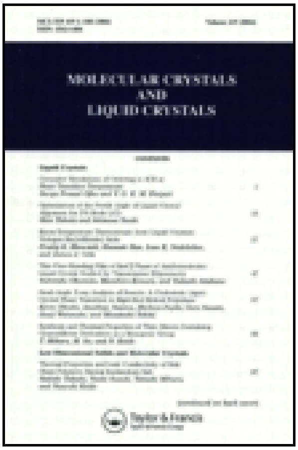


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Influence Of The Substitutionpattern Of Acridizinium Salts On The Regioselectivity Of The Solid-State Photodimerization

Heiko Ihmels [a], Sara Bosio [a], Milena Bressanini [a], Andreas Schmitt [a], Kathrin Wissel [a], Dirk Leusser [b] & Dietmar Stalke [b]

[a] Institutes of Organic Chemistry, University of Würzburg, Am Hubland, Würzburg, D-97074, Germany

[b] Institutes of Inorganic Chemistry, University of Würzburg, Am Hubland, Würzburg, D-97074, Germany

Version of record first published: 18 Oct 2010

To cite this article: Heiko Ihmels, Sara Bosio, Milena Bressanini, Andreas Schmitt, Kathrin Wissel, Dirk Leusser & Dietmar Stalke (2002): The Influence Of The Substitutionpattern Of Acridizinium Salts On The Regioselectivity Of The Solid-State Photodimerization, Molecular Crystals and Liquid Crystals, 390:1, 105-112

To link to this article: http://dx.doi.org/10.1080/10587250216168

Mol. Cryst. Liq. Cryst., Vol. 390, pp. 105–112
Copyright © 2003 Taylor & Francis
1542-1406/03 $12.00 + .00
DOI: 10.1080/15421400390193486

THE INFLUENCE OF THE SUBSTITUTION PATTERN OF ACRIDIZINIUM SALTS ON THE REGIOSELECTIVITY OF THE SOLID-STATE PHOTODIMERIZATION

Heiko Ihmels, Sara Bosio, Milena Bressanini,*
Andreas Schmitt, and Kathrin Wissel
University of Würzburg, Institutes of Organic Chemistry,
Am Hubland, D-97074 Würzburg, Germany

Dirk Leusser and Dietmar Stalke
University of Würzburg, Institutes of Inorganic Chemistry,
Am Hubland, D-97074 Würzburg, Germany

Irradiation of 8-bromoacridizinium bromide in the solid state gave preferentially the anti-*head-to-head dimmer whereas a benzo-annelated acridizinium salt gives exclusively the corresponding* anti-*head-to-tail photodimer. The results are discussed on the basis of X-ray diffraction analysis and DFT calculations.*

Keywords: solid-state photochemistry; [4+4] photocycloaddition; acridizinium salts; DFT calculations

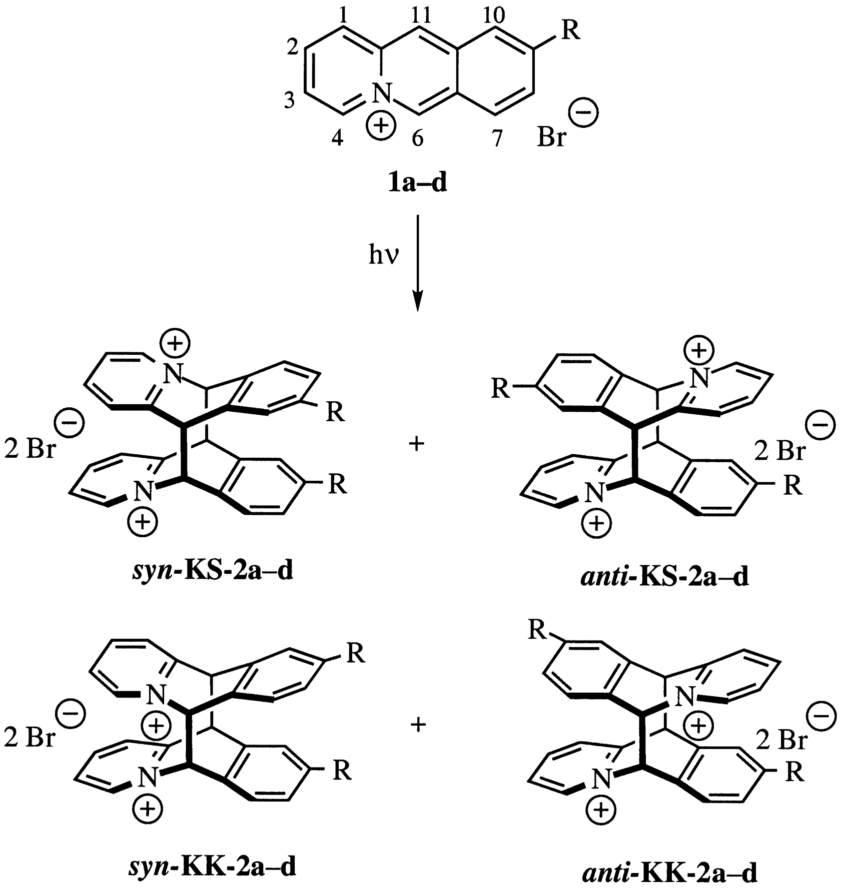
INTRODUCTION

Acridizinium derivatives [1] represent ideal model compounds to study the [4+4] photocycloaddition in the solid state (Scheme 1) [2]. *Single-crystals* of the parent compound **1a** and 9-chloroacridizinium (**1b**) undergo a topochemical dimerization on solid-state irradiation to give exclusively the *anti*-head-to-tail dimmers ***anti*-ht-2a,b**; however, it was also shown that the irradiation of salts **1a** [3] and **1b** [4] in the *poly-crystalline state* yields all four possible regioisomers of **2**. By contrast, it was demonstrated that the

---

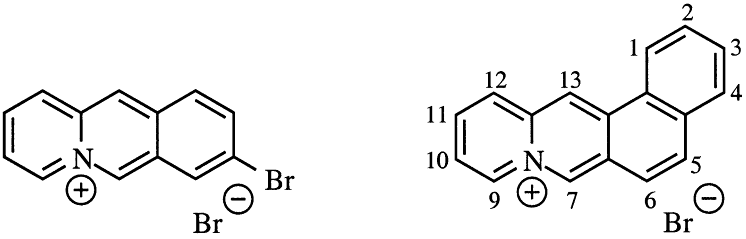
This work was generously financed by the *Fonds der Chemischen Industrie*, the *Bundesministerium für Bildung und Forschung*, and the *Deutsche Forschungsgemeinschaft*. Constant encouragement and generous support by Prof. W. Adam is gratefully appreciated.

*Corresponding author. E-mail: ihmels@chemie.uni-wuerzburg.de introduction of moderate π-donor substituents in 9-bromoacridizinium (**1c**) and 9-methoxyacridizinium (**1d**) leads to the regioselective formation of the *anti*-head-to-tail dimmers ***anti*-ht-2c,d** exclusively either in the single crystal or in the polycrystalline state [4,5]. During our studies of the influence of the substitution pattern on the regioselectivity of the solid-state photodimerization of acridizinium derivatives, we investigated the photoreactivity of acridizinium salts **1e** and **1f** in the crystalline state. The results will be outlined in this extended abstract.



a: R = H; **b**: R = Cl; **c**: R = Br; **d**: R = OMe;

SCHEME 1 (Continued)



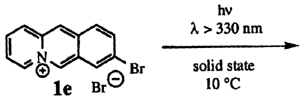
1e **1f**

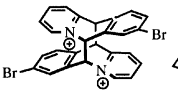
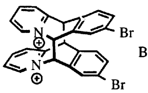
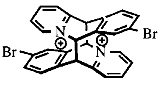
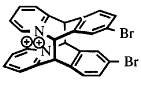
SCHEME 1 Photodimerization of acridizinium derivatives **1a**–**1d**.

RESULTS AND DISCUSSION

The 8-bromoacridizinium bromide (**1e**) was crystallized from several solvents and solvent mixtures and subsequently irradiated in the solid state to give all four regioisomers (Table 1). The identification of the reaction products was carried out by ^{1}H-NMR-spectroscopic analysis of the reaction

TABLE 1 Solid-State Photodimerization of 8-Bromoacridizinium Bromide (**1e**)

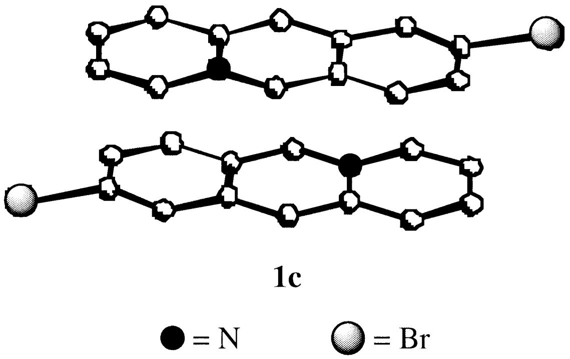


Crystallized from, (Irradiation time, conversion)	 *anti*-**hh-2e**[a]	 *syn*-**hh-2e**[a]	 *anti*-**hh-2e**[a]	 *syn*-**hh-2e**[a]
MeOH/Dioxane (8 h, 28%)	60	12	14	14
MeOH/Acetone (13 h, 13%)	69	8	12	11
MeOH/CH_3CN (8 h, 14%)	77	7	8	8
EtOH (8 h, 41%)	60	11	15	14
EtOH (24 h, 94%)	30	18	26	26
EtOH/Et_2O (8 h, 24%)	75	10	8	7
EtOH/Ethyl Acetate (7 h, 18%)	75	9	8	8
EtOH/CH_3CN (7 h, 19%)	64	12	12	12

[a] ht = head-to-tail; hh = head-to-head, ratio determined from ^{1}H-NMR-spectroscopic analysis of the reaction mixture; error: ± 5% of the given value.

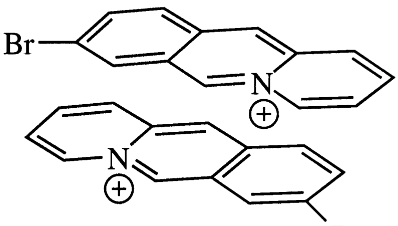
mixture. A preference (60–77%) for the *anti*-head-to-head dimer ***anti*-hh-2e** was observed in each case. This regioselectivity decreases with increasing conversion, i.e. enhanced reaction time. Thus, irradiation of solid samples of **1e** (crystallized from ethanol) for 8 h (conversion: 41%) gave 60% of the dimer ***anti*-hh-2e** whereas the amount of this dimer decreases to 30% in the reaction mixture after 60 h of irradiation (conversion: 94%).

This photoreaction represents the *first example* of a head-to-head selectivity in a acridizinium photodimerization and is in contrast to the solid-state photodimerization of the isomeric 9-bromoacridizinium bromide (**1c**), which yields the *anti*-head-to-tail dimer ***anti*-ht-2c** exclusively [4,5]. The latter regioselectivity, which still remains at full conversion, is explained in terms of a strong directional π stacking of two molecules of **1c** in the solid state. Such a directional effect results from the introduction of a distinct dipole moment into the acridizinium, which forces the π-stacked molecules to arrange in an antiparallel orientation (Fig. 1). In analogy, it may be deduced that the selective formation of the dimmer ***anti*-hh-2e** on



1c

FIGURE 1 Arrangement of two 9-bromoacridizinium molecules in the solid state.



1e

FIGURE 2 Proposed arrangement of two 8-bromoacridizinium molecules in the solid state.

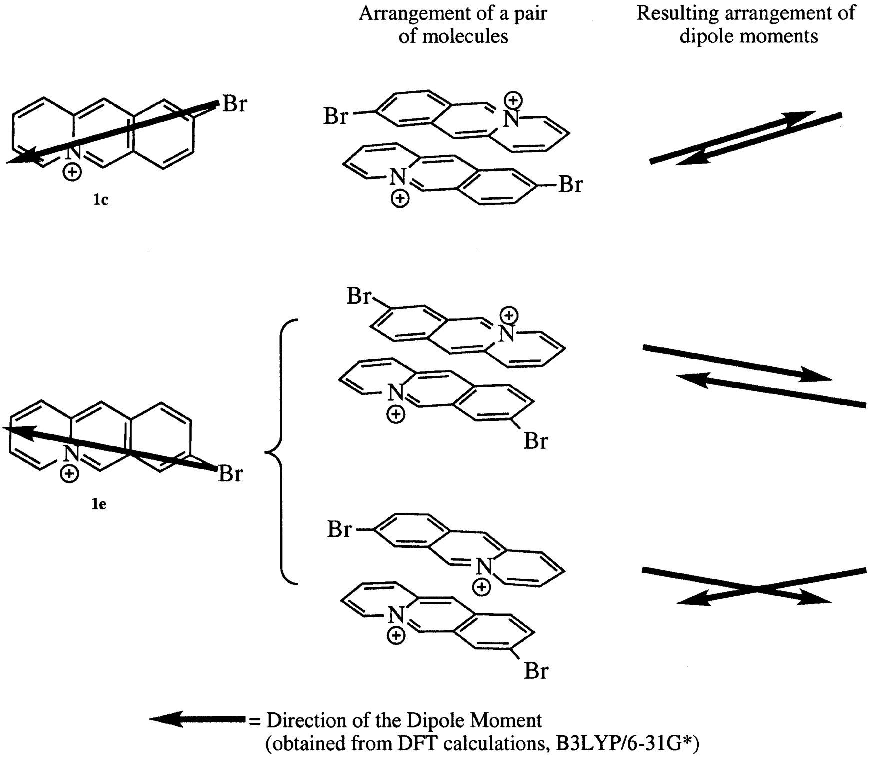


FIGURE 3 Calculated dipole moments of acridizinium salts **1c** and **1e**, possible arrangements in the solid state and resulting dipole-dipole interactions.

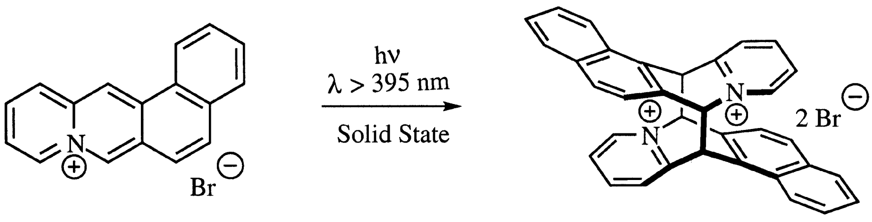
solid-state irradiation of **1e** results from a preferential formation of two molecules in a *anti*-head-to-head arrangement in the crystalline state (Fig. 2). Also, the results of the solid-state photodimerization suggest that not all of the acridizinium molecules adopt such an arrangement. Presumably, this significant disorder is also the reason that no single crystals could be obtained so far.

Why do the two isomers **1d** and **1e** exhibit significantly different solid-state arrangements and, thus, solid-state photoreactivity? In an attempt explain this difference it may be proposed that the orientation of the two aromatic molecules towards each other is governed by a combination of π stacking and dipole-dipole interactions. Whereas the π stacking provides the coplanar arrangement of the two molecule planes, the tendency of two dipole moments to arrange antiparallel may determine the orientation of the molecule axes towards each other [6]. Such an arrangement leads to a net dipole moment of nearly zero and should be energetically favorable.

It should, however, be noted that a statistical analysis of selected data from the Cambridge Structural Database (CSD) reveals that dipole-dipole interactions do not necessarily lead to an anti-parallel orientation of two molecules in the solid state [7].

The theoretical direction of the dipole moments of the isomeric acridizinium derivatives **1c** and **1e** were determined by DFT calculations (B3LYP/6-31G*) and are shown in Figure 3. Thus, an antiparallel orientation of the two dipole moments of **1c** may result in an *anti*-head-to-tail arrangement of two molecules in the solid state (Fig. 3). In fact, this arrangement is confirmed by X-ray diffraction analysis (Fig. 1). Moreover, if the dipole moments in the isomer **1e** tend to superpose in antiparallel orientation, an *anti*-head-to-tail orientation of two molecules of **1e** may also be expected; however, a distorted *anti*-head-to-head arrangement of two molecules in the solid state also results a low net dipole moment (Fig. 3). Thus, the head-to-head arrangement of **1e** in the solid state may also be considered. In fact, the prefential formation of the *anti*-head-to-head dimer ***anti*-hh-2e** on solid-state irradiation suggests that this arrangement is adopted by the majority of molecules in the crystal lattice. So far, this unprecedented preferential arrangement in the solid state is rather speculative and it is not quite clear *why* these molecules arrange in a *anti*-head-to-head orientation. Maybe other intermolecular interactions such as hydrogen bonding or ionic interactions support this arrangement. Further attempts are in progress to analyze the structure in the solid state by X-ray-diffraction analysis.

The benzo-annelated acridizinium salt **1f** was crystallized from ethanol and subsequently irradiated in the crystalline state to afford the *anti*-head-to-head dimer ***anti*-ht-2f** exclusively (Scheme 2). A maximum conversion of 81% was achieved after three days. After recrystallization, the dimer ***anti*-ht-2f** was isolated in 53% yield. The structural assignment of the isolated dimer ***anti*-ht-2f** was made on the basis of chemical shifts and signal patterns of the bridgehead protons in the ^{1}H-NMR spectrum and on ROESY-NMR experiments, as already described for other acridizinium photodimers [3,5].



1f ***anti*-ht-2f**

SCHEME 2 Solid-state photodimerization of acridizinium derivative **1f**.

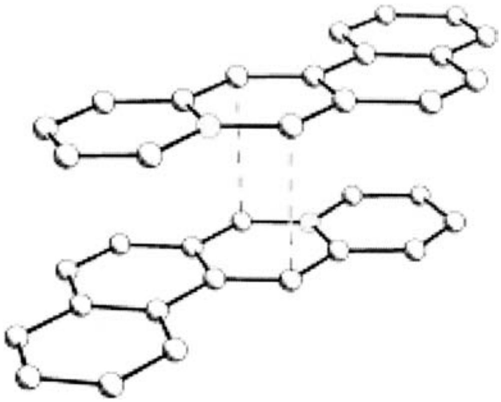


FIGURE 4 Arrangement of two benzoacridizinium molecules **1f** in the solid state (dotted lines indicate the C–C bond which is formed in the course of the [4+4] photocycloaddition).

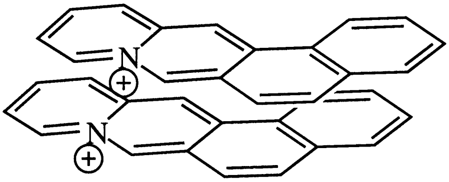


FIGURE 5 *anti*-Head-to-head arrangement of a two molecules of **1f**.

If one considers topochemical behavior during the solid-state photoreaction of the benzoacridizinium salt **1f**, the regioselectivity of the solid-state dimerization may be explained by an arrangement of the chromophores in the crystalline state, which is favorable for a *anti*-head-to-tail dimerization. X-ray diffraction analysis of single crystals of the acridizinium salt **1f** confirmed this proposed solid-state arrangement (Fig. 4). The crystal lattice consists of pairs of molecules which are well arranged for *anti*-head-to-tail dimerization. The observed structural features of compounds **1f** resemble those of the acridizinium salts **1a–c** [2,4,5]. Thus, the distance **d** between the reaction centers; C-6–C-13′ and C13′–C7, is suitable for a solid-state photodimerization ($\mathbf{d} = \mathbf{d}' = 362\,\text{pm}$); however, the two molecules are slightly shifted towards each other and exhibit the characteristic "offset" of π-stacked aromatic molecules [8]. This slight deviation from an ideal overlap of the π systems may be the reason why a topotactic single-crystal-to-single-crystal transformation is not observed [9], as in the case of the parent acridizinium bromide (**1a**) [2].

This result shows that the increase of the π system in aromatic compounds does not necessarily lead to maximum overlap of the molecules, because in that case a *syn*-head-to-head arrangement of two molecules should have been observed (Fig. 5). The similarity between the structures of the parent compound **1a** and **1f** in the solid state shows that the positive charge of the cation may have more influence on the orientation of the two molecules towards each other than the π stacking.

In summary, further examples have been presented which may help to evaluate the structural features that govern the arrangement of acridizinium derivatives in the solid state. It has been shown that the presence of a distinct dipole moment within the acridizinium has a profound influence on the direction of the π stacking. Moreover, the extension of the π system does not lead to significant changes of the π-stacked molecules compared to the parent acridizinium salt **1a**.

REFERENCES AND NOTES

[1] Bradsher, C. K. (1985). In: *Comprehensive Heterocyclic Chemistry*, Boultier, A. J. & McKillop, A. (Eds.), Pergamon Press, Oxford, Vol. 2, p. 525.

[2] (a) Wang, W. N. & Jones, W. (1987). *Tetrahedron*, *43*, 1273.
  (b) Wang, W. N. & Jones, W. (1994). *Mol. Cryst. Liq. Cryst.*, *242*, 227.
  (c) Kearsley, D. K. (1987). In: *Organic Solid State Chemistry*, Desiraju, G. R. (Eds.), Elsevier: Amsterdam, p. 69.

[3] Lehnberger, C., Scheller, D., & Wolff, T. (1997). *Heterocycles*, *10*, 2033.

[4] Ihmels, H., Leusser, D., Pfeiffer, M., & Stalke, D. (2001). *Mol. Cryst. Liq. Cryst.*, *356*, 433.

[5] Ihmels, H., Leusser, D., Pfeiffer, M., & Stalke, D. (1999). *J. Org. Chem.*, *64*, 5715.

[6] Glusker, J. P. (1998). *Top. Curr. Chem.*, *198*, 1.

[7] Whitesell, J. K., Davis, R. E., Saunders, L. L., Wilson, R. J., & Feagins, J. P. (1991). *J. Am. Chem. Soc.*, *113*, 3267.

[8] Hunter, C. (1994). *Chem. Soc. Rev.*, 101.

[9] For an almost complete compilation of single-crystal-to-single-crystal photoreactions, see Reference 30 in: Leibovitch, M., Olovsson, G., Scheffer, J. R., & Trotter, J. (1998). *J. Am. Chem. Soc.*, *120*, 12755.