# REGIOISOMERS IN THE PHOTODIMERIZATION OF ACRIDIZINIUM BROMIDE

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**Abstract** - Products of the photodimerization of acridizinium bromide (**1**) were analyzed by means of $^1$H NMR spectroscopy. Upon irradiation in solution and in the solid state four distinct isomeric photodimers were identified, two of which may exist in enantiomeric forms which could not be distinguished. Solubilization of **1** in anionic micellar solutions affected the regioselectivity of the photodimerization: as compared to a homogeneous aqueous solution the yield of dimers exhibiting higher dipole moments was enriched in the reaction mixture.

The irradiation of acridizinium salts (**1**) (cf. Figure 1) has been known to yield photodimers of acridizinium ions since the work of Bradsher and coworkers forty years ago.[2] In this and all subsequent papers on the subject[3-5] the respective authors were convinced that only one of the possible six isomeric photodimers is formed, i.e. **2** in Figure 1, because it allows the largest distance of the two positive charges in the molecule. This assumption appeared to be supported by crystallographic work:[5] single crystals of acridizinium bromide were photochemically converted to dimers to which the structure **2** was assigned *via* X-Ray analysis.

In this paper we present NMR spectroscopic data on the photodimers of acridizinium bromide in

homogeneous and micellar solution as well as in the solid state clearly demonstrating the formation of regioisomers under all conditions.

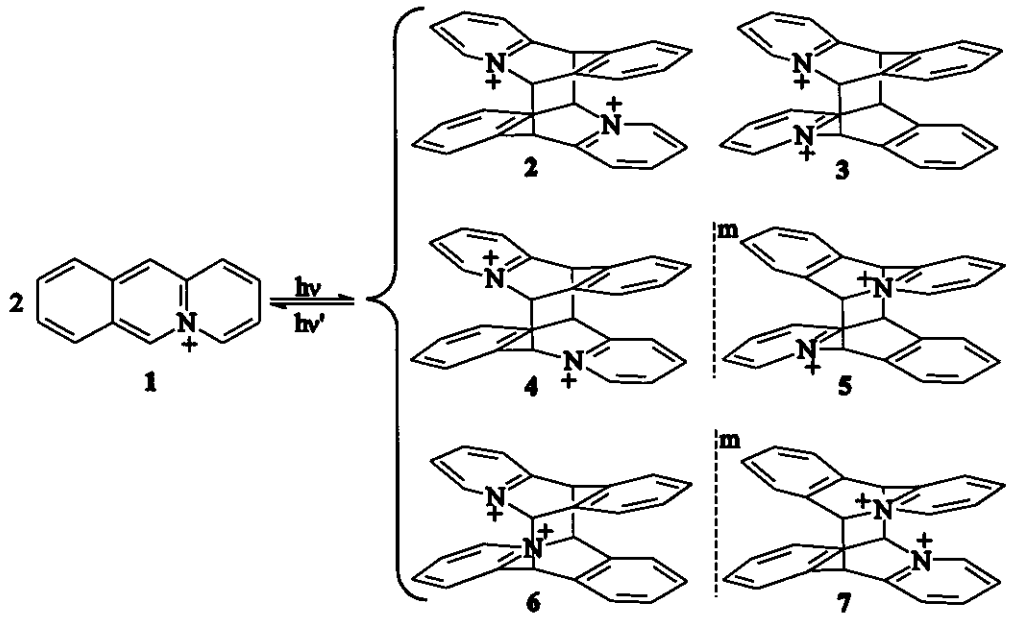


Figure 1: Reaction scheme showing possible photodimers of acridizinium cations

## RESULTS AND DISCUSSION

Figure 2(a) shows the $^1$H NMR spectrum of acridizinium bromide after photodimerization. Data from the spectrum are comprised in Table 1 along with PM3 calculations of atomic charges and of dipole moments. The NMR data allowed the identification of four isomeric dimerization products: the achiral dimers (**2** and **3**), and the enantiomeric pairs (**4,5** and **6,7**), respectively. Assignment of the dimers was made by considering the signals of the four dimer protons that are denoted H(1A), H(1B), H(2), and H(3) in Figure 3. Separate signals are revealed for the protons H(1A) (ranging from 5.93 to 6.17 ppm) as well as for the aromatic protons neighbouring the nitrogen atom H(2) (ranging from 9.12 to 9.38 ppm). The former appear as singlets in **3** and **4,5** because of chemical equivalence with H(1B), while in **2** and **6,7** doublets ($^3J_{AB}$ = 10.7 Hz) appear. The H(2) signals are doublets due to coupling with H(3) ($^3J_{23}$ = 6.2 Hz). The smallest and the

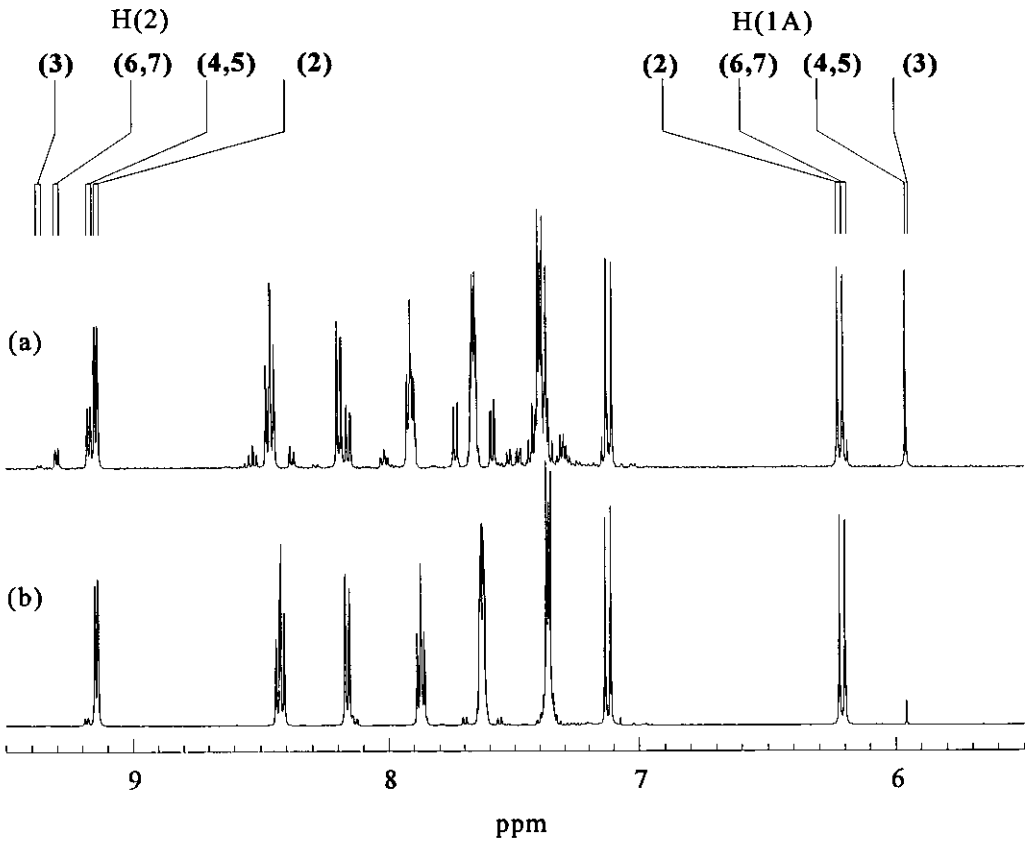


Figure 2: $^1$H NMR spectra of (a) photodimerized acridizinium bromide and (b) of the isolated isomer **2**

largest δ values can be expected in the isomers (**2**) and (**3**), respectively, since these show the largest and the smallest distance of the two nitrogen atoms bearing positive charges. It is reasonable that the chemical shift of H(2) in **3** exceeds that in **2** because of different interactions of two rings containing $N^+$, which are neighbouring each other in **3**. Analogously, **4,5** and **6,7** may be classified. Our assignment is supported by PM3 calculations[6] of electron densities at H(2) which are significantly smaller in **3** and **6,7** as compared to **2** and **4,5**, respectively (see Table 1). The enantiomers of the enantiomeric pairs (**6,7**) and (**4,5**) cannot easily be distinguished. Without chiral induction they can be expected to be formed in 1:1 ratios.

Because of different molecular dipole moments of the dimers, the isomer (**2**) can be isolated *via* repeated recrystallizations of the photodimer mixture. PM 3 calculations[6] show that the dipole moments decrease in the order **3** > **6,7** > **4,5** > **2** (Table 1). We yielded 93% of isomer (**2**) impurified by 7% of isomer **4,5** (Figure

2b) after 30 recrystallizations. The isomer (**2**) as well as the dimer mixture does not fluoresce significantly. **2** can be split into the monomers without side products upon irradiation at *ca.* 270 nm.

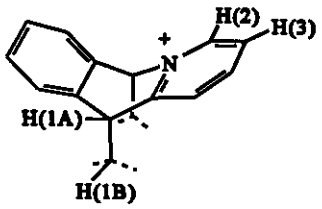


Figure 3: Relevant protons for the assignment of NMR signals to isomeric photodimers

Table 1: Chemical shifts δ (in ppm), coupling constants *J* (in Hz) and PM3 calculation data of selected acridizinium bromide dimer protons relevant for the assignment of isomers (cf. Figure 3).

| dimer | $\delta_{H(1A)}$ | $^3J_{AB}$ | $\delta_{H(2)}$ | $^3J_{23}$ | charge at H(2) | molecular dipole moment / Debye |
|---|---|---|---|---|---|---|
| **(2)** | 6.17 | 10.7 | 9.12 | 6.2 | 0.1751 | 0.006 |
| **(3)** | 5.93 | - | 9.38 | 6.2 | 0.1766 | 9.587 |
| **(4,5)** | 5.94 | - | 9.15 | 6.2 | 0.1734 | 1.204 |
| **(6,7)** | 6.16 | 10.7 | 9.30 | 6.2 | 0.1789 | 9.519 |

The different dipole moments also influence the regioselectivity of the photodimerization of acridizinium bromide, see Figure 4: in an aqueous solution containing anionic micelles of sodium 1-dodecanesulphonate the yield of high dipole moment isomers (**3** and **6,7**) increases at the expense of **2** and **4,5** as compared to the yields in pure water. In micelles of sodium dodecylsulphate the yield of **2** further decreases whereas the yield of the dimer **4,5** - exhibiting intermediate polarity (Table 1) - is strongly enhanced. **4,5** becomes the major product in micellar solution of sodium bis-2-ethylhexylsulfosuccinate (AOT). Yields were determined from integrals of the according NMR signals.

Generally, the surfactant effect can be rationalized in terms of preorientation of acridizinium monomers at the oppositely charged micellar surface directing to the formation of polar dimers. The shape of the surfactant aggregate is less important since there is not much difference in the product ratios when AOT micelles and AOT lamellae are compared. Distinctions among the surfactant micelles may be due to the type

of solubilization: when the acridizinium monomer is associated with the micelles mainly by electrostatic interactions (such as in sodium 1-dodecanesulphonate) the polar dimer **6,7** is favoured. When there is strong ion pair formation (such as in AOT as revealed by an increased tendency to precipitation) the medium polar dimer **4,5** predominates. Sodium dodecylsulphate behaves intermediately in this respect.

To achieve constancy of absorption spectra irradiation times of *ca.* 80 min in water and 12 min in micellar solution were needed. This enhancement of quantum yields can be ascribed to the high local concentration of reactants associated with micelles as known for various photodimerization reactions.[7]

In irradiations of solid acridizinium bromide only a minor change in regioselectivity is observed when crystals recrystallized from ethanol and from water are irradiated, respectively (Figure 4). The latter crystals

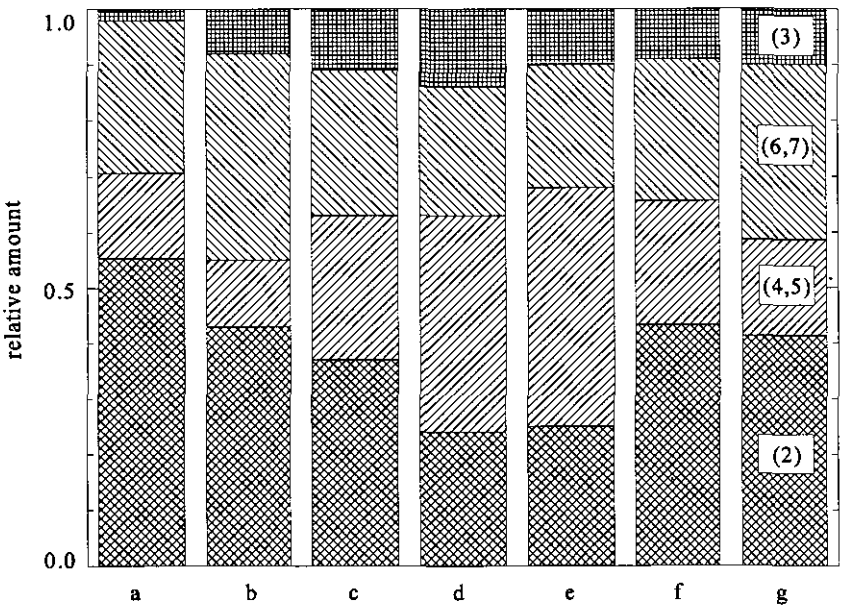


Figure 4: Relative amounts of the isomeric photodimers (**2**), (**3**), (**4,5**), (**6,7**) formed under various conditions: a) 20 mM acridizinium bromide (**1**) in water; b) 20 mM **1** in 20 mM sodium 1-dodecane-sulphonate; c) 20 mM **1** in 20 mM sodium dodecylsulphate; d) 2.5 mM **1** in 25 mM AOT (micelles); e) 20 mM **1** in 10%w/w AOT (lamellae); f) solid **1** recrystallized from ethanol; g) solid **1** recrystallized from water.

were expected to yield **2** exclusively according to the work of Wang and Jones[5] who used material crystallized from water. These authors, however, employed single crystals instead of polycrystalline acridizinium bromide in their investigation which might have affected the result.

## EXPERIMENTAL

**Materials**: Acridizinium bromide (**1**) was prepared as described in the literature[3] and recrystallized from ethanol: mp 240-242°C (lit.,[3] 240-241°C). For a repetition of the irradiation in the solid state described by Wang and Jones,[5] this material was recrystallized from water: mp 240-242°C. Sodium 1-dodecanesulphonate (Merck) was recrystallized three times from ethanol/acetone (1:1 ratio), sodium dodecylsulphate (Fluka) two times from ethanol. Sodium bis-2-ethylhexylsulfosuccinate (AOT, Fluka, >99%) was used without further purification.

**Irradiations**: (i) In solution: 12 mL of a stirred 20 mM solution of **1** in water, in 20 mM sodium 1-dodecanesulphonate, in 20 mM sodium dodecylsulphate, 2.5 mM **1** in 25mM sodium bis-2-ethylhexylsulfosuccinate (AOT, micellar[8]), or 20mM **1** in 10% AOT (lamellar[8]) was irradiated at 40 °C under a nitrogen atmosphere through the gas/liquid interface. A 100 W high pressure mercury lamp fitted with a 300 nm cut-off filter served as irradiation source. Irradiations were processed until constancy of absorption spectra (in water for *ca.* 80 min, in micellar solution for *ca.* 12 min) indicating 85 % conversion to dimers. The solvent then was evaporated. (ii) In the solid state: the same apparatus was used to irradiate solid acridizinium bromide. Irradiations were processed until the yellow colour of the crystals almost vanished (*ca.* 5 min). Storing of irradiated samples did not alter the ratios of isomeric products, so that complications due to thermal splitting of dimers and subsequent redimerization (or due to the work up procedure) are remote. For the photochemical back reaction a $10^{-5}$ M dimer solution was subjected to the mercury lamp.

Isomer (**2**) was purified by thirty recrystallizations of the irradiation product from a 1,4-dioxane-water mixture (9:1 ratio).

**Analysis**: $^1$H NMR spectra of samples dissolved in deuterated methanol (if necessary after addition of ≈10% heavy water) were run on a Bruker MSL 300 spectrometer at 300 MHz.

## ACKNOWLEDGEMENTS

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