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Solid-state photoreactivity of 9-substituted acridizinium bromide salts†

Samuel A. Stratford,^a Mihails Arhangelskis,^a Dejan-Krešimir Bučar^{*ab} and William Jones^{*a}

A series of 9-X-acridizinium bromide salts (where X = F, Cl, Br, I, CH₃, C(CH₃)₃) was synthesised, and their solid-state [4 + 4] photoreactivity was investigated using crystallographic and spectroscopic methods, while their thermal stability was studied using thermal gravimetry and differential-scanning calorimetry. The study aimed to identify how the nature and size of the substituent on the acridizinium cation affected the regioselectivity of the [4 + 4] cycloaddition reactions, the reaction yields and relative reaction rates. Computational methods were utilised to rationalize the unexpectedly high regioselectivity of the solid-state photodimerisation of the 9-Cl-acridizinium bromide salt.

Introduction

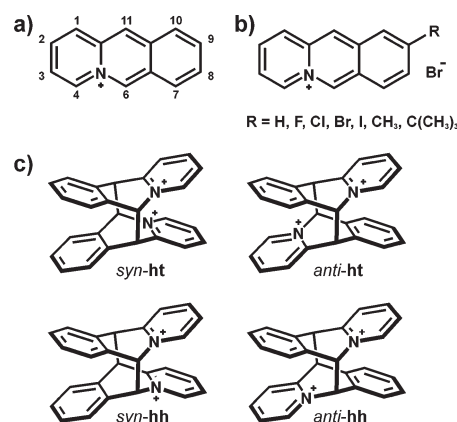
Acridizinium cations are highly conjugated, rigid anthracene-like molecules (Scheme 1a), which upon exposure to UV irradiation undergo a reversible [4 + 4] cycloaddition reaction, both in solution and the solid state.^{1–3} Acridizinium salts have been shown to be useful as molecular switches,⁴ fluorescent probes^{5,6} and sensors.^{7,8} Furthermore, acridizinium-based dendrimers were revealed as promising materials in the context of optical data-storage devices (*e.g.* Blu-ray Disc technology).⁹

While acridizinium derivatives have been reported to photodimerise in solution with low regioselectivity, it has been demonstrated that the regioselectivity of the solution-based reaction can be improved through appropriate derivatisation of the acridizinium cation. A study by Ihmels *et al.* showed that UV-irradiation of 9-Cl-, 9-Br- and 9-OCH₃-substituted acridizinium cations gives rise to four regioisomers, namely *syn*-hh, *anti*-hh, *syn*-ht, *anti*-ht (where ht = “head-to-tail” and hh = “head-to-head”, Scheme 1c), while the 9-NH₂ derivative yields only two.¹⁰ The solid-state [4 + 4] photodimerisation, on the other hand, exhibits further improved regioselectivity.²

Initial reports of photoreactivity studies of polycrystalline acridizinium salts suggested that only the *anti*-ht photodimers form.¹¹ Later studies, however, showed that polycrystalline acridizinium salts yield mixtures of all four possible regioisomers.^{3,12} Single crystals of the corresponding salts, on

the other hand, yield exclusively the *anti*-ht photodimer,^{12,13} thus indicating that the photodimerisation is affected by the orientation of the molecules within the single crystal (*i.e.* the reaction is topochemical). The fact that a high degree of regioselectivity can only be achieved within single crystals (possibly because of the high surface area associated with polycrystalline materials and the inability to control the surface) presents a limitation in terms of functionality. Specifically, the growth of single crystals may not be straightforward and they are also susceptible to mechanical stress and, thus, may be difficult to be processed and incorporated into functional devices.

We assessed in a previous study how the nature of the counter ion in the acridizinium salt affects the reaction yields and the regioselectivity of the solid-state [4 + 4] photodimerisation.^{13,14} It was shown that larger anions (*e.g.* picrate) and those with a tetrahedral geometry (*e.g.* perchlorate,



Scheme 1 Molecular structures of: a) an acridizinium cation, b) the studied 9-substituted acridizinium cations and c) possible regioisomers of the acridizinium photodimer. The nomenclature of the regioisomers was adapted from Ihmels *et al.*^{1,2} for clarity and comparison purposes.

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: wj10@cam.ac.uk

^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK. E-mail: d.bucar@ucl.ac.uk

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hexafluorophosphate, tetrafluoroborate) distort the packing of the acridizinium ions to affect the photoreactivity in two ways: they either lower the reaction rates (e.g. perchlorate, tetrafluoroborate), or they render the solid photostable (e.g. hexafluorophosphate). Spherical anions (e.g. bromide and iodide) were found to improve reaction kinetics. The effect of the counterion was also shown to be different in the case of the 9-methylacridizinium cation, as compared to the 9-bromoacridizinium cation.¹⁴ While the perchlorate and the bromide salts reacted very quickly, the iodide salt reacted very slowly and exhibited a long induction period. In a related study, Ihmels *et al.* also showed that 9-bromoacridizinium bromide resulted in exclusively the *anti*-ht isomer.¹ This contrasted with the regioselectivity of 8-bromoacridizinium bromide, a solid that was reported to yield all four regioisomers upon UV-irradiation in the solid state.²

The work reported here focuses on how the substituents on the acridizinium framework influence the solid-state photoreactivity of the salts. With this in mind, we have synthesised a series of 9-X-acridizinium bromide salts (9-X) (where X = F, Cl, Br, I, CH₃, C(CH₃)₃; Scheme 1b) in order to study how the nature and the size of the substituent controls reaction rates and regioselectivity. We chose to study 9-substituted acridizinium salts with bromide as the counterion, as it has been previously shown that related acridizinium bromide salts yield photodimers in a regioselective fashion and in high yields.¹

Results and discussion

1. Structural analyses of the 9-substituted acridizinium salts

The diffraction data for compounds 9-X were collected at room temperature (*i.e.* 298 K) in order to study their structural features at conditions under which the photoreactivity studies were conducted. Room temperature diffraction experiments were considered to be necessary, as the photoreactivity is temperature dependent (low temperatures are reported to induce shifts of acridizinium cations in the crystal lattice, or even phase transitions).²

Single crystal and powder X-ray diffraction studies showed that the structures of all studied single crystals are identical to those of the corresponding bulk materials. All the 9-X-acridizinium bromides were found to crystallise as hydrates. The acridizinium cations in the majority of the studied salts exhibit a preference to arrange in an *anti*-ht fashion. This is attributed to the repulsion forces occurring between the quaternary nitrogen atoms, as well as to the donor-acceptor $\pi\cdots\pi$ interactions between the electron rich phenyl moiety and the pyridinium moiety. Based on the alignment of the acridizinium cations in their crystal lattices and assuming topochemical control, it was anticipated that the majority of solids would yield only *anti*-ht photodimers upon UV-irradiation. The cations in 9-F, 9-Cl and 9-C(CH₃)₃, however, display different packing modes and were thus expected to yield other photodimers. Specifically, the 9-Cl cations are arranged in an *anti*-ht and *syn*-ht fashion, while

the 9-F cations stack in both an *anti*-ht and *anti*-hh manner (as a consequence of molecular disorder). The photoreactions of 9-F and 9-Cl were, therefore, expected to be less regioselective than those of the other salts. 9-C(CH₃)₃, on the other hand, displays stacks wherein the cations are exclusively aligned in a *syn*-ht fashion for the formation of only one photodimer.

Our studies have also revealed the unexpected formation of 9-I triiodide. It should be noted that this compound is not a major constituent of the bulk material, but rather appears as an impurity in the bulk of 9-I bromide. It is presumed that the triiodide counter anion was formed at some point during the synthesis of 9-I. The crystal structure of the triiodide stands out because it does not include a water molecule, thus, suggesting that the triiodide might exhibit greater thermal stability than other acridizinium salts described herein. The structural features of all solids are described below in succession.

1.1. 9-Fluoroacridizinium bromide monohydrate (9-F). Single crystal X-ray diffraction studies showed that salt 9-F crystallises in the monoclinic $P2_1/c$ space group with one 9-fluoroacridizinium cation, one bromide anion and one water molecule in the asymmetric unit. The acridizinium cation is disordered over two positions (occupancies: 0.50 : 0.50), thus resulting in an *anti*-ht and *anti*-hh arrangement of the acridizinium cation pairs (Fig. 1a). The reaction centres in the acridizinium pair are separated by 3.99 Å. The pairs are connected by four-component centrosymmetric bromide-water hydrate assemblies *via* C-H \cdots Br and C-H \cdots O interactions, and form a one-dimensional array (highlighted in Fig. 1b). The four-component bromide-water assembly is sustained by O-H \cdots Br interactions (highlighted in Fig. 1b). The one-dimensional molecular array is extended into a planar two-dimensional structure *via* C-H \cdots F forces. The two-dimensional sheets are stacked (Fig. 1b) and held together by Br $\cdots\pi$ forces.

1.2. 9-Chloroacridizinium bromide hydrate (9-Cl). Single crystal X-ray diffraction was used to show that salt 9-Cl crystallises in the triclinic $P\bar{1}$ space group. The asymmetric unit consists of two 9-chloroacridizinium cations, two bromide counter anions and two molecules of water. The cations stack infinitely in an offset manner leading to *anti*-ht and *syn*-ht packing arrangements. The reaction centres of *anti*-ht arranged cations in the stack are separated by 3.80 Å, while

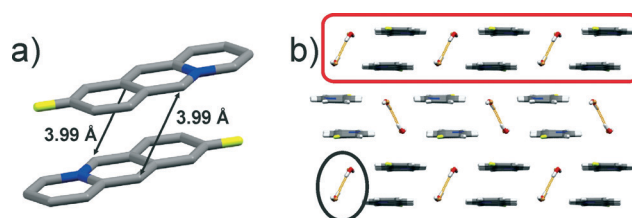


Fig. 1 X-ray crystal structure of: a) two stacked 9-F cations in an *anti*-ht arrangement (hydrogen atoms are omitted for clarity, only one occupancy is shown), and b) crystal packing of 9-F viewed along a^* .



the reaction centres of the *syn*-ht arranged cations are separated by 3.63 and 3.83 Å (Fig. 2a). While the reaction centres in the *anti*-ht and *syn*-ht acridizinium pairs display similar separation distances, their alignment differs noticeably. More specifically, the *anti*-ht acridizinium cations align in a parallel offset fashion, while the acridizinium cations of the *syn*-ht pairs display an angular offset (Fig. 2b). The acridizinium stacks are separated by four-component centrosymmetric bromide-water assemblies *via* C–H⋯Br and C–H⋯O interactions. The bromide-water assemblies are held together by O–H⋯Br hydrogen bonds. The crystal lattice of 9-Cl (Fig. 2c) is sustained by C–H⋯Br interactions.

The diffraction data suggested that the studied 9-Cl single crystal was partially dehydrated (more specifically, one of the two water molecules in the asymmetric unit exhibited a partial occupancy of ~50%). Considering the low dehydration temperature of the solid (see Table 2), the fact that the diffraction data was collected at room temperature, and that all other studied acridizinium salts crystallise as monohydrates, it is likely that 9-Cl in fact crystallises as a (thermally unstable) monohydrate.

Another polymorph of 9-Cl was earlier identified by Ihmels *et al.* (CCDC reference code: CIPQUN, Form I).¹ Unlike the 9-Cl polymorph described herein (Form II), Form I features 9-chloroacridizinium cations being arranged exclusively in an *anti*-ht fashion, similarly to the 9-bromoacridizinium cations in the structure of 9-Br (described below).

1.3. 9-Bromoacridizinium bromide monohydrate (9-Br). The crystal structure of 9-Br was determined using single crystal X-ray diffraction. The salt crystallises in the triclinic $P\bar{1}$ space group with one 9-bromoacridizinium cation, one bromide anion and one water molecule in the asymmetric unit. The acridizinium cations pack pair-wise in an *anti*-ht manner forming infinite stacks. The reaction centres in the cation pair are separated by 3.78 Å, while the reaction centres of cations belonging to neighbouring pairs are separated by 3.95 Å (Fig. 3a).

The stacks of 9-bromoacridizinium cations are separated by bromide-water hydrate assemblies (as seen in the previously

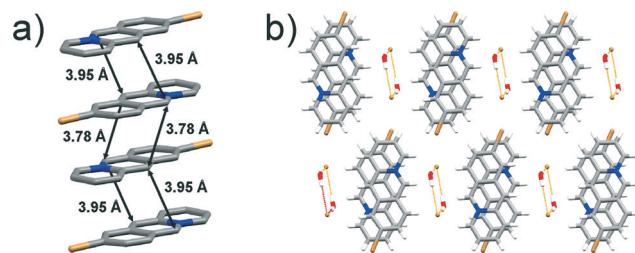


Fig. 3 X-ray crystal structure of: a) an infinite stack of 9-Br cations (hydrogen atoms are omitted for clarity), and b) crystal packing of 9-Br viewed along the crystallographic axis *a*.

described structures), and held together by C–H⋯Br and C–H⋯O interactions to form a two-dimensional molecular array. These molecular arrays further stack and are held together by van der Waals forces (Fig. 3b). The herein reported room-temperature crystal structure of 9-Br is identical to one determined at low temperature by Ihmels *et al.* (CCDC reference code: CIPQOH).¹

1.4. 9-Iodoacridizinium bromide monohydrate (9-I-Br) and 9-iodoacridizinium triiodide (9-I-I₃). The 9-iodoacridizinium cation was found to crystallise in two forms that differ in colour, one occurring as colourless needles, while the other occurs as brown blocks. Both crystals were subjected to single crystal X-ray crystallographic analyses that revealed that the 9-iodoacridizinium cation forms salts with different counterions, *i.e.* Br[−] and I₃[−].

Colourless single crystals corresponding to the bulk material were identified as 9-iodoacridizinium-bromide monohydrate (9-I-Br). The compound crystallises in the monoclinic $P2_1/c$ space group with one 9-iodoacridizinium cation, one bromide anion and one water molecule in the asymmetric unit. The structure features pairs of acridizinium cations that stack infinitely in an *anti*-ht manner. The reaction centres of the cations within the pairs are separated by 3.81 Å, while the reaction centres of cations belonging to neighbouring acridizinium pairs are separated by 4.04 Å (Fig. 4a). Neighbouring stacks are, as in the other described structures, separated by hydrogen-bonded bromide-water hydrate assemblies. The crystal structure of 9-I-Br is sustained by C–H⋯O, C–H⋯Br and I⋯O and interactions (Fig. 4b).

The brown single-crystalline blocks were identified as an anhydrous form of 9-iodoacridizinium triiodide, 9-I-I₃.

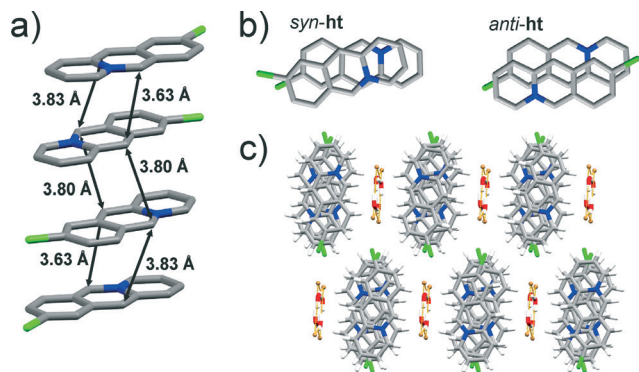


Fig. 2 X-ray crystal structure of: a) an infinite stack of 9-Cl cations (hydrogen atoms are omitted for clarity), b) parallel and angular offsets in pairs of *syn*-ht and *anti*-ht pairs of acridizinium cations, and c) crystal packing of 9-Cl viewed along the crystallographic plane (-110) .

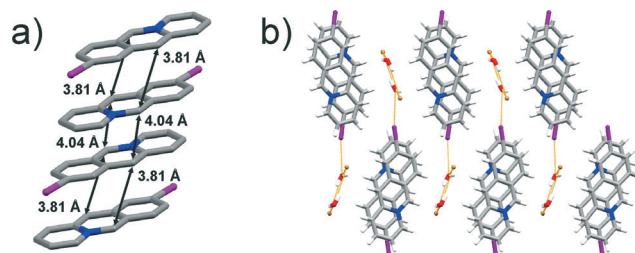


Fig. 4 X-ray crystal structure of: a) an infinite stack of 9-I cations (hydrogen atoms are omitted for clarity), and b) crystal packing of 9-I-Br viewed along the crystallographic axis *a*.



The solid crystallises in the triclinic space group $P\bar{1}$, with one 9-iodoacridizinium cation and one triiodide anion in the asymmetric unit. The cations stack pair-wise in an *anti*-ht fashion. The cation pairs are isolated by triiodide anions. The reaction centres within each cation pair are separated by 3.79 Å (Fig. 5a). The crystal structure of **9-I-I₃** is held together by C-H...I, I... π and I...I interactions (Fig. 5b).

1.5. 9-Methylacridizinium bromide monohydrate (9-CH₃). Single crystal X-ray diffraction studies showed that salt **9-CH₃** crystallises in the triclinic $P\bar{1}$ space group with one 9-methylacridizinium cation, one bromide anion and one water molecule in the asymmetric unit. The cations pack pair-wise in an *anti*-ht manner forming infinite slanted stacks. The reaction centres of the cations within the pairs are separated by 3.69 Å, whereas the reaction centres of cations belonging to the neighbouring cation pairs are separated by 4.53 Å (Fig. 6a), *i.e.* a distance that is believed not to support a [4 + 4] photodimerisation in the solid state.¹⁵ The stacks of **9-CH₃** cations are segregated by bromide-water hydrate assemblies, and held together by C-H...O and C-H...Br interactions (Fig. 6b) to form a two-dimensional molecular array. The molecular arrays stack and are held together by van der Waals forces, as seen in **9-Cl** (Fig. 3b).

1.6. 9-*tert*-Butyl-acridizinium bromide monohydrate (9-C(CH₃)₃). Attempts to grow single crystals of **9-C(CH₃)₃** for X-ray diffraction studies were unsuccessful after numerous trials (see ESI†). The crystal structure solution of **9-C(CH₃)₃** was therefore achieved utilising powder X-ray diffraction data and a combination of simulated annealing, Rietveld refinement and DFT calculations (see ESI†). The solution-based crystallisation experiments have, however, unexpectedly yielded single crystals of the *anti*-ht photodimer of

9-C(CH₃)₃, which formed in a closed crystallisation vial that was unintentionally left exposed to sunlight for about a week (for the crystal data of the photodimer see ESI†).

The **9-C(CH₃)₃** monomer crystallises in the orthorhombic $Pca2_1$ space group with one acridizinium cation, one bromide anion and one water molecule in the asymmetric unit. The slightly twisted acridizinium cations are stacked in a *syn*-ht fashion (Fig. 7a) whereby neighbouring cations exhibit an angular offset (Fig. 7b). The reaction centres of the cations are separated by 3.42 and 3.95 Å and are thus conforming to the topochemical postulates. The stacks are separated by infinite zigzag-shaped bromide-water chains, which are held together by O-H...Br interactions (Fig. 7b). The chains interact with the acridizinium cations *via* C-H...Br and C-H...O interactions.

2. Photoreactivity studies – yields and regioselectivity

Powder samples of salts **9-Cl**, **9-Br** and **9-CH₃** formed *anti*-ht photodimers in almost quantitative yields after 5 hours of irradiation (**9-Br**: 95.7%, **9-Cl**: 95.4%, **9-CH₃**: 97.4%; the overall yields of photoproducts are >99% in all three solids). Solids **9-F**, **9-I-Br** and **9-C(CH₃)₃** photoreacted to a lesser extent. In particular, UV irradiation of **9-I-Br** for 24 hours yielded the *anti*-ht photodimer in only 8.6% yield, despite the fact that the alignment of the monomers conforms to Schmidt's topochemical postulate.¹⁵ The photoreaction of **9-I-Br** also yielded other regioisomers as by-products with a 4.4% yield. Salt **9-C(CH₃)₃** generated a mixture of different regioisomers in 25.9% yield (including the *anti*-ht dimer). The **9-F** salt was UV-irradiated for 24 hours to undergo the formation of a mixture of regioisomers in 58.4% yield (see ESI†).

The high regioselectivity of the photodimerisation of **9-Br** and **9-CH₃** was not surprising considering that their respective cations are exclusively aligned in an *anti*-ht fashion (Fig. 3a and 6a). The high regioselectivity of the **9-Cl** (Form II) photodimerisation (>95%), on the other hand, is unexpected bearing in mind that the cations in this structure are aligned in both an *anti*-ht and *syn*-ht manner, and that the separation distances of the reactive centres in the *anti*-ht and *syn*-ht cation pairs in Form II both conform to Schmidt's topochemical

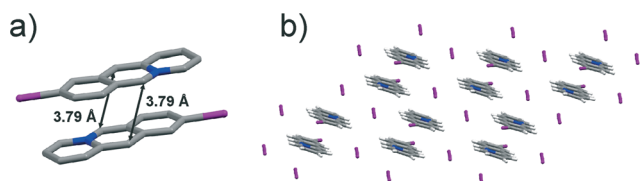


Fig. 5 X-ray crystal structure of: a) an infinite stack of **9-I** cations (hydrogen atoms are omitted for clarity), and b) crystal packing of **9-I-I₃** viewed along the crystallographic plane (-101).

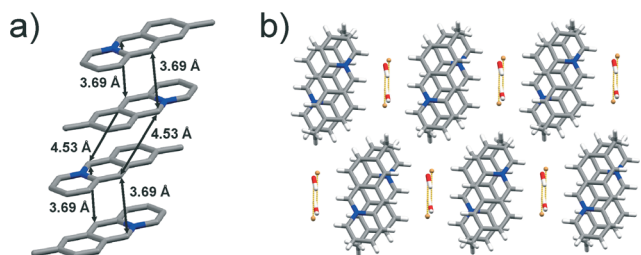


Fig. 6 X-ray crystal structure of: a) an infinite stack of **9-CH₃** cations (hydrogen atoms are omitted for clarity), and b) crystal packing of **9-CH₃** viewed along the crystallographic axis *a*.

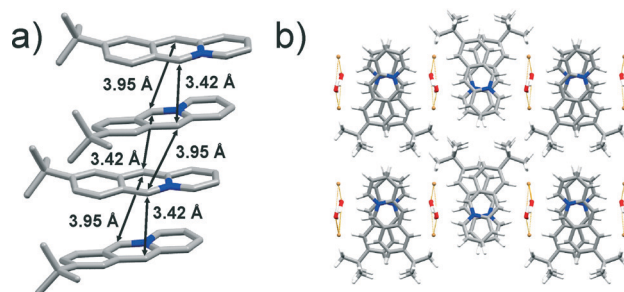


Fig. 7 X-ray crystal structure of: a) an infinite stack of **9-C(CH₃)₃** cations (hydrogen atoms are omitted for clarity), and b) crystal packing of **9-C(CH₃)₃** viewed along the crystallographic axis *c*.



postulate. It is, therefore, reasonable to expect that the photodimerisation reaction of Form II would be regioselective than that of 9-Br and 9-CH₃. The high regioselectivity of the Form II photoreaction suggested that Form II potentially transformed into its initially reported polymorph Form I (which is expected to yield exclusively the *anti*-ht isomer¹) either before or while the solid was UV irradiated. This proposition was supported by the finding that an unreacted portion of the initially prepared Form II batch transformed into Form I after being in storage for more than six months (see ESI† Fig. S21). Attempts to confirm whether the initially obtained Form II actually yields one regioisomer in >95% yield, or whether the solid undergoes a phase transition prior to or during the UV-irradiation, have *initially* failed, as Form II could not be reproduced. The inability to prepare a crystal form that has previously been synthesised (or to prepare elusive crystal forms^{16,17}) is a frustrating issue that solid-state scientists occasionally face.¹⁸ Although the crystallization conditions for the consistent production of a 'disappearing polymorph' can be determined as a result of systematic and copious crystallization studies,¹⁹ our efforts to obtain the initially observed polymorph Form II through recrystallization were unsuccessful after numerous attempts. The initially observed polymorph Form II was finally obtained from a freshly synthesised batch of the 9-chloroacridizinium cation. We believe that the formation of Form II eventually succeeded through heteronuclear seeding^{20,21} by an unidentified material in the reaction mixture. After Form II was reproduced and structurally characterized, the solid was immediately subjected to UV irradiation for five hours to produce the *anti*-ht regioisomer in 96% yield. *Ex situ* analysis of a Form II bulk after only 30 min of UV irradiation confirmed that the majority of the unreacted bulk in the solid corresponds to Form II, which suggests that the Form II might not convert into Form I while being exposed to UV irradiation (see ESI† Fig. S21).

Preliminary computational studies (see ESI†) point to the fact that the high regioselectivity of the photodimerisation reaction might be attributed to a more efficient molecular orbital overlap between the cations in the *anti*-ht pair, as compared to the cations in the *syn*-ht pair. More specifically, DFT calculations showed that the electron distribution in the LUMO of the *anti*-ht cation pair is localised in the area between two cations where carbon-carbon single bonds are expected to form upon UV irradiation. The LUMO of the *syn*-ht pair, on the other hand, does not feature any electron distribution that could correspond to the formation of the carbon-carbon single bonds, thus indicating that the [4 + 4] photodimerisation is not likely to occur between the cations of the *syn*-ht pair (Fig. 8).

The results of the photoreactivity studies are summarised in Table 1. The NMR spectra of the acridizinium-based solids are shown in the ESI† document. The assignment of the ¹H NMR signals to the dominant regioisomers of the photodimers is detailed in the ESI†.

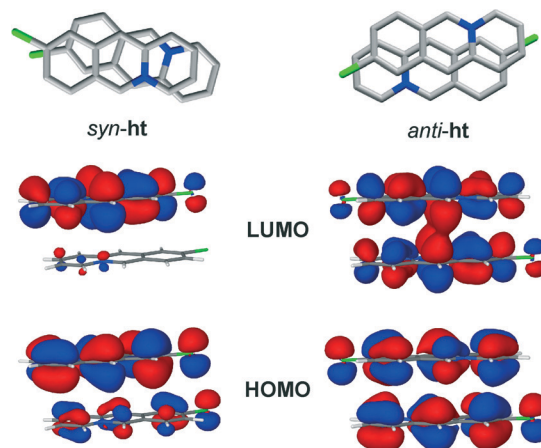


Fig. 8 HOMO and LUMO orbitals of the *syn*-ht (left) and *anti*-ht (right) pairs of 9-chloroacridizinium cations in 9-Cl.

3. Photoreactivity studies – reaction rates

Photoreactivity studies were also carried out using a UV source (366 nm) of significantly lower intensity (namely 10 W) to study the relative rates of the [4 + 4] photodimerisation reaction involving 9-Cl, 9-Br and 9-CH₃. Salts 9-F, 9-I-Br and 9-C(CH₃)₃ were not considered in this part of the study owing to the low yields and the low regioselectivity of their photodimerisation reaction. The relative conversion rates were obtained by measuring the integrals of ¹H NMR signals corresponding to monomers and dimers of the studied acridizinium cations (see ESI†).

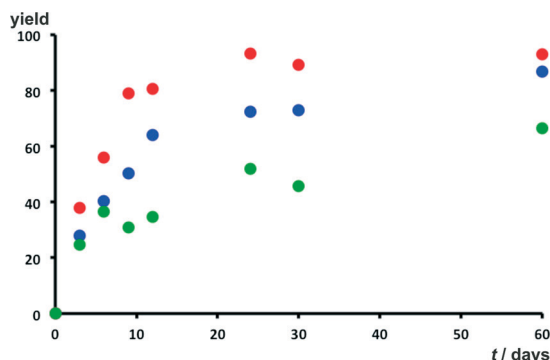
Irradiation of the salts was again shown to result in the formation of the *anti*-ht regioisomer. Fig. 9 shows that salt 9-Cl undergoes photodimerisation with the fastest reaction rate in nearly quantitative yields (*i.e.* 93%) after low-intensity UV irradiation for 60 days. The reaction of salts 9-Br proceeded somewhat slower in the same timeframe to react up to 87% yield, whereas 9-CH₃ reacted at the lowest rate up to yield 67%. The relative conversion rates for solids are shown in Fig. 9. The low-intensity UV-irradiation of the three studied solids surprisingly revealed that the regioselectivity of the dimerisation had diminished. A two-fold increase in the formation of the *syn*-ht 9-Cl and 9-Br photodimers was observed, while a four-fold increase of the *syn*-ht photodimer formation was observed in the case of 9-CH₃. The increased formation of the *syn*-ht photodimer during the low-intensity UV-irradiation studies might be attributed to the low thermal stability of the solids, which were found to dehydrate at relatively low temperatures (*i.e.* 40–98 °C, Table 2). The low thermal stability of the salts is thought to lead to structural rearrangement of the acridizinium cations in their respective crystal lattices, which feasibly enables the increased formation of the *syn*-ht isomers. In addition, long UV-irradiation times might lead to partial melting of the solids, which facilitates the alignment of the acridizinium cations favouring the formation of other regioisomers.

In addition to the observed differences in reaction yields, reaction rates and thermal behavior, we note that the



Table 1 Separation distances of the reaction centres in 9-X cations in their respective solids, their arrangement, and their photodimerisation yields

Salt	$d(\text{C}\cdots\text{C})/\text{\AA}$	Arrangements	Overall yield (irradiation time)	Main isomer (yield)
9-F	3.99	<i>anti</i> -hh, <i>anti</i> -ht	58.4% (24 h)	<i>anti</i> -ht (18.2%)
9-Cl	3.63, 3.83	<i>anti</i> -ht, <i>syn</i> -ht	>99.0% (5 h)	<i>anti</i> -ht (96.2%)
9-Br	3.78, 3.95	<i>anti</i> -ht	>99.0% (5 h)	<i>anti</i> -ht (95.7%)
9-I-Br	3.81, 4.04	<i>anti</i> -ht	13.0% (24 h)	<i>anti</i> -ht (8.6%)
9-CH ₃	3.69, 4.53	<i>anti</i> -ht	>99.0% (5 h)	<i>anti</i> -ht (97.4%)
9-C(CH ₃) ₃	3.42, 3.95	<i>syn</i> -ht	25.9% (5 h)	<i>syn</i> -ht (17.0%)

**Fig. 9** Relative rates of conversions for salts 9-Cl (red), 9-Br (blue), and 9-CH₃ (green) using a low intensity single wavelength UV lamp.

acridizinium salts exhibit distinct hydration behavior, as well as various degrees of crystallinity upon exposure to UV irradiation. Studies are underway to explain the complex relationship between the solid-state reactivity (*i.e.* reaction yields and rates), the reaction conditions (*e.g.* humidity) and the molecular dynamics of the acridizinium cations within the solid during UV irradiation.

Conclusions

A series of 9-X-acridizinium bromide salts (where X = F, Cl, Br, I, CH₃, C(CH₃)₃) (9-X) was synthesised and characterised using crystallographic, thermal, spectroscopic and computational methods. The structural studies revealed that the salts mainly pack in an *anti*-ht fashion in their crystal structures. Exceptions to such packing behaviour are 9-F, 9-Cl and 9-C(CH₃)₃, wherein the cations pack in either an *anti*-ht and *anti*-hh fashion (9-F), a *syn*-ht and *anti*-ht manner (9-Cl), or a

syn-ht fashion (9-C(CH₃)₃). All studied bromide salts were shown to crystallise as hydrates.

All structurally characterised acridizinium salts were found to conform to Schmidt's topochemical postulate. Photoreactivity studies showed that the *anti*-ht photodimer was formed in 97% yield for 9-CH₃ and 96% yield for 9-Cl and 9-Br. The overall photodimerisation yields (*i.e.* the extent of the formation of all possible regioisomers) for these salts was >99%. The photodimerisation reactions of salts 9-I-Br, 9-F and 9-C(CH₃)₃ were less regioselective and also yielded less photoproducts. Only one crystal structure of a photodimer, namely that of the *anti*-ht 9-C(CH₃)₃ photodimer, was determined.

Thermal investigations showed that all studied acridizinium salts exhibit similar thermal stabilities with respect to dehydration. Salt 9-Cl was found to have the lowest stability towards dehydration, while the 9-Br salt exhibited the highest stability.

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Table 2 Dehydration temperatures (t_d) and melting points (t_m) of the 9-X salts (for more details see ESI)

Salt	$t_d/^\circ\text{C}$	Determined mass loss/%	Calculated mass loss/%	$t_m/^\circ\text{C}$
9-F	45	4.20	6.00	230
9-Cl	40	4.33	5.76	249
9-Br	98	5.17	5.04	270
9-I-Br	67	3.70	4.46	257
9-CH ₃	55	6.15	6.16	179
9-C(CH ₃) ₃	45	4.65	5.38	145



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