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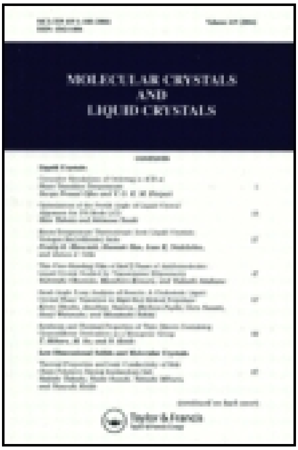

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Solid-State Photodimerization of 9-Substituted Acridizinium Salts - Selectivity by Directional π Stacking

HEIKO IHMELS[a], DIRK LEUSSER[b], MATTHIAS PFEIFFER[b] and DIETMAR STALKE[b]

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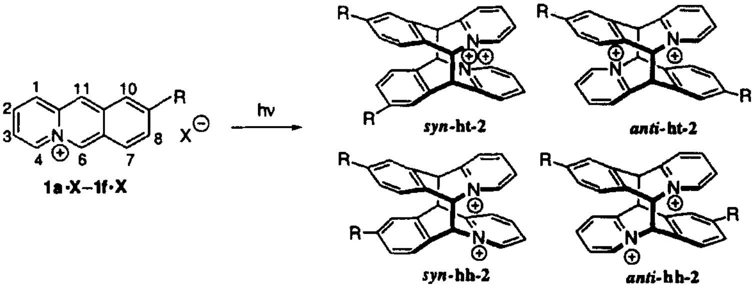
Irradiation 9-donor-substituted acridizinium salts in the solid state gave exclusively the *anti*-head-to-tail dimers. The regioselectivity of the photodimerization of the bromo-substituted derivative was independent of the morphology of the solid sample, and this selectivity is proposed to be the result of efficient directional π stacking in the solid state. X-ray structure analysis and solid-state emission spectroscopy are used to characterize the solid samples.

Keywords: solid-state photochemistry; [4+4] photocycloaddition; crystal engineering; solid-state emission spectroscopy

INTRODUCTION

Bimolecular solid-state photoreactions require a close proximity of two photoreactive molecules in the crystalline state.[1] The directional attractive π-π interaction between two aromatic molecules, which results in π stacking on crystallization,[2] may be a useful tool to provide such an arrangement. To investigate the use of this directional crystallization for selective solid-state photoreactions, acridizinium salt derivatives **1**[3] seem to be ideal compounds. These polycyclic aromatic heterocycles are high-melting, crystalline compounds which dimerize quantitatively in a [4+4] photocycloaddition on solid-state irradiation (Scheme 1).[4,5] However, only few investigations of the solid-state photochemistry of this class of compounds are known.[4,5] Single crystals of the parent compound **1a** and the methyl-substituted derivative **1b** dimerize on irradiation in the solid state to give exclusively the *anti*-head-to-tail dimer ***anti*-ht-2**;[4] but it was also shown that irradiation of the acridizinium salt **1a** in the polycrystalline state yields all four possible regioisomers **2**.[5]



SCHEME 1. Photodimerization of acridizinium salts
a: R = H; X = Br, ClO_4; **b**: R = Me; **c**: R = Cl; X = Br, BF_4; **d**: R = Br; X = Br, ClO_4; **e**: R = OMe; X = ClO_4; **f**: R = NH_2; X = Br, BF_4

The selectivity of the solid-state photodimerization may be enhanced by the introduction of a π-donor substituent such as in compounds **1c**–**1f**: The attractive π-π interactions between the π-donor substituted benzene moiety and the pyridinium ring may result in directional π stacking and thus provide an ideal *anti*-head-to-tail preorganization of two molecules in the solid-state (Figure 1).[6] Although, such donor-acceptor interactions have been used in crystal engineering for the selective photodimerization of alkenes in the crystalline state[7] and for selective solid-state cross-cycloadditions of mixed two-component crystals,[8]

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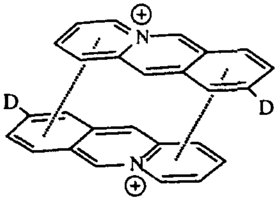

FIGURE 1. *Anti*-head-to-tail arrangement of donor-substituted acridizinium salts resulting from directional π stacking (D = Donor)

there are no examples to control the regioselectivity of [4+4] photodimerization in the solid state by this method.

EXPERIMENTAL

Acridizinium salts **1** were synthesized according to literature procedures.[3] Experimental details of the solution and solid-state photolysis, physical properties of the reaction products and full crystallographic data have been already reported.[9] Solid-state fluorescence spectra were recorded with a Perkin-Elmer LS-50 spectrometer with a Front Surface Accessory. The emission spectra of the solid salts **1c•Br** and **1c•BF$_4$** were recorded from single crystals whose solid-state structure was known from X-ray structure analysis. The solid samples under investigation were classified according to the solvent from which they have been crystallized (given in parentheses) and their morphology (single crystal vs. polycrystalline). Note that grinding a single crystal does not lead to a polycrystalline sample since the order of the single crystal still remains in the obtained microcrystals.

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RESULTS AND DISCUSSION

Irradiation of the acridizinium salts **1c–1e** in acetonitrile or methanol solution resulted in unseparable mixtures of all four regioisomers **2c-e**, as was determined by ^{1}H-NMR spectroscopy.[9] Photolysis of the amino-substituted acridizinium salt **1f** gave exlusively the head-to-tail dimers in a 1:1 ratio. However, solid-state irradiation of acridizinium salts **1c·Br** (single crystal, crystallized from methanol), **1d·Br** (single crystal, methanol/ethyl acetate) and **1e·ClO$_4$** (polycrystalline, water) afforded the *anti*-head-to-tail dimers exclusively at full conversion. In the case of acridizinium salt **1d·Br**, recrystallization from MeOH, MeOH/ethyl acetate, MeOH/isopropanol, or MeOH/acetone, followed by irradiation of the solid sample, led exclusively to the dimer ***anti*-ht-2d** in each case even at 100% conversion and with polycrystalline samples. However, in the case of salt **1c·Br**, only the irradiation of a single crystal grown from methanol gave the *anti*-head-to-tail dimer, whereas the formation of both the *anti*- and the *syn*-head-to-tail dimer in a 2:1 ratio was observed on photolysis of polycrystalline samples recrystallized from methanol/ethyl acetate. The acridizinium salts **1c·BF$_4$** (water or methanol/toluene), **1d·ClO$_4$** (water or acetonitrile), **1f·Br** (methanol), **1f·BF$_4$** (methanol), and **1f·ClO$_4$** (water) were photoinert in the solid state.

X-ray structure analyses of selected samples **1c·Br**, **1c·BF$_4$** and **1d·Br** revealed that in the case of the photoactive derivatives **1c·Br** and **1d·Br**, the crystal lattices consist of pairs of chromophores which are arranged in a *anti*-head-to-tail orientation, respectively (Figure 2). Within the crystal lattice of the photoinert salt **1c·BF$_4$** there is also a close pair of arenes; however, two acridizinium molecules face each other in a highly distorted *syn*-head-to-head arrangement. For a quantitative analysis, the distances **d** and **d'** between the opposite reactive *meso*

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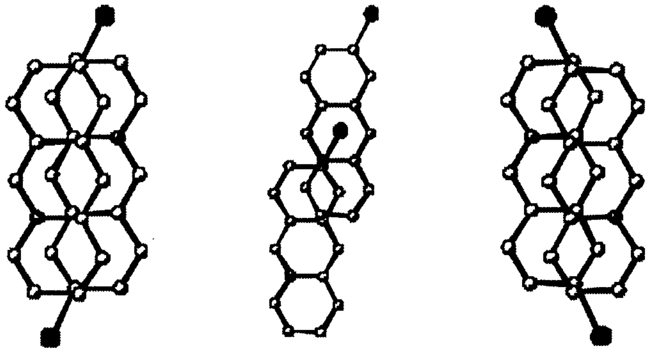

1c·Br **1c·BF$_4$** **1d·Br**

FIGURE 2. Diagram of the solid-state structure of acridizinium salts **1c·Br**, **1d·Br** and **1c·BF$_4$**; a pair of the two closest molecules is shown; counter anions are omitted for clarity.

positions (i.e. C-6 and C-11), which may form the new C–C bonds in the photodimerization, were taken as structural parameters, whose ideal value should be **d** < 400 pm.[1] Moreover, the deviation from an ideal superposed position of two molecules was quantified by the shift of one molecule along the long and the short molecule axis, Δx and Δy, respectively. In the case of a perfect superposition the ideal values are $\Delta x = \Delta y = 0$ pm.

The observed structural features of compounds **1c·Br** and **1d·Br** (Table 1) are comparable to those of the acridizinium salts **1a** and **1b**.[4b] Although the distance between the reaction centers is suitable for the photoreactive acridizinium salts **1c·Br** and **1d·Br**, 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. Thus, the two acridizinium molecules need to shift along the short and long molecular axis, respectively, to align properly for the dimerization process. Thus, the required movement for the dimerization presumably

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causes a destructive phase transition in the crystal, so that a topotactic single-crystal-to-single-crystal transformation was not observed.[10]

TABLE 1. Stuctural parameters of the solid-state arrangement of the acridizinium salts **1c·Br**, **1c·BF₄** and **1d·Br**

	space group	**d** [pm]	**d'** [pm]	Δx [pm]	Δy [pm]
1c·Br	$P\bar{1}$	388.6	388.6	18	112
1d·Br	$P\bar{1}$	378.2	378.2	24	124
1c·BF₄	$P2_1/n$	620.7	620.7	507	126

In the case of the photoinert salt **1c·BF₄** the distances **d** and **d'** and the Δx and Δy values deviate significantly from the ideal parameters and photodimerization is no longer possible. It may be assumed that this arrangement results from π stacking between one pyridinium moiety and one chloro-substituted benzene ring which are separated by only 360.

Photodimerizations usually proceed via the initial formation of an excimer which may exhibit a red-shifted fluorescence, whose band shift and structure are determined by the orientation of the two monomers towards each other.[11] Thus, solid-state fluorescence spectroscopy may be a useful tool to characterize the arrangement of the chromophores in the solid state, because the appearance of excimer fluorescence should be related to the solid-state photoactivity. Figure 3 shows the solid-state fluorescence spectra of the acridizinium salts **1c·Br** and **1c·BF₄** compared with the solution fluorescence spectrum. Each solid sample exhibits a significant bathochromic shift of the emission compared to the solution fluorescence band. However, a remarkable difference was observed between the photoinert and the photoactive solid samples. The photoinert salt **1c·BF₄** shows a similar band shape than in solution, however, a bathochromic shift of 40 nm was observed. The photoactive salt **1c·Br** exhibits a more complex band structure with local maxima.

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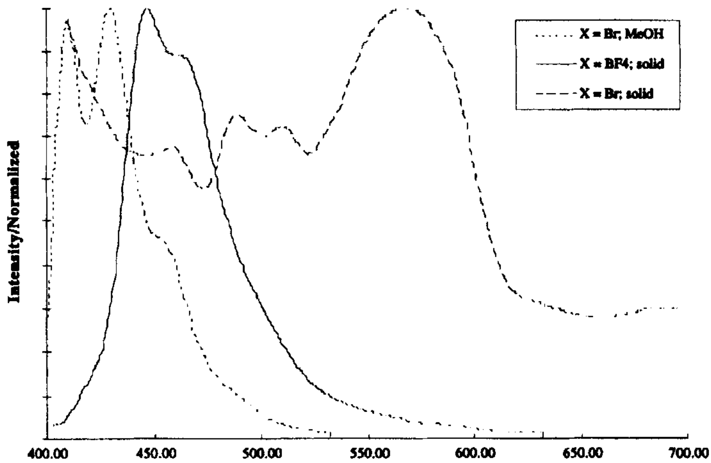

FIGURE 3. Fluorescence spectra of salt **1c·X** (counter anion X = Br or BF_4) in methanol solution and in the solid state (λ_{ex} = 380 nm)

The two maxima at 492 nm and 512 nm resemble the band shape of the solution spectrum, whereas the broad band at 566 nm shows the typical fluorescence shift and structure of acridizinium salt excimers.[12] We suggest that the observed emission of the solid salt **1c·BF$_4$** represents a red-shifted monomer fluorescence, whereas the luminescence spectrum of **1c·Br** represents an ensemble of monomer (492 and 512 nm) and excimer fluorescence (566 nm). The bathochromic shift of the monomer emission of the solid salts may be due to the interaction of the π systems of the opposing aromatic rings, which does not result in excimer formation. The degree of the red-shift correlates well with the π orbital overlap of the compounds in the solid state. In the case of salt **1c·Br** the observed monomer emission along with the excimer fluorescence reflects the fact that the arene molecules are not perfectly superposed and the deactivation process by monomer emission competes with the excimer

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formation. However, all reactive acridizinium salts exhibit a resembling emission band structure. Thus, the general photoactivity of these compounds can be deduced from the emission spectrum whereas the regioselectivity of the dimerization process cannot be monitored by this method.

The observation that the regioselectivity of the solid-state photodimerization of acridizinium salt **1d•Br** is not influenced by the morphology of the solid sample leads to the conclusion that the donor-acceptor interplay, which was observed in the single crystal of **1d•Br** (crystallized from methanol/ethyl acetate), is also effective in the polycrystalline phase of this compound. However, irradiation of polycrystalline samples of chloro-substituted acridizinium salt **1c•Br** yielded the two head-to-tail dimers. Thus, in contrast to the bromo functionality, the donor properties of the chloro substituent are not strong enough to provide a *anti*-head-to-tail arrangement of two chromophores in the polycrystalline state.

In summary, it was shown that the solid-state irradiation of appropriately tailored donor-substituted acridizinium salt derivatives gives rise to a highly regioselective and quantitative photodimerization. This is not observed in the solution photolysis and may be used for synthetic purposes; moreover, single crystals are not necessarily required for this selective transformation.

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