatic interaction *versus* ion pair formation) of the acridizinium (**1a**) by the surfactant. The quantum yields of the photodimerization are also enhanced because of the high local concentration of monomers associated with micelles.

The propensity of acridizinium ions to be adsorbed on surfactants along with their photochromic behavior was used to modify the rheological properties of aqueous solutions of tetramethylammoniumhydrogen-2-dodecyl malonate (TAMH). Thus, the addition of the acridizinium (**1a**) to TAMH changes the viscoelastic properties of the latter, whereas the *in situ* photodimerization of the adsorbed acridizinium bromide leads to the reversion of this effect and regains essentially the original rheological properties of the surfactant solution [66].

The photochromic behavior of the acridizinium ion (**1a**) may also be used to switch the percolation temperature of microemulsions, i.e., the temperature at which the conductivity of a microemulsion with constant composition increases significantly [67]. Thus, in microemulsions composed of the surfactant aerosol OT (AOT), isooctane, and water (mass ratio: 1:0.75:1.54), the addition of the acridizinium (**1a**) (final conc.: 10 mM) results in an increase of the percolation temperature, i.e., from a non-conducting to a conducting microemulsion, from 33 to 38 °C. The irradiation of these microemulsions leads to the photodimerization of **1a** along with a further increase of the percolation temperature to 43 °C. It was proposed that the adjacent cation centers in the acridizinium dimers are bound to the relatively large anionic AOT head groups and that the interactions between the dimer and the surfactant at the oil–water interface stabilize the microemulsions against percolation. The different percolation temperatures in the presence of the acridizinium monomers or dimers allow, in principle, the photoinduced switching of conductivity in the employed microemulsion systems between 38 and 43 °C; although it was not demonstrated explicitly that the photocycloaddition is reversible in these systems.

6. Conclusion

In this review, the photochemical and photophysical aspects of the reversible [4 + 4] photocycloaddition of acridizinium derivatives, as well as their applications as photochromic materials are presented and discussed. It is shown that the photoinduced dimerization of the acridizinium ion is an ideal model system that may be employed for the detailed investigation of the factors that govern the selectivity and efficiency of the [4 + 4] photocycloaddition in general. Moreover, it is demonstrated that the reversible photocycloaddition of acridizinium derivatives represents a versatile platform for the design of efficient photochromic materials. Thus, considering the resemblance of the photochemical properties of the acridizinium ion to the ones of anthracene, the acridizinium derivatives may be used as complementary systems to the well-established photochromic anthracene, for example when the photochromic property should be applied in aqueous solution, i.e., when water solubility is required.

References

[1] H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, Chem. Soc. Rev. 29 (2000) 43.
[2] H. Bouas-Laurent, J.-P. Desvergne, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism, Molecules and Systems, Elsevier, Amsterdam, 1990, p. 561.
[3] Cross-dimerizations: D.E. Bailey, V.E. Williams, J. Org. Chem. 71 (2006) 5778.
[4] [4 + 4] Cycloaddition in organic synthesis: S.McN. Sieburth, N.T. Cunard, Tetrahedron 52 (1996) 6251.
[5] Theoretical aspects: S. Grimme, C. Diedrich, D. Korth, Angew. Chem. 118 (2006) 641.
[6] [4 + 4] Cycloaddition by photochemical upconversion: R. Islangulov, F.N. Castellano, Angew. Chem. 118 (2006) 6103.
[7] C. Schäfer, R. Eckel, R. Ros, J. Mattay, D. Anselmetti, J. Am. Chem. Soc. 129 (2007) 1488.
[8] H. Masu, I. Mizutani, T. Kato, I. Azumaya, K. Yamaguchi, K. Kishikawa, S. Kohmoto, J. Org. Chem. 71 (2006) 8037.
[9] C. Schäfer, J. Mattay, Photochem. Photobiol. Sci. 3 (2004) 331.
[10] R.O. Al-Kaysi, A.M. Müller, C.J. Bardeen, J. Am. Chem. Soc. 128 (2006) 15938.
[11] T. Ihara, T. Fuji, M. Mukae, Y. Kitamura, A. Jyo, J. Am. Chem. Soc. 124 (2004) 8880.
[12] J. Daub, M. Beck, A. Knorr, H. Spreitzer, Pure Appl. Chem. 68 (1996) 1399.
[13] M. Irie, Pure Appl. Chem. 68 (1996) 1367.
[14] A.P. de Silva, C.P. McCoy, Chem. Ind. (1994) 992.
[15] A.S. Dvornikov, I. Cokgor, F. McCormick, R. Piyaket, S. Esener, P.M. Rentzepis, Opt. Commun. 128 (1996) 205.
[16] A.S. Dvornikov, P.M. Rentzepis, Res. Chem. Intermed. 22 (1996) 115.
[17] G. McSkimming, J.H.R. Tucker, H. Bouas-Laurent, J.-P. Desvergne, S.J. Coles, M.B. Hursthouse, M.E. Light, Chem. Eur. J. 8 (2002) 3331.
[18] H. Ihmels, in: D. Black (Ed.), Science of Synthesis, vol. 15. Six-Membered Hetarenes with One Nitrogen or Phosphorus Atom, Georg Thieme Verlag, Stuttgart, 2004, p. 907.
[19] G. Jones, Adv. Heterocycl. Chem. 31 (1982) 1.
[20] C.K. Bradsher, in: A.R. Katritzky, C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, vol. 2. Six-Membered Rings with One Nitrogen Atom, Pergamon, Oxford, 1984, p. 525.
[21] S. Arai, M. Hida, Adv. Heterocycl. Chem. 55 (1992) 261.
[22] C.K. Bradsher, L.E. Beavers, J.H. Jones, J. Org. Chem. 129 (1957) 1740.
[23] C.K. Bradsher, L.E. Beavers, J. Am. Chem. Soc. 77 (1955) 4812.
[24] C. Lehnberger, D. Scheller, T. Wolff, Heterocycles 45 (1997) 2033.
[25] H. Ihmels, D. Leusser, M. Pfeiffer, D. Stalke, J. Org. Chem. 64 (1999) 5715.
[26] H. Ihmels, C.J. Mohrschladt, A. Schmitt, M. Bressanini, D. Leusser, D. Stalke, Eur. J. Org. Chem. (2002) 2624.
[27] H. Ihmels, Tetrahedron Lett. 39 (1998) 8641.
[28] H. Ihmels, B. Engels, K. Faulhaber, C. Lennartz, Chem. Eur. J. 6 (2000) 2854.
[29] R.W. Warrner, M. Golic, D.N. Butler, Tetrahedron Lett. 39 (1998) 4717.
[30] C.K. Bradsher, T.W.G. Solomons, J. Am. Chem. Soc. 82 (1960) 1808.
[31] J. Bendig, U. Bauer, D. Kreysig, Z. Phys. Chem. 262 (1981) 1041.
[32] H. Ihmels, D. Otto, A. Faccio, G. Viola, J. Org. Chem. 71 (2006) 8401.
[33] R.K.Y. Zee-Cheng, C.C. Cheng, J. Med. Chem. 19 (1976) 883.
[34] J. Bendig, B. Geppert, D. Kreysig, J. Prakt. Chem. 320 (1978) 739.
[35] J. Bendig, D. Kreysig, Z. Phys. Chem. 260 (1979) 663.
[36] J.W. Buchwitz, J. Fischer, D. Kreysig, J. Prakt. Chem. 323 (1981) 485.
[37] J. Wagner, J. Bendig, D. Kreysig, J. Prakt. Chem. 326 (1984) 757.
[38] J. Wagner, J. Bendig, A. Felber, A. Sommerer, D. Kreysig, Z. Chem. 25 (1985) 64.
[39] G.M.J. Schmidt, Pure Appl. Chem. 27 (1971) 647.
[40] R.G. Weiss, V. Ramamurthy, G.S. Hammond, Acc. Chem. Res. 26 (1993) 530.
[41] For a critical view on topochemical photoreactions in the solid state and the postulation of a “phase rebuilding concept”, that considers dynamic effects during the photoreaction, see: G. Kaupp, in: J.E.D. Davies, J.A. Ripmeester (Eds.), Comprehensive Supramolecular Chemistry, vol. 8. Physical Methods in Supramolecular Chemistry, Elsevier, Oxford, 1996, p. 381.
[42] A.E. Keating, M.A. Garcia-Garibay, in: V. Ramamurthy, K.S. Schanze (Eds.), Organic and Inorganic Photochemistry, Marcel Dekker Inc., New York, 1998, p. 195.
[43] F. Toda, Top. Curr. Chem. 254 (2005) 1.
[44] M. Sakamoto, Top. Curr. Chem. 254 (2005) 207.
[45] J.R. Scheffer, W. Xia, Top. Curr. Chem. 254 (2005) 233.
[46] H. Ihmels, J.R. Scheffer, Tetrahedron 55 (1999) 885.
[47] D.P. Craig, P. Sarti-Fantoni, J. Chem. Soc., Chem. Commun. (1966) 742.
[48] M.D. Cohen, Z. Ludmer, J.M. Thomas, J.O. Williams, J. Chem. Soc., Chem. Commun. (1969) 1172.
[49] M.D. Cohen, G.M.J. Schmidt, J. Am. Chem. Soc. 86 (1964) 1996.
[50] J.G. Gamlin, R. Jones, M. Leibovitch, B. Patrick, J.R. Scheffer, J. Trotter, Acc. Chem. Res. 29 (1996) 203.
[51] D.K. Kearsley, in: G.R. Desiraju (Ed.), Organic Solid State Chemistry, Elsevier, Amsterdam, 1987, p. 69.
[52] W.N. Wang, W. Jones, Tetrahedron 43 (1987) 1273.
[53] W.N. Wang, W. Jones, Mol. Cryst. Liq. Cryst. 242 (1994) 227.
[54] J.P. Glusker, Top. Curr. Chem. 198 (1998) 1.
[55] A. Nangia, G.R. Desiraju, Top. Curr. Chem. 198 (1998) 57.
[56] C.V.K. Sharma, K. Panneerselvam, L. Shimoni, H. Katz, H.L. Carrell, G.R. Desiraju, Chem. Mater. 6 (1994) 1282.
[57] H. Ihmels, D. Leusser, M. Pfeiffer, D. Stalke, Mol. Cryst. Liq. Cryst. 356 (2001) 433.
[58] H. Ihmels, S. Bosio, M. Bressanini, A. Schmitt, K. Wissel, D. Leusser, D. Stalke, Mol. Cryst. Liq. Cryst. 390 (2003) 105.
[59] H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, R. Lapouyade, Chem. Soc. Rev. 29 (2001) 248.
[60] R.A. Barber, P. de Mayo, K. Okada, S.K. Wong, J. Am. Chem. Soc. 104 (1982) 4995.
[61] J.M. Masnovi, J.K. Kochi, J. Am. Chem. Soc. 107 (1985) 6781.
[62] R. Mitzner, J. Bendig, R. Ziebig, F. Graichen, D. Kreysig, F. Pragst, J. Prakt. Chem. 327 (1985) 241.
[63] W.J. Tomlinson, E.A. Chandross, R.L. Fork, C.A. Pryde, A.A. Lamola, Appl. Opt. 11 (1972) 533.
[64] G. Smets, J. Polym. Sci. Polym. Chem. Ed. 13 (1975) 2223.
[65] D. Kuckling, I.G. Ivanova, H.P. Adler, T. Wolff, Polymer 43 (2002) 1813.
[66] C. Lehnberger, D. Scheller, T. Wolff, J. Colloid Interface Sci. 213 (1999) 187.
[67] D. Nees, U. Cichos, T. Wolff, Ber. Bunsenges. Phys. Chem. 100 (1996) 1372.