4-Styrylquinolines: synthesis and study of [2 + 2]-photocycloaddition reactions in thin films and single crystals†‡

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Four new (*E*)-4-styrylquinoline compounds containing two methoxy substituents or an 18-crown-6-ether fragment were synthesized in order to investigate the [2 + 2]-photocycloaddition (PCA) reaction in the solid state. These compounds reveal different abilities to undergo the photoreaction depending on the packing of the quinoline molecules in thin polycrystalline films and single crystals. The only products from the irradiation of (*E*)-4-styrylquinolines were an *rctt* isomer of 1,2,3,4-tetrasubstituted cyclobutane and, rarely, a *Z* isomer of the styrylquinoline. The *rctt* cyclobutane derivative was formed as a result of the PCA of centrosymmetric *syn*-'head-to-tail' dimeric pairs of the reactant species that are preorganized in such a way as to promote this reaction. Peculiarities in the crystal packing motifs that are typical for single crystals of 4-styrylquinoline compounds are discussed. The solvate molecules can affect significantly the packing of styrylquinolines. Benzene solvate molecules create a soft, flexible, shell about the dimeric pairs that facilitates the PCA in the single crystal without causing degradation of the crystal. In crystal packing that contains CH_2Cl_2 and H_2O solvate molecules, they are prone to form complicated systems of hydrogen bonds with crown-ether oxygen atoms and each other. This results in distorting the organic molecule geometry toward non-planarity and accomplishing a new type of crystal packing uncommon for styrylheterocycles, in which the PCA is impossible. The topochemical single-crystal-to-single-crystal PCA reaction was monitored for one of the species. Two cyclobutane derivatives obtained in single crystals were subjected to recrystallization from a solution. The new single crystals formed belong to different crystal systems, with different unit cell parameters as compared with initial single crystals; significant differences in the geometry of the cyclobutane molecules were also found. This implies that the cyclobutane derivatives obtained in the solid phase have a molecular geometry that is somewhat stressed.

Introduction

Unsaturated compounds containing ethylene C=C bonds, such as stilbenes, their aza analogues and vinylogues, are known to undergo [2 + 2]-photocycloaddition (PCA) in the solid state, or in concentrated solutions.[1] It has been established that there are important specific geometric requirements for the olefin dimer that is a precursor for this reaction. These requirements are: (1) the two olefin units should be situated in parallel planes one above the other and (2) the interplanar distance between these units, d_1, should be equal to 3.6–4.2 Å (Scheme 1). In the most cases these requirements are realized although several exceptions to these requirements are known and associated with more distant mutual arrangement of the ethylene groups participating in the PCA or crossed arrangement of the ethylene groups in the parallel planes.[1n,o]

Previously, we have found that crown-ether stilbene-like compounds participate in stereoselective PCA reactions.[2,3] For crown-ether styryl and butadienyl dyes bearing an *N*-sulfonatoalkyl spacer, this reaction usually takes place in solution in the presence of metal cations. Crown-ether styryl dyes containing an ammonioalkyl group in their heterocyclic moiety undergo efficient and stereospecific PCA both in solution and in the crystal state. We have established[2] that the presence of an additional functional group (SO_3^- or NH_3^+) in the dye molecule assists in the preorganization of the structural units to give specific dimeric complexes with a parallel arrangement of the ethylene fragments (Scheme 1). Metal cations with large ionic radii (Sr^{2+}, Ba^{2+}) and alkanediammonium compounds were also found to be able to assemble unsaturated crown ethers into sandwich-like structures to enable the PCA reaction to proceed.[3]

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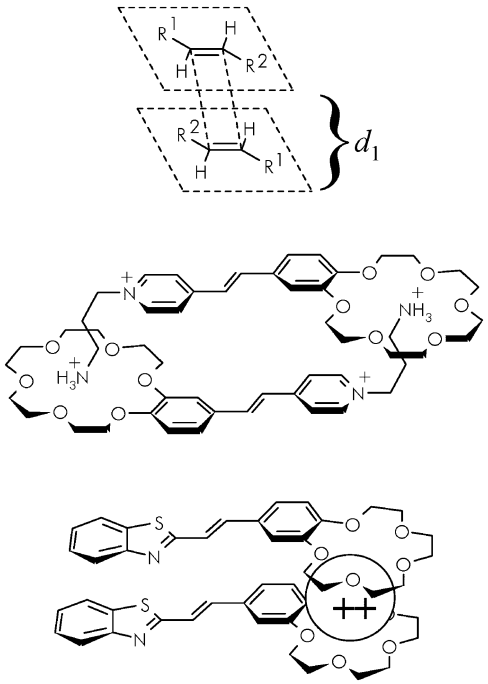
† Electronic supplementary information (ESI) available: formation of cyclobutane *rctt*-**11**, crystal structures and packings, crystal data, and selected geometric parameters. See DOI: 10.1039/b615056j
‡ The HTML version of this article has been enhanced with colour images.



Scheme 1 The precursor dimer for the PCA reaction, and examples of the self-assembly in solution of two crown-ether stilbene-like molecules.

This specific sandwich-like mutual arrangement of two units may also be supported by a crystal lattice, consequently PCA reactions are often observed in the solid state. It is obvious that the PCA reaction should proceed inside the volume specified by the initial dimer unit. Therefore, this reaction may be accomplished without crystal degradation, which is to say, as a single-crystal-to-single-crystal transformation. In the last few years many observations of these processes in single crystals have been reported.[1f,4] However, so far systematic investigations, and predictions as to the particular type of crystal packing that permits such a transformation to occur without crystal degradation, are lacking.

Herein we report the synthesis, ^{1}H NMR and X-ray studies, of the structure and PCA reaction for four new 4-styrylquinoline compounds, namely, the neutral 1-quinolyl-2-phenylethylenes **1** and **3**, and the related cationic styryl dyes **2** and **5**, and the products of their PCA reactions, and some other related compounds. Peculiarities in their crystal packing motifs and geometric characteristics are also discussed.

Results and discussion

Synthesis

The synthetic route for the preparation of the compounds is presented in Scheme 2. Recently obtained[5] 4-styrylquinoline **1** was quaternized with ethyl *p*-toluenesulfonate, followed by anion exchange with perchloric acid to give rise to the corresponding styryl dye **2** in good overall yield. The new compound **3** was synthesized by condensation of (4-formylbenzo)-18-crown-6 ether with lepidine in a near equimolar ratio in DMF under basic conditions. This reaction afforded the target product **3** (yield 48%) along with the bisheterocyclic derivative **4**, which is produced as a result of the Michael addition of a second molecule of lepidine to the double bond of **3**. It should be noted that compound **4** was formed in a manner that is unlike the similar condensation reaction between lepidine and (4-formylbenzo)-15-crown-5 ether.[5] Furthermore, using a five-fold excess of lepidine was found to substantially increase the yield of **4** (45 *vs.* 10%), which became the only product of the reaction. The crown containing styryl dye, **5**, was obtained from **3** in a similar way to the synthesis of **2** from **1**.

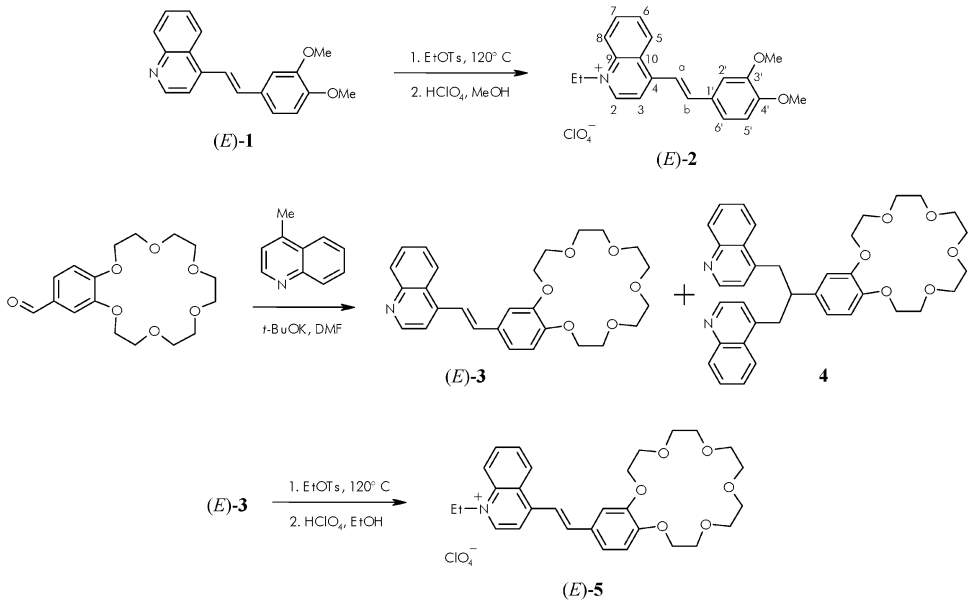
According to the vicinal coupling constants for the ethylene bond protons, $^3J_{H(a),H(b)}$ = 15.7–16.1 Hz, compounds **1–3**, and **5** were obtained as *E* isomers.

^{1}H NMR study

In solution, compound (*E*)-**1** was revealed[5] to be present as a mixture of s-*cis*- and s-*trans*-conformers, which differ by the orientation of dimethoxybenzene moiety with respect to ethylene fragment of the molecule. Dyes **2** and **5** and the neutral compound **3** have a similar conformational composition in DMSO-d_6 solution; this is confirmed by the presence of intense NOE cross signals between protons H(2′), H(6′), H(a), and H(b) (see Scheme 2 for atom numbering). Irradiation of solutions of **1–3** and **5** with visible light only brings about the reversible *E–Z* isomerization of the compounds about the ethylene bond. This type of photoreaction has been observed for the styryl dyes of a pyridine series, and in related compounds studied by us previously.[2b,e,6]

Visible light irradiation of compounds **1**, **2**, and **5** as thin polycrystalline films resulted in the relatively fast and substantial reduction in their colour. Analysis of ^{1}H NMR data for the photoproducts showed that the initial compounds disappeared gradually and that in each case only a single product was present in the final reaction mixture. For these photoproducts, the signals for the protons and carbon atoms of the ethylene bond are absent from the aromatic region of the spectra, and two new signals appear at δ 5.1–5.5 ppm (Fig. 1) and at δ 43–50 ppm in the ^{1}H and ^{13}C NMR spectra, respectively. The positions of these peaks are typical of the cyclobutane derivatives of styryl dyes that have been observed previously, and are known to form upon the photoirradiation of these dyes.[2b,e,6]

Thus, the solid-phase photoreactions of **1**, **2**, and **5** gave rise to cyclobutane derivatives **6**, **7**, and **9**, respectively. The presence of only one set of signals in the NMR spectra is indicative of the formation of a single stereoisomer. The proton signals due to the cyclobutane fragments within the resulting photoadducts appear as symmetric AA′BB′ spin systems (Fig. 1), with vicinal coupling constants of 9.1–10.5 and 5.6–7.0 Hz. The difference in the coupling constants is associated with the difference in the endocyclic dihedral angles in the cyclobutane moieties. Since the signals for the cyclobutane protons comprise two doublets of doublets,[6] the solid-phase photocycloaddition affords the *rctt* stereoisomers of cyclobutanes **6**, **7**, **9** and, hence, the cycloaddition of (*E*)-**1**, (*E*)-**2**, and (*E*)-**5** takes place within the *syn*-'head-to-tail' arrangement of the dimeric pairs (Scheme 3).



Scheme 2 The synthetic route affording 4-styrylquinoline compounds **2**, **3**, **5** and the bisheterocycle **4**.

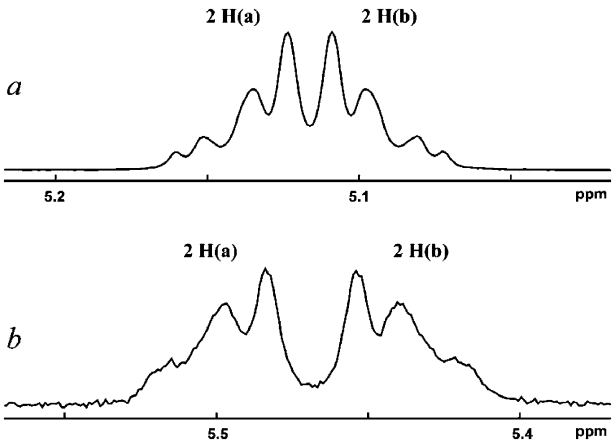


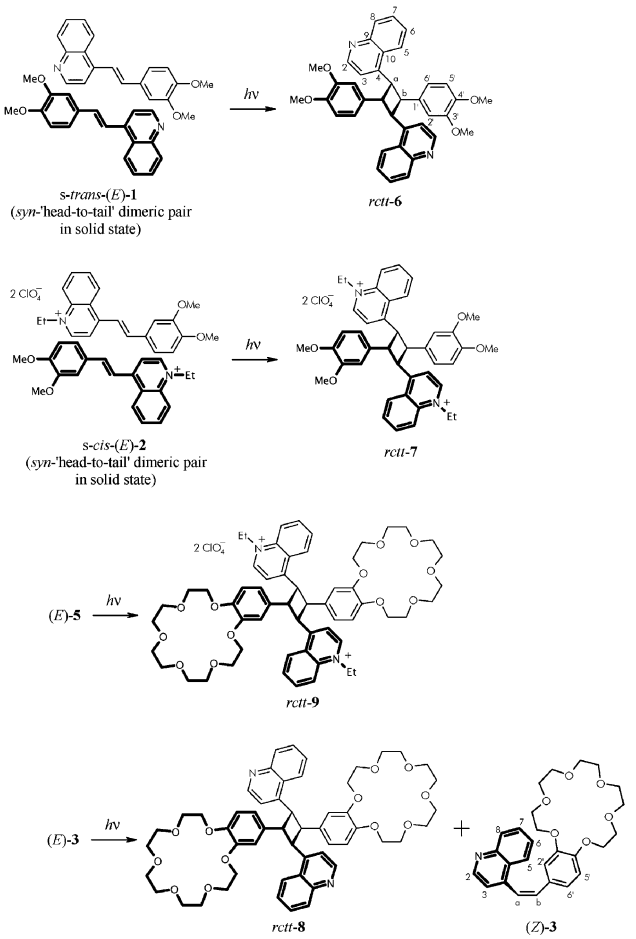
Fig. 1 The ^{1}H NMR spectra (region of the cyclobutane protons) in DMSO-d_6 at 25 °C: (a) the product of the photoirradiation of (*E*)-**1** as a thin film for 20 h (*rctt*-**6**); (b) product of the photoirradiation of (*E*)-**2** as a thin film for 35 h (*rctt*-**7**).

In contrast to compounds **1**, **2**, and **5**, irradiation of a thin film prepared from the crown-containing 4-styrylquinoline **3** led to cyclobutane *rctt*-**8** formation, along with $E \rightarrow Z$ isomerization of the initial compound (Scheme 3). The presence of the *Z* isomer of **3** in the reaction mixture is caused by a special mutual arrangement of the molecules (*E*)-**3** in the solid state, affording a molecular arrangement that is less favourable with respect to allowing the PCA reaction to proceed (see also X-ray section). A change in the geometry of the *Z* isomer compared to that of the *E* isomer results in a substantial decrease in the conjugation within the chromophoric fragment, and to a twist of this fragment due to the steric interactions of the bulky aromatic substituents at the ethylene bond. This is displayed in the ^{1}H NMR spectrum as upfield shifts of the signals for the majority of the protons, the most substantial shifts being observed for the protons of the ethylene fragment, protons H(5) and H(2′) of the quinoline and benzene fragments, respectively, and for the protons of the 3′-OCH_2 group ($\Delta\delta_H$ = 0.52–1.03 ppm). This suggests that the quinoline residue is arranged under the benzocrown-ether fragment in (*Z*)-**3** in the predominant conformation shown in Scheme 3. The above-mentioned protons are shielded by the aromatic units and consequently the signals for these protons appear at higher field compared to those of (*E*)-**3**.

It is interesting to compare the rates of cyclobutane formation in thin films of compounds **1**–**3** and **5**. Irradiation of the films under the same conditions (visible light, 10 h) resulted in different extents of conversion to the cyclobutane derivatives for these compounds, being much higher for **1** and **5** than for **2** and **3** (Table 1). This difference might arise due to the different mutual arrangement of the two styryl molecules in the precursor dimeric pair and, hence, owing to the different distances separating the C=C bonds that are to react. The results from the X-ray study of dye **2** showed that a closed mutual arrangement of the reacting molecules in the dimeric pair is attained by inserting benzene solvate molecules into the crystal lattice of the compound (see X-ray section). Preparation of a thin film of **2** in the presence of benzene did lead to a considerable increase in the extent of conversion to cyclobutane *rctt*-**7** (70 *vs.* 23%). Thus, altering the solvent of crystallization allows ones to control the efficiency of the [2 + 2]-photocycloaddition reaction in the solid state. It should be noted that prolonged irradiation of the films of **1** and **5** resulted in complete photoconversion (total 20 h). In contrast to this, complete photoconversion did not occur for **2** and **3** even after irradiation for a total of 150 h. This means that films prepared from compounds **2** and **3** are probably a mixture of crystals with different crystal packings, some of which are unfavourable for PCA.

X-Ray diffraction study

Recently,[6] we reported a solid phase PCA of the crown-ether styryl dye of the pyridine series (*E*)-**10** (Scheme 4) that



Scheme 3 Solid-phase synthetic routes for the formation of cyclobutanes *rctt*-**6**–**9**.

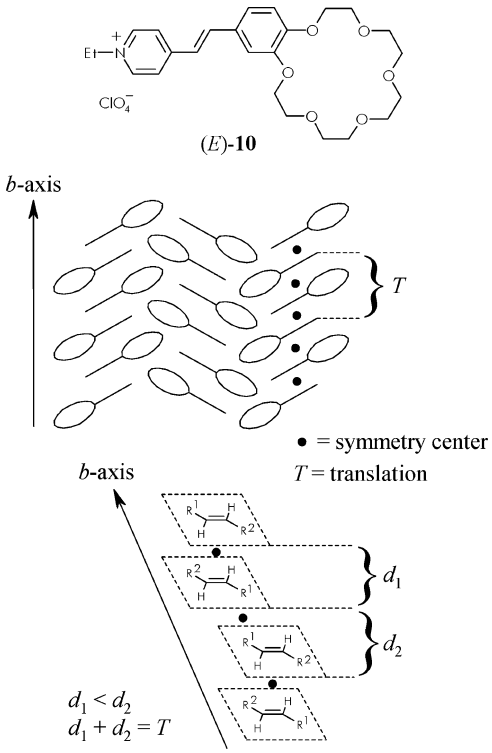
occurred without crystal degradation (Scheme 1S, ESI†). In single crystals of the starting compound **10**, charged dye molecules are arranged in centrosymmetric *syn*-'head-to-tail' sandwiches, in which two ethylene units are in close vicinity to each other. These sandwiches form stacks running along the *b* axis (Scheme 4; ovals and R^1 denote benzocrown-ether substituents and R^2 denotes pyridine substituents at the ethylene bonds).

Adjacent stacks are separated by a double layer of very loosely packed crown-ether fragments. In a given stack, any

Table 1 The content of the photoproducts,[a] and the extent of conversion of the reactants to cyclobutane derivatives, after irradiation for 10 h of thin films of the 4-styrylquinolines **1**–**3**, and **5**

Initial compound	Photoproduct content[a]/ molar ratio			Conversion extent into cyclobutane derivative (%)
	E isomer	*Z* isomer	*rctt* Cyclobutane derivative	
(*E*)-**1**	1	0	4.3	90
(*E*)-**2**	6.9	0	1	23
(*E*)-**2**[b]	1	0	1.2	70
(*E*)-**3**	5.7	3.7	1	18
(*E*)-**5**	1	0	2.5	83

[a] From ^{1}H NMR data. [b] The film was prepared using benzene.



Scheme 4 Structure of dye **10** (above), its crystal packing (middle) and a schematic showing the structure of a stack of molecular sandwiches (below).

two adjacent sandwiches are related by a symmetry center, but in general they are spaced farther from one another than the two molecules within a sandwich ($d_2 > d_1$, see Scheme 4). Moreover, the nearest ethylene groups to a given sandwich belong to adjacent sandwiches, and are significantly shifted with respect to each other within the parallel planes because the *b* axis is inclined to the ethylene planes. It is important that if the solid phase PCA reaction is accomplished within a sandwich that no change in the local symmetry of crystal occurs as a result of the transformation. Actually, the cyclobutane derivative **11** formed from **10** was generated as the *rctt* centrosymmetric isomer (Scheme 1S, ESI†) and, therefore, the symmetry of the single crystal after the reaction finished turned out to be unchanged from the initial crystal.

The above mentioned stacking type of crystal packing is the most abundant (there are two forms of stacking: 'head-to-tail' and 'head-to-head'), this is typical for crown-ether styryl and butadienyl dyes.[7] We suggested that PCA reactions in the solid state, including those that proceed without crystal degradation, may be expected for the many compounds of this class that display the 'head-to-tail' stacking motif in their crystal packing. In order to check this idea, we performed an X-ray structural analysis of an orange single crystal of styryl dye **2**, irradiated it with visible light, and then repeated the X-ray structural investigation.

Structure of dye 2 and cyclobutane 7. The structure of the benzene solvate of compound **2** is shown in Fig. 2. The dye molecule is nearly planar. The dihedral angles between the quinoline and ethylene groups, and between the ethylene and

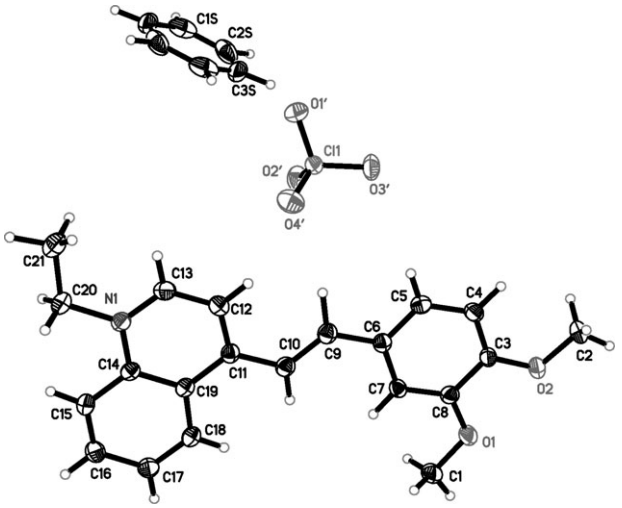


Fig. 2 Structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level.

benzene groups, are equal to 6.9 and 6.5°, respectively. The dihedral angle between the quinoline and benzene groups is 0.7°. The bond lengths in the C(6)–C(9)–C(10)–C(11) fragment are 1.460(2), 1.343(2), and 1.456(2) Å, respectively, being indicative of a rather localized C═C ethylene bond.

Compound **2** crystallizes in the space group $P2_1/n$. Benzene solvate molecules occupy symmetry centers, so that half a benzene molecule per dye molecule is found in this crystal. The crystal packing of this compound, in two projections, is shown in Fig. 3. The dye molecules are packed in stacks, with a centrosymmetric 'head-to-tail' arrangement between any two adjacent molecules, similar to the packing of dye **10** (Scheme 4). In this packing arrangement, adjacent stacks of sandwiches are isolated from one another by perchlorate anions and benzene solvate molecules.

The structure of a single sandwich is shown in Fig. 4. The interatomic distances between the ethylene carbon atoms C(9)···C(10B) and C(10)···C(9B) are rather short, 3.492 Å, and satisfy the above mentioned geometric requirements for the PCA reaction to occur.

After finishing the data collection, the single crystal was taken off the diffractometer and subjected to irradiation with visible light over a period of 30 h. The crystal became much lighter in colour. Then this single crystal was mounted back on the diffractometer and a second X-ray data collection was performed. The complete conversion of the initial compound **2** into the *rctt* isomer of cyclobutane **7** had occurred (Fig. 5). The molecule *rctt*-**7** is situated on the symmetry center; the formation of the product compound in the single crystal does not destroy the crystal symmetry. The crystal system and the space group have remained as for **2**, that is, monoclinic $P2_1/n$. During the PCA reaction, the volume of the crystal unit cell was insignificantly increased from 2172.1(3) $Å^3$ for **2** to 2206.2(4) $Å^3$ for **7**, a 1.6% increase.

The dihedral angle between the quinoline and benzene fragments [N(1)...C(11)–C(19) and C(3A)...C(8A)] is equal to 25.7°. The bond distances C(9)–C(10A), C(9)–C(10), C(6)–C(9), and C(10)–C(11) are equal to 1.568(10),

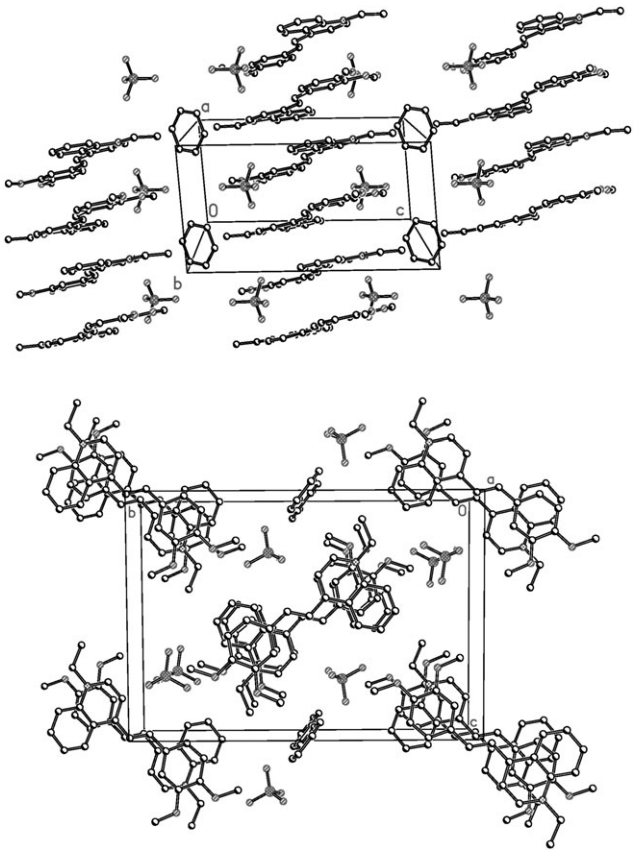


Fig. 3 Crystal packing of **2** as viewed down the *b* axis (above) and down the *a* axis (below).

1.615(12), 1.508(10), and 1.503(10) Å, respectively. The bond angles C(9)–C(10)–C(11), C(11)–C(10)–C(9A), C(9)–C(10)–C(9A), C(6)–C(9)–C(10A), C(6)–C(9)–C(10), and C(10)–C(9)–C(10A) are 113.1(6), 119.3(6), 90.2(6), 118.0(6), 117.2(6), and 89.8(6)°, respectively.

It is interesting to note that not only the structural units participating in the PCA changed their positions within the crystal unit cell. Fig. 6 shows a superposition of the same areas of the unit cell in the initial compound **2**, and the product of its PCA transformation, **7**. The perchlorate anions and the benzene molecules have also changed their positions. The benzene molecules and perchlorate anions create a soft flexible shell around the sandwiches (see Fig. 3), and thus can compensate somewhat for the stress that is generated in the crystal as the result of the large atomic displacements that happen within the sandwiches during the course of the PCA reaction. In the above mentioned single-crystal-to-single-crystal transformation **10** → **11** the function of the 'soft environment' was performed by the crown-ether moieties and perchlorate anions that were wrapped about the stacks. These species also changed their geometry within crystal as a result of the PCA transformation.

It should be added that our attempts to monitor the PCA reaction in **2** failed. X-Ray data collected on the initial crystal after 6 and 15 h of irradiation resulted only in structural models displaying an increase in thermal displacement parameters for all atoms, and only after 30 h of irradiation were

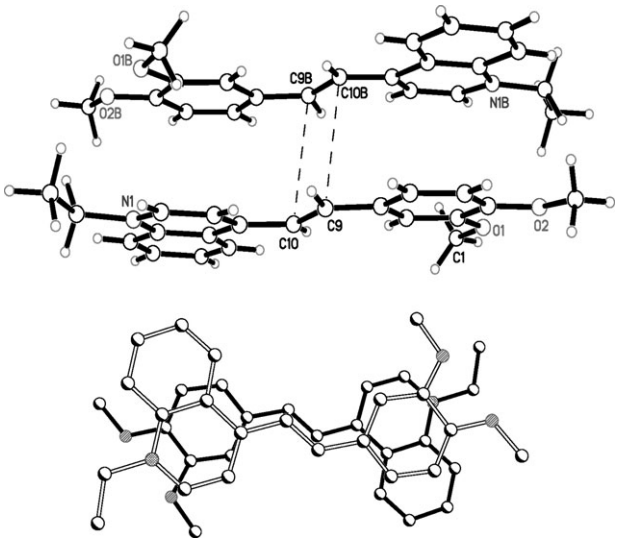


Fig. 4 Structure of a sandwich of **2** in two projections. In the below projection the upper molecule is drawn with hollow lines, and all hydrogen atoms are omitted for clarity; the additional letter 'B' indicates that atoms are at $(1 - x, 1 - y, 1 - z)$.

informative data obtained. Perhaps a reason for these findings is that the reaction starts slowly at a localised site, most likely within a defect of the crystal lattice, and then the PCA transformation proceeds rapidly throughout the remainder of the crystal.

Structure of cyclobutane 7a. It was of interest to compare the geometry of cyclobutane **7** obtained in the course of a solid phase PCA, with that of a crystal of **7** grown from solution. Such crystals were obtained by recrystallization of *rctt*-**7** from a MeCN–benzene mixture. The resultant crystals belong to the triclinic $P\bar{1}$ space group; the structure of this compound (**7a**) is shown in Fig. 7. Compound **7a** is also a benzene solvate, but the *rctt*-**7** : benzene ratio turned out to be different from the ratio seen for compound **7** obtained from the PCA reaction, 1 : 3 *vs.* 1 : 1.

The *rctt* isomer of the substituted cyclobutane, and one of the benzene solvate molecules, are situated at symmetry centers; the other benzene molecules and the perchlorate anions occupy general positions. Selected geometric parameters for **7a** are as follows: bond lengths C(3)–C(10), C(10)–C(11A), C(10)–C(11), C(11)–C(12) are 1.504(3), 1.552(3), 1.587(3), 1.507(3) Å; bond angles C(3)–C(10)–C(11A), C(3)–C(10)–C(11), C(11)–C(10)–C(11A), C(12)–C(11)–C(10A), C(10)–C(11)–C(12), C(10)–C(11)–C(10A) are 120.1(2), 118.7(2), 90.8(1), 117.2(2), 120.0(2), 89.2(1)°, respectively. The torsion angle C(3)–C(10)–C(11A)–C(12A) is equal to 112.0°, and the dihedral angle between the quinoline N(1)–C(11)...C(19) and benzene C(12A)...C(17A) planes, is 54.9°. These data show that the differences between the angular parameters found in **7** and in **7a** are significant. Fig. 8 clearly demonstrates this difference.

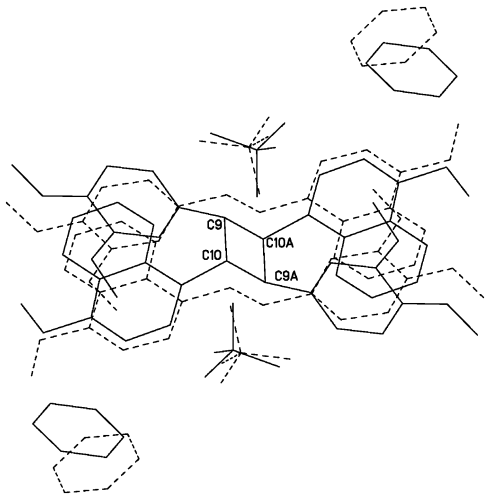


Fig. 6 Superposition of the same areas of crystal unit cell for **2** (dashed lines) and **7** (solid lines); the additional letter 'A' indicates that atoms are at $(1 - x, 1 - y, 1 - z)$.

Thus, the geometry of the organic skeleton of **7** obtained as a result of the solid phase PCA reaction is rather stressed. This geometry cannot be reproduced in solution. Therefore, crystals of **7** belonging to the monoclinic space group $P2_1/n$ cannot be crystallized from solution, instead they are only formed as a result of a single-crystal-to-single-crystal PCA reaction.

Other possible packing motifs in styryl dyes and their neutral precursors. In general, styryl dyes display only two types of

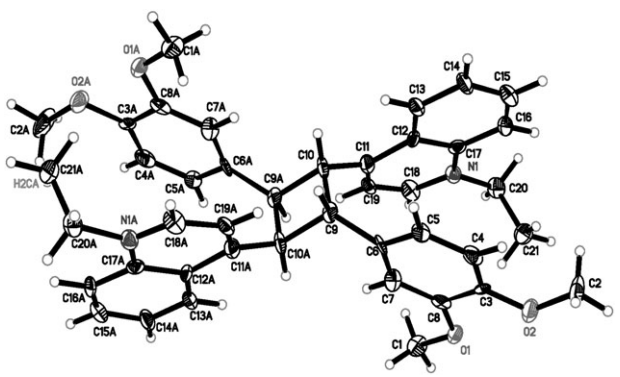


Fig. 5 Structure of the *rctt* cation of compound **7**; the additional letter 'A' indicates that atoms are at $(1 - x, 1 - y, 1 - z)$.

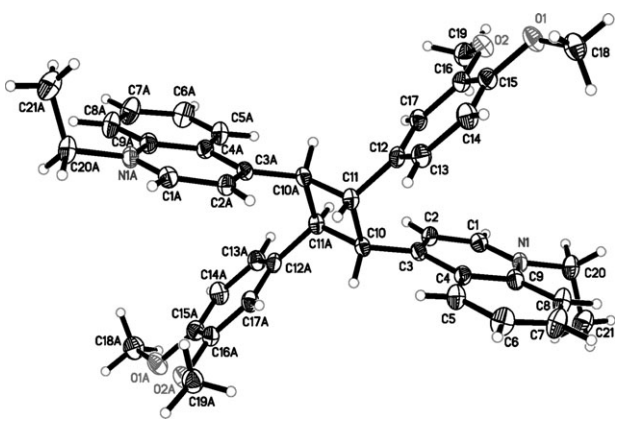


Fig. 7 The structure of *rctt*-**7a**; the additional 'A' letter indicates that atoms are at $(1 - x, -y, 1 - z)$.

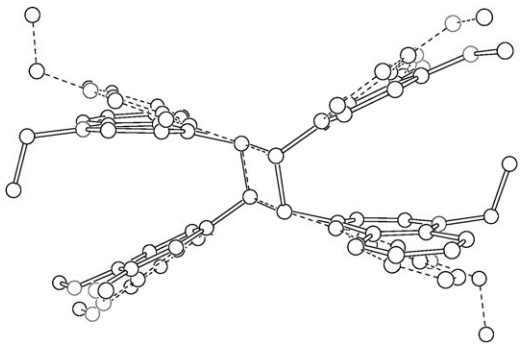
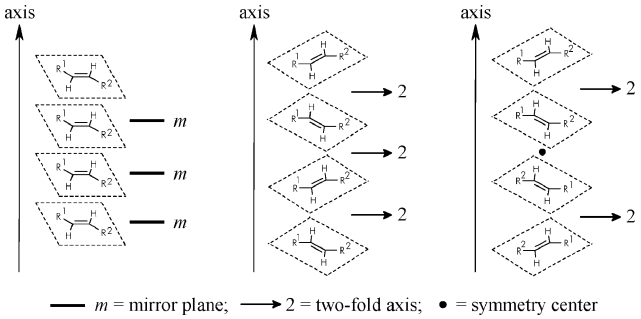


Fig. 8 Superposition of the cyclobutane molecules in **7** (hollow lines) and **7a** (dashed lines).



Scheme 6 Stacks of unsaturated molecules formed *via* mirror planes (left side), two-fold axes (middle), and a combination of a two-fold axis with symmetry center (right side).

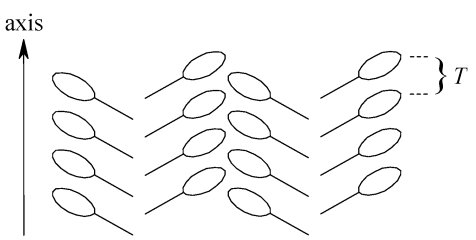
crystal packing, but both incorporate stacks of the dye molecules. One type involves the 'head-to-tail' stacking of the molecules (Scheme 4),[6,7a–d] and the other is 'head-to-head' stacking.[7b,e] In the latter packing motif, any two adjacent molecules are related by translation (Scheme 5). This motif is usually characterized by a significant shift of two adjacent molecules that lie in parallel planes with respect to each other, so that the ethylene bonds in these molecules are well spaced from one another. Even if the adjacent molecules were not shifted, the PCA reaction between any two adjacent molecules would result in an alteration in the local symmetry of the crystal, a development which would create a set of defects within the crystal lattice that would eventually lead to crystal degradation. However, nothing prevents this reaction from proceeding successfully in solution.[3]

In principle, one may deduce other variations in the symmetry relationships between adjacent molecules in a stack that would not result in a local symmetry infraction during the course of a PCA solid phase reaction (Scheme 6).

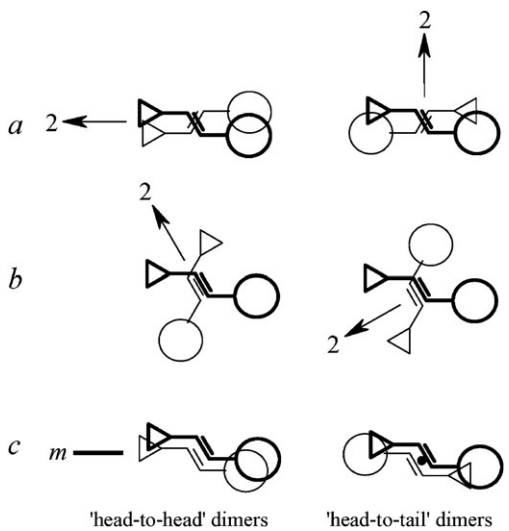
In the left-hand stack in Scheme 6 the molecules are related by mirror planes. In reality this variant cannot be achieved in crystals formed by molecules with essential intramolecular charge separation because with this symmetry identically charged moieties of two adjacent molecules within a stack are in the vicinity of each other, which is not optimal because this arrangement is associated with a high degree of electrostatic repulsion. Indeed, we never observe this type of molecule packing for styryl dyes and related compounds.

In the middle stack in Scheme 6 the molecules are related by two-fold axes. In general, this symmetry means a mutually crossed arrangement of two adjacent ethylene bonds, which is not optimal for the PCA reaction. However, 2-fold symmetry does not restrict the twist of two adjacent ethylene bonds about a theoretical axis joining the middles of the ethylene bonds. This symmetry also permits a relatively small twist in the mutual arrangement of the ethylene groups (case *b* rather than case *a*, Scheme 7) to give a close to optimal disposition for the PCA reaction to occur.

In most cases the twist of two conjugated molecules with *E* configuration about a line joining the middles of the ethylene bonds means less efficient overlapping of the conjugated systems (Scheme 7, *a* and *b*) with respect to the centrosymmetrically or mirror-plane related molecules (Scheme 7, *c*). Therefore, if stacking interactions and Coulomb repulsion forces are important in molecular self-assembly, it is most likely that the centrosymmetric dimers form, rather than dimers in which the molecules are related by 2-fold axes or mirror-planes. In principle, a specific case could arise in which a relatively small twist in the ethylene moieties allows for orbital overlap. Such an arrangement should bring about the *rtct* isomer of cyclobutane derivative as a result of the PCA reaction. However, we observed this geometry of the styryl dye dimers, and the subsequent formation of the *rtct*-cyclobutanes, only in solution.[2b,d]



Scheme 5 'Head-to-head' crystal packing motif.

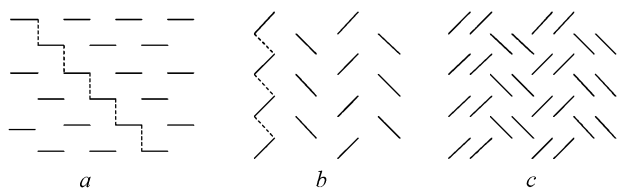


Scheme 7 Possible mutual arrangements of styryl dye molecules in dimeric pair. Here circles denote phenyl substituents and triangles are heterocyclic moieties.

The right-hand case in Scheme 6 represents molecular stacks that are generated by a combination of two-fold axes and symmetry centers. This type of packing motif has been observed previously within crystals of a KI complex of a 15-crown-5-ether styryl dye of the quinoline series.[8] In this crystal, 2-fold related crown-ether dye sandwiches formed *via* interactions of the crown-ether fragments with the K^+ ions are observed (Fig. 1S, ESI†). Only the quinoline fragments of the dye molecules overlap in these sandwiches. In the crystal these sandwiches are packed in stacks. Any two adjacent sandwiches in a stack are related by symmetry centers, and have short interatomic distances between the ethylene bonds, and extensive overlapping over the conjugated systems. This geometry might only allow the solid phase PCA reaction to occur between the sandwiches rather than inside them. However, no cases of two-fold related units within a stack were observed in styryl compounds without foreign support (*e.g.* metal cations).

Contrary to styryl dyes, their neutral precursors, 1-hetaryl-2-phenylethylenes, are usually characterized[5,7d] by three packing motifs: staircase (*a*), parquet (*b*), and parquet sandwich (*c*) (Scheme 8). No stacking motifs that are characteristic of styryl dyes were observed for these compounds. However, in the parquet sandwich packing motif *c*, centrosymmetric sandwiches pre-organized towards the PCA reaction occur. Previously,[5] we have performed an X-ray structural determination of 4-styrylquinoline **1** and established that a parquet sandwich packing motif, with centrosymmetric 'head-to-tail' sandwiches, is present in the crystals. We presumed that the single-crystal-to-single-crystal PCA might be observed for this compound too. In order to check this idea we performed an X-ray investigation of a single crystal of compound **1**, followed by its irradiation with visible light, and then repeated the X-ray determination.

Structure of quinolylphenylethylene 1 and cyclobutane 6. The molecule of the light yellow compound **1** is nearly planar (Fig. 2S, ESI†). The dihedral angles between the ethylene group C(3)–C(10)–C(11)–C(12) and its substituents, the quinoline and benzene fragments, are equal to 16.0 and 16.6°, whereas the dihedral angle between the planes of the quinoline and benzene moieties is 2.3°. The geometric parameters in the ethylene unit have the following values: the C(3)–C(10), C(10)–C(11), and C(11)–C(12) bond lengths are equal to 1.471(1), 1.341(2), and 1.469(2) Å, respectively; the angles C(3)–C(10)–C(11) and C(10)–C(11)–C(12) are 123.8(1) and 127.1(1)°, respectively; the torsion angle C(3)–C(10)–C(11)–C(12) is 179.8°. These values agree well with those observed by us in our previous X-ray determination of this compound.[5]



Scheme 8 Packing motifs in crystals of 1-hetaryl-2-phenylethylenes: staircase (*a*), parquet (*b*), and parquet sandwich (*c*). Solid lines denote the profiles of the conjugated fragments of the molecules.

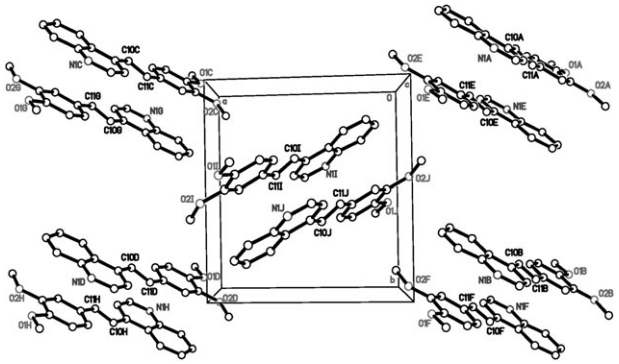


Fig. 9 A fragment of crystal packing of **1**.

Single crystal of the initial compound **1** belongs to the monoclinic crystal system and the $P2_1/c$ space group. A fragment of the crystal packing is shown in Fig. 9. It can be seen that the molecular packing displays the parquet sandwich motif *c* (see Scheme 8). In a centrosymmetric sandwich unit (Fig. 3S, ESI†) the ethylene fragments are situated in parallel planes, and the C(10A)···C(11E) and C(11A)···C(10E) interplanar distances between the ethylene carbon atoms (Fig. 9) are equal to 3.629 Å. These geometric parameters satisfy the aforementioned geometric conditions to enable the PCA reaction to happen.

After the data collection with a single crystal of **1** was completed, this single crystal was taken off the diffractometer and subjected to irradiation with visible light for 6 h. It has become lighter in colour. This single crystal was then re-mounted on the diffractometer, and the X-ray structural experiment was repeated.

The result of irradiation of **1** for 6 h is shown in Fig. 10. Two compounds, **1** and **6**, simultaneously occur in the same single crystal in the ratio 0.66 : 0.34. The centrosymmetric *rctt* isomer of cyclobutane **6** is partly formed as a result of the PCA reaction that occurs in the single crystal of **1**. The formation of this isomer does not affect the local symmetry of the crystal. Significant atomic displacements during the course of the reaction do not alter the crystal environment of the sandwich because they proceed inside the volume specified by the initial sandwich. The geometric parameters for the central fragment of the substituted cyclobutane product are as follows: bond lengths C(3′)–C(10′) 1.519(12), C(10′)–C(11′) 1.560(7), C(11′)–C(12′) 1.504(16), C(10′)–C(11B) 1.610(8) Å; bond angles C(3′)–C(10′)–C(11′) 117.9(7), C(3′)–C(10′)–C(11B) 115.4(6), C(11′)–C(10′)–C(11B) 90.7(4), C(10′)–C(11′)–C(12′) 118.0(7), C(12′)–C(11′)–C(10B) 114.0(5), C(10′)–C(11′)–C(10B) 89.3(4)°; torsion angle C(12′)–C(11′)–C(10′)–C(3′) 123.5°.

Interestingly, in crystals of quinoline **1** the PCA reaction required less than 6 h of irradiation to start, whereas, in our previous experiments with the related dye **2**, the reaction required a much longer exposure. It should be noted that the crystal of this compound does not contain other structural units (such as the perchlorate anions and solvate benzene molecules in **2**) that could create a flexible shell around the sandwich unit. It is likely that a parquet sandwich packing motif provides a more spacious environment for the molecular sandwiches than a stacking packing motif.

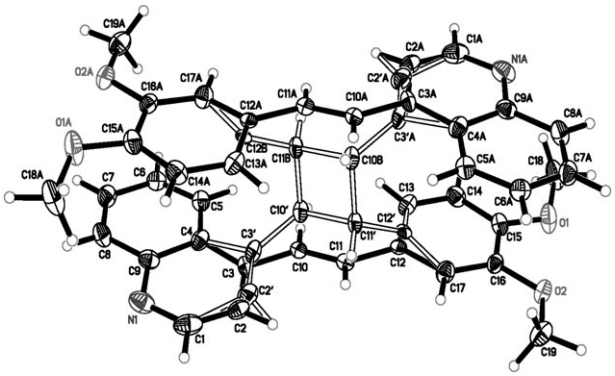


Fig. 10 The X-ray structure of **1**/**6** obtained after 6 h irradiation of **1**. The atoms belonging to **6** are connected by hollow lines; the additional letter 'A' or 'B' indicates that atoms are at $(3 - x, 1 - y, 1 - z)$. The thermal ellipsoids are drawn at the 50% probability level.

After conducting the second X-ray experiment, this particular single crystal was taken off the diffractometer and subjected to further irradiation for 24 h. The single crystal became colourless. It was then mounted on the diffractometer again, and its X-ray structure determined for the third time.

After the irradiation of compound **1** for a total of 30 h, full PCA transformation of the initial compound **1** to the *rctt* isomer of cyclobutane **6** was observed. The structure of the product compound is shown in Fig. 11. The *rctt* isomer of cyclobutane **6** is situated at the symmetry center. It is important that the formation of this new compound in the single crystal does not destroy crystal symmetry. The crystal system and the space group remain as for **1**, that is, monoclinic $P2_1/c$.

The dihedral angle between the quinoline and benzene fragments [N(1)–C(1)...C(9) and C(12A)...C(17A)] is equal to 16.0°. The geometric parameters for the central fragment of the substituted cyclobutane product are as follows: bond lengths C(3)–C(10) 1.505(3), C(10)–C(11A) 1.549(3), C(11)–C(12) 1.510(3), C(10)–C(11) 1.603(3) Å; bond angles C(3)–C(10)–C(11A) 119.9(2), C(3)–C(10)–C(11) 113.6(2), C(11)–C(10)–C(11A) 90.3(2), C(10A)–C(11)–C(12) 118.1(2), C(10)–C(11)–C(12) 115.3(2), C(10)–C(11)–C(10A) 89.7(2)°; torsion angle C(3)–C(10)–C(11A)–C(12A) −123.5°.

During the PCA reaction the volume of the crystal unit cell is insignificantly decreased from 1457.39(7) $Å^3$ in **1** to 1444.8(3) $Å^3$ in **6**, a change in volume corresponding to 0.9%.

Structure of cyclobutane 6 · 2HClO$_4$. It was of interest to know whether it is possible to grow crystals of **6** from solution that are of the same polymorphic form as those obtained from the PCA reaction. Our attempts to grow crystals of **6** from different solutions turned out to be successful only in the presence of perchloric acid. The compound crystallized as a salt **6** · 2HClO$_4$, the crystals of which belong to the triclinic space group $P\bar{1}$ with $Z = 2$. The structure of formula units is shown in Fig. 12. The cation of the compound occupies a general position within the unit cell. Both nitrogen atoms are protonated. Although the compound is a salt rather than a neutral compound, we may expect that the geometric parameters for the central parts of the substituted cyclobutanes formed from quinolines **1** and **2** should be identical.

The bond lengths in the cyclobutane fragment of the cation in **6** · 2HClO$_4$ are insignificantly different to these in **6**: C(10)–C(11) and C(29)–C(30) are 1.544(4) and 1.554(4) Å, C(10)–C(30) and C(11)–C(29) are 1.584(4) and 1.579(4) Å, C(3)–C(10) and C(22)–C(29) are 1.493(4) and 1.485(4) Å, C(11)–C(12) and C(30)–C(31) are 1.499(4) and 1.490(4) Å, respectively. Whereas the bond and dihedral angles have markedly different values: C(3)–C(10)–C(11) and C(22)–C(29)–C(30) are both 120.1(2)°, C(3)–C(10)–C(30) and C(11)–C(29)–C(22) are 120.3(2) and 119.7(2)°, C(10)–C(11)–C(12) and C(29)–C(30)–C(31) are 116.5(2) and 114.8(2)°, C(12)–C(11)–C(29) and C(10)–C(30)–C(31) are 122.5(2) and 123.3(2)°, respectively, torsion angles C(3)–C(10)–C(11)–C(12) and C(22)–C(29)–C(30)–C(31) are 106.6 and −108.3°, respectively, and dihedral angles N(1)–C(1)...C(9)/C(12)...C(17) and N(2)–C(20)...C(28)/C(31)...C(36) are 60.6 and 65.0°, respectively. Interestingly, the dihedral angles between the aromatic moieties in this molecule (60.6 and 65.0°) are markedly greater than the corresponding value (54.9°) in cyclobutane **7a**.

The difference in the geometry of the substituted cyclobutanes **6** and **6** · 2HClO$_4$ is well demonstrated in Fig. 13. This significant difference in geometry shows that in crystals of **6** the molecular structure is stressed. This stressed geometry cannot be reproduced in solution. Hence, crystals belonging to the monoclinic space group $P2_1/c$ with geometric parameters close to those in **6** cannot be obtained from solution.

Structure of quinolylphenylethylene 3. The nearest relative of quinoline **1** is its 18-crown-6-containing analogue **3**. We have managed to grow crystals of compound **3** but only in a

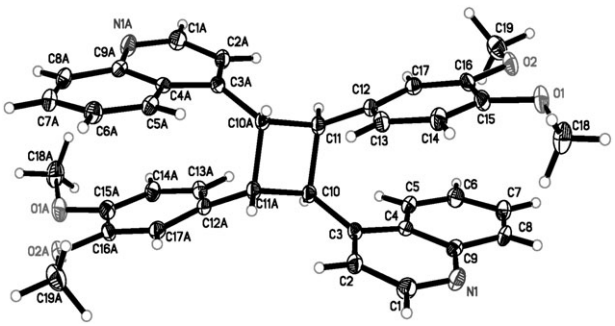


Fig. 11 The structure of compound **6** obtained after 30 h irradiation of **1**; the additional letter 'A' indicates that atoms are at $(2 - x, 2 - y, 1 - z)$. Thermal ellipsoids are drawn at the 50% probability level.

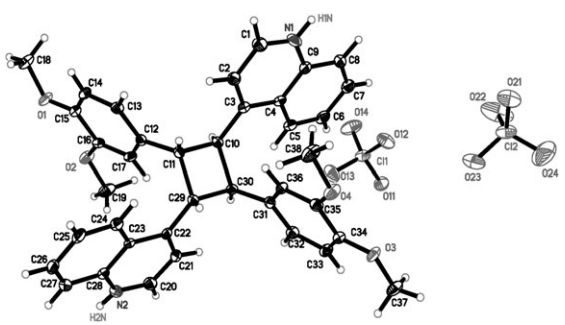


Fig. 12 The structure of **6** · 2HClO$_4$. Thermal ellipsoids are drawn at the 50% probability level.

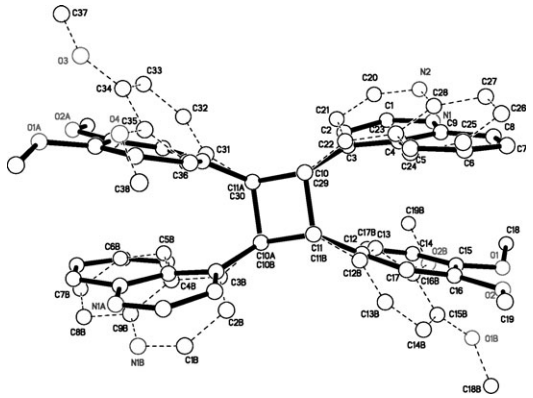


Fig. 13 Superposition of cyclobutane units in **6** (full lines) and **6** · $2HClO_4$ (dashed lines). All hydrogen atoms are omitted for clarity.

solvated form incorporating water and dichloromethane molecules. The X-ray structure of this compound is shown in Fig. 14.

The presence of the solvate molecules, water and dichloromethane, which tend to form hydrogen bonds, significantly affects the geometry of the molecule of **3** and its packing arrangement in the crystal. First of all, the molecule is not planar: the dihedral angle between the quinoline and benzene substituents of the ethylene group is equal to 55.0°, between the ethylene group and benzene ring it is 13.3°, and between the ethylene and quinoline groups it is 41.7°. Thus, the quinoline residue is strongly twisted from the styrene mean plane. Additionally, the packing motif exhibited in the crystal structure of this compound cannot be classified as one of the above mentioned packing motifs that are typical for 1-hetaryl-2-phenylethylenes. In these motifs all the conjugated moieties are usually planar.[5,7d]

In the crystal adjacent molecules of **3** are related by translations along the *b* axis to give a staircase packing motif (Fig. 4S, ESI†). Two adjacent staircases are related by symmetry centers. The staircase arrangement is due to a system of hydrogen bonds in which the crown-ether fragments, water and dichloromethane molecules all participate (Fig. 15). Both hydrogen atoms of the dichloromethane molecule form bifurcate hydrogen bonds with atoms O(2), O(3) and O(5), O(6) of the crown-ether fragment (the corresponding H···O distances are 2.51, 2.59 and 2.67, 2.55 Å). Atom Cl(1) of this molecule participates in a hydrogen bond with the water molecule (the Cl(1)···O(1S) distance is 3.343 Å). In turn the water molecule forms at least two more bifurcate hydrogen bonds with atoms O(1) and O(6) of a crown-ether fragment of a translation-related molecule of **3**. The corresponding H···O distances are 2.37 and 2.53 Å and the angles O–H···O(1)/O(6) are equal to 155, 142°. It is this system of hydrogen bonds that defines the staircase packing motif.

In the two nearest centrosymmetrically related molecules of **3** that are in adjacent staircases, the linear ethylene groups are not projected onto one another (Fig. 16), and their carbon atoms C(10A), C(11B) and C(11A), C(10B), are spaced at a distance of 4.945 Å from each other, a distance that exceeds the above mentioned upper limit for the PCA reaction to be possible.

These data mean that the PCA reaction is impossible in this single crystal. Just in case, the compound was subjected to irradiation with visible light for a period of two weeks without any change in the crystal, as expected.

Conclusions

Solid phase PCA reactions involving styryl dyes, including those that proceed without crystal degradation, can be accomplished in many of the compounds reported herein that exhibit the 'head-to-tail' molecular stacking motif in their crystal packing. The stacks comprise molecular sandwiches, with

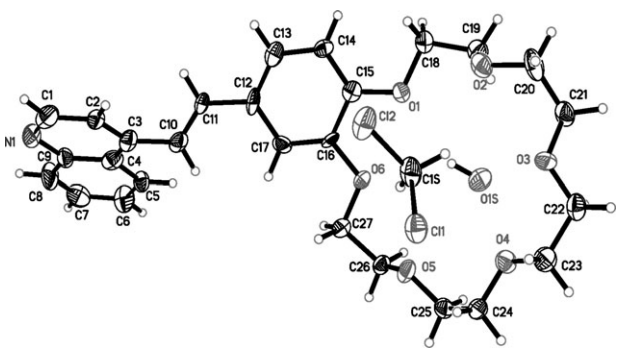


Fig. 14 The structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

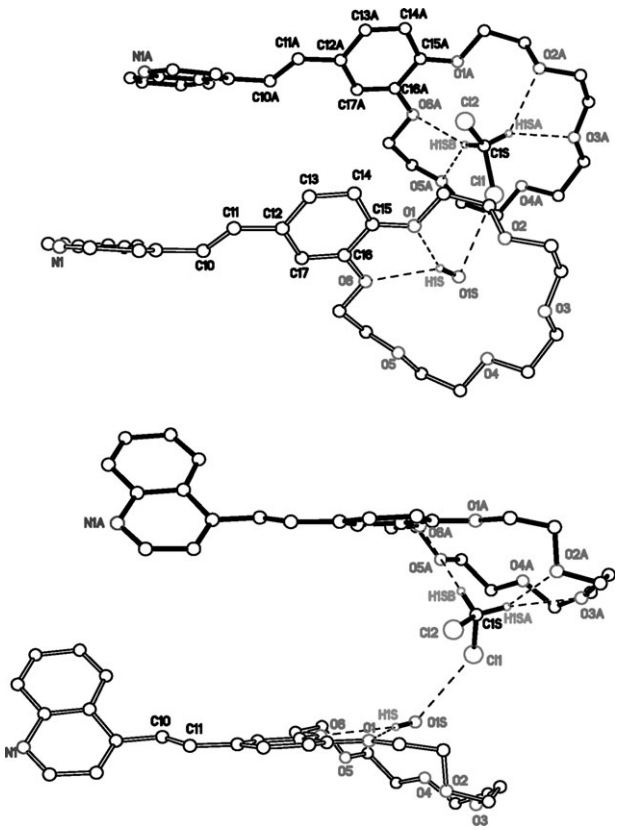


Fig. 15 Two projections of two adjacent molecules of **3** in a staircase; the additional 'A' letter indicates that atoms are at (x, 1 + y, z). Hydrogen bonds are shown as dashed lines. Hydrogen atoms of **3** that are not involved in secondary interactions are omitted for clarity.

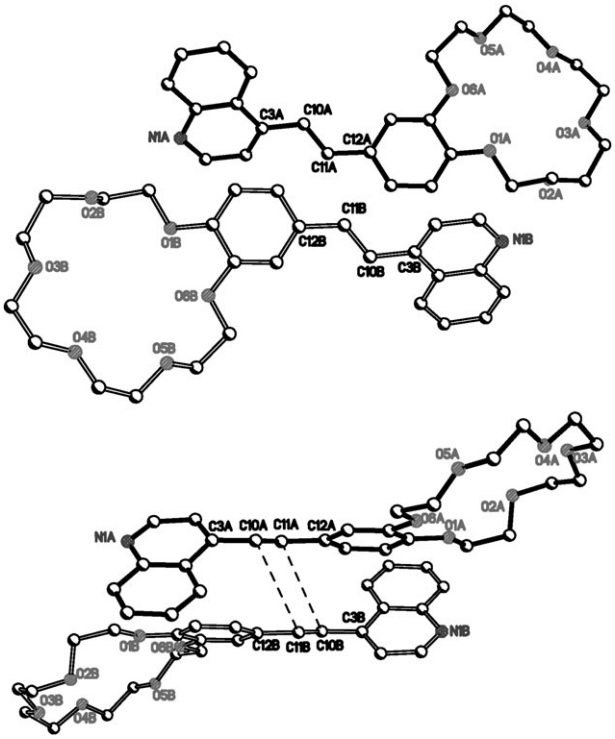


Fig. 16 Two centrosymmetrically related molecules of **3** in different projections; the additional letter 'B' indicates that atoms are at ($2 - x$, $1 - y$, $1 - z$). All hydrogen atoms and solvate molecules are omitted for clarity.

shorter distance between the ethylene fragments inside a sandwich than between adjacent sandwiches. The general problem of unpredictability in the crystal packing is overcome here, based on the general observation that compounds of this class form only stacking packing motifs, the 'head-to-tail' stacking that is favorable for PCA reactions being more abundant than the 'head-to-head' stacking packing arrangement that is unfavorable for PCA. The presence of benzene solvate molecules, together with perchlorate anions, that are able to rotate within the crystal are important for creating a soft flexible shell about each sandwich. This shell permits significant atomic displacements to occur during the course of the PCA transformation by 'absorbing' the lattice stress caused by these displacements. Analogous PCA reactions also can be accomplished in related neutral compounds, 1-hetaryl-2-phenylethylenes. However, in this case only one of three typical packing motifs turned out to be favorable for the solid phase PCA, enabling the reaction to proceed without crystal degradation, and this was the parquet sandwich motif.

Experimental

General methods

The melting points were measured with a MEL-Temp II apparatus with in a capillary, and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 instrument in DMSO-d_6 or $CDCl_3$ using the solvent as internal reference; ^{1}H–^{1}H COSY and NOESY spectra and ^{1}H–^{13}C COSY (HSQC and HMBC) spectra were used to assign the proton and carbon signals.§ Absorption spectra were measured on a UV-3101PC spectrophotometer (Shimadzu) in the range of 200–550 nm with an increment of 0.5 nm. The mass spectra were obtained on a Varian MAT 311A instrument with direct inlet of the sample into the ionization source; the ionization energy was 70 eV. Elemental analyses were performed at the microanalytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russian Federation); the samples for elemental analyses were dried *in vacuo* at 80 °C.

Preparations

Lepidine, veratraldehyde, (4-formylbenzo)-18-crown-6 ether, ethyl *p*-toluenesulfonate, and anhydrous DMF were used as received (Aldrich, Merck).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)ethenyl]quinoline ((*E*)-1). This was prepared by the condensation of lepidine with veratraldehyde in anhydrous DMF in the presence of *t*-BuOK; yellowish crystals (yield 46%), mp 130–132 °C (lit. data:[5] mp 130–132 °C). ^{1}H NMR ($CDCl_3$, 30 °C) δ: 3.96 (s, 3H, 4′-MeO), 4.01 (s, 3H, 3′-MeO), 6.95 (d, J = 8.2 Hz, 1H, H(5′)), 7.20 (d, J = 1.6 Hz, 1H, H(2′)), 7.23 (dd, J = 8.2 Hz, J = 1.6 Hz, 1H, H(6′)), 7.39 (d, J = 15.9 Hz, 1H, H(b)), 7.66 (m, 1H, H(6)), 7.68 (d, J = 4.8 Hz, 1H, H(3)), 7.70 (d, J = 15.9 Hz, 1H, H(a)), 7.81 (m, 1H, H(7)), 8.29 (m, 2H, H(5), H(8)), 8.89 (d, J = 4.8 Hz, 1H, H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 55.44 (4′-OMe), 55.61 (3′-OMe), 109.86 (C(2′)), 111.57 (C(5′)), 116.05 (C(3)), 119.74 (C(a)), 121.50 (C(6′)), 124.11 (C(5)), 125.68 (C(10)), 126.17 (C(6)), 129.17 (C(7)), 129.30 (C(1′)), 129.38 (C(8)), 135.02 (C(b)), 142.40 (C(4)), 148.28 (C(9)), 148.97 (C(3′)), 149.64 (C(4′)), 150.02 (C(2)). UV-Vis ($c = 5 \times 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 353 nm (ε = 29 500 M^{-1} cm^{-1}).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)ethenyl]-1-ethylquinolinium perchlorate ((*E*)-2). A mixture of compound (*E*)-**1** (103 mg; 0.35 mmol) and ethyl *p*-toluenesulfonate (212 mg; 1.06 mmol) was heated at 120 °C (oil bath) for 2 h. The resulting red mass was extracted with hot benzene (10 mL) and the insoluble residue was decanted and then dissolved in methanol (5 mL). Then 70% aq. $HClO_4$ (61 μL; 0.71 mmol) was added to the methanolic solution and after cooling to −10 °C, the precipitate formed and was filtered and washed with cold methanol (3 × 2 mL) to give dye (*E*)-**2** as orange powder in 71% overall yield; mp 168–171 °C. ^{1}H NMR (DMSO-d_6, 25 °C) δ: 1.60 (t, J = 7.2 Hz, 3H, $MeCH_2$), 3.86 (s, 3H, 4′-MeO), 3.92 (s, 3H, 3′-MeO), 5.00 (q, J = 7.2 Hz, 2H, CH_2), 7.11 (d, J = 8.1 Hz, 1H, H(5′)), 7.50 (dd, J = 8.1 Hz, J = 2.3 Hz, 1H, H(6′)), 7.66 (d, J = 2.3 Hz, 1H, H(2′)), 8.05 (m, 1H, H(6)), 8.16 (d, J = 15.9 Hz, 1H, H(b)), 8.20 (d, J = 15.9 Hz, 1H, H(a)), 8.26 (m, 1H, H(7)), 8.45 (d, J = 6.6 Hz, 1H, H(3)), 8.53 (d, J = 8.6 Hz, 1H, H(8)), 9.07 (d, J = 8.1 Hz, 1H, H(5)), 9.33 (d, J = 6.6 Hz, 1H, H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 14.96 ($MeCH_2$), 51.87 (CH_2), 55.58 (4′-MeO), 55.75 (3′-MeO), 110.54 (C(2′)), 111.57 (C(5′)), 115.74 (C(3)), 117.07 (C(a)), 118.80 (C(8)), 124.20 (C(6′)), 126.45 (C(10)), 126.73 (C(5)), 128.29 (C(1′)),

§ See Scheme 2 for atom numbering.

128.82 (C(6)), 134.94 (C(7)), 137.53 (C(9)), 143.51 (C(b)), 146.70 (C(2)), 149.05 (C(3′)), 151.49 (C(4′)), 152.99 (C(4)). UV-Vis ($c = 5 \cdot 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 440 nm (ε = 23 200 M^{-1} cm^{-1}). Anal. calcld for $C_{21}H_{22}ClNO_6$: C, 60.07; H, 5.28; N, 3.34; found: C, 59.93; H, 5.49; N, 3.20%.

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-1-ethenyl]quinoline ((*E*)-3) and 4-[2-(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-3-(4-quinolyl)propyl]quinoline (4). A mixture of lepidine (0.43 mL, 3.0 mmol) and potassium *tert*-butoxide (prepared by dissolution of potassium (0.127 g, 3.2 mmol) in dry *tert*-butyl alcohol followed by concentration to dryness), in anhydrous DMF (15 mL) was stirred at room temperature for 30 min. Then (4-formylbenzo)-18-crown-6 ether (1.00 g, 2.9 mmol) was added and the reaction mixture was stirred at room temperature for 25 h. After adding water (150 mL), the reaction mixture was extracted with benzene (4 × 70 mL), the organic extracts were concentrated *in vacuo* at 90 °C, and the residue was chromatographed on a column with Al_2O_3 (Aluminium oxide 150 basic, Typ E, 0.063–0.200 mm, Merck) using an acetonitrile–benzene gradient (up to 50% of the former) as the eluent. Two fractions were collected. The first contained compound (*E*)-**3** (0.65 g, 48%) as yellowish powder, mp 88–90 °C (from hexane). ^{1}H NMR (DMSO-d_6, 25 °C) δ: 3.55 (s, 4H, 2 CH_2O), 3.58 (m, 4H, 2 CH_2O), 3.64 (m, 4H, 2 CH_2O), 3.79 (m, 2H, 4′-OCH_2CH_2), 3.82 (m, 2H, 3′-OCH_2CH_2), 4.14 (m, 2H, 4′-OCH_2), 4.24 (m, 2H, 3′-OCH_2), 7.01 (d, J = 7.9 Hz, 1H, H(5′)), 7.28 (dd, J = 7.9 Hz, J = 1.8 Hz, 1H, H(6′)), 7.52 (d, J = 1.8 Hz, 1H, H(2′)), 7.52 (d, J = 15.9 Hz, 1H, H(b)), 7.66 (m, 1H, H(6)), 7.78 (m, 1H, H(7)), 7.81 (d, J = 4.9 Hz, 1H, H(3)), 7.96 (d, J = 15.9 Hz, 1H, H(a)), 8.03 (d, J = 7.9 Hz, 1H, H(8)), 8.55 (d, J = 8.5 Hz, 1H, H(5)), 8.86 (d, J = 4.9 Hz, 1H, H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 68.10 (4′-OCH_2), 68.24 (3′-OCH_2), 68.59 (4′-OCH_2CH_2), 68.68 (3′-OCH_2CH_2), 69.71 (4 OCH_2), 69.81 (2 OCH_2), 111.09 (C(2′)), 112.79 (C(5′)), 116.03 (C(3)), 119.76 (C(a)), 121.67 (C(6′)), 124.13 (C(5)), 125.67 (C(10)), 126.16 (C(6)), 129.16 (C(7)), 129.37 (C(8), C(1′)), 134.97 (C(b)), 142.39 (C(4)), 148.27 (C(9)), 148.34 (C(3′)), 149.05 (C(4′)), 150.01 (C(2)). UV-Vis ($c = 5 \cdot 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 354 nm (ε = 32 600 M^{-1} cm^{-1}). MS (I_{rel} (%)) m/z: 466 (30), 465 $[M]^+$ (100), 290 (50), 289 (28), 288 (20), 276 (19), 263 (41), 217 (13), 216 (13), 109 (16). Anal. calcd for $C_{27}H_{31}NO_6$: C, 69.66; H, 6.71; N, 3.01; found: C, 69.84; H, 6.79; N, 2.96%.

The second fraction contained **4** (0.18 g, 10%) as yellowish solid, mp 64–66 °C. ^{1}H NMR (DMSO-d_6, 25 °C) δ: 3.47 (m, 1H, $CH(CH_2)_2$), 3.48 (m, 2H, $(CH_aH_b)_2CH$), 3.52 (s, 4H, 2 OCH_2), 3.53–3.58 (m, 8H, 4 OCH_2), 3.59 (m, 2H, $(CH_aH_b)_2CH$), 3.67 (m, 4H, 2 CH_2CH_2OAr), 3.90 (m, 2H, 4′-OCH_2), 3.98 (m, 2H, 3′-OCH_2), 6.39 (dd, J = 8.2 Hz, J = 1.6 Hz, 1H, H(6′)), 6.59 (d, J = 8.2 Hz, 1H, H(5′)), 6.89 (d, J = 1.6 Hz, 1H, H(2′)), 7.16 (d, J = 4.3 Hz, 2H, 2 H(3)), 7.52 (m, 2H, 2 H(6)), 7.71 (m, 2H, 2 H(7)), 7.97 (d, J = 8.2 Hz, 2H, 2 H(8)), 8.03 (d, J = 8.6 Hz, 2H, 2 H(5)), 8.66 (d, J = 4.3 Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 37.85 ($CH(CH_2)_2$), 46.45 ($CH(CH_2)_2$), 67.83 (4′-CH_2O), 68.05 (3′-CH_2O), 68.62 (2 CH_2CH_2OAr), 69.66 and 69.71 (6 CH_2O), 112.54 (C(2′), C(5′)), 119.99 (C(6′)), 121.97 (2 C(3)), 123.66 (2 C(5)), 126.08 (2 C(6)), 127.01 (2 C(10)), 128.76 (2 C(7)), 129.60 (2 C(8)), 135.29 (C(1′)), 145.78 (2 C(9)), 146.66 (C(4′)), 147.75 (2 C(4), C(3′)), 149.64 (2 C(2)). UV-Vis ($c = 5 \times 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 274 nm (ε = 13 400 M^{-1} cm^{-1}). MS (I_{rel} (%)) m/z: 609 (23), 608 $[M]^+$ (61), 467 (29), 466 (100), 378 (18), 290 (15), 154 (95), 143 (31), 142 (20), 115 (12). Anal. calcd for $C_{37}H_{40}N_2O_6$: C, 73.00; H, 6.62; N, 4.60; found: C, 73.17; H, 6.64; N, 4.56%.

4-[(*E*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)ethenyl]-1-ethylquinolinium perchlorate ((*E*)-5). A mixture of compound (*E*)-**3** (46 mg, 0.1 mmol) and ethyl *p*-toluenesulfonate (60 mg; 0.3 mmol) was heated at 120 °C (oil bath) for 3 h. The resulting mass was extracted with hot benzene (4 × 20 mL) and the insoluble residue was decanted and then dissolved in a minimal quantity of hot ethanol. Then 70% aq. $HClO_4$ (13 μL, 0.15 mmol) was added to the ethanolic solution and after cooling to −10 °C, the precipitate formed and was filtered to give dye (*E*)-**5** as an orange powder (33 mg, 54% overall yield); mp 136–139 °C. ^{1}H NMR (DMSO-d_6, 25 °C) δ: 1.59 (t, J = 7.2 Hz, 3H, Me), 3.55 (s, 4H, 2 OCH_2), 3.58 (m, 4H, 2 OCH_2), 3.65 (m, 4H, 2 OCH_2), 3.80 (m, 2H, 4′-OCH_2CH_2), 3.84 (m, 2H, 3′-OCH_2CH_2), 4.19 (m, 2H, 4′-OCH_2), 4.27 (m, 2H, 3′-OCH_2), 4.99 (q, J = 7.2 Hz, 2H, CH_2N), 7.11 (d, J = 8.2 Hz, 1H, H(5′)), 7.47 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H, H(6′)), 7.68 (d, J = 1.8 Hz, 1H, H(2′)), 8.04 (m, 1H, H(6)), 8.12 (d, J = 15.7 Hz, 1H, H(b)), 8.19 (d, J = 15.7 Hz, 1H, H(a)), 8.26 (m, 1H, H(7)), 8.44 (d, J = 6.6 Hz, 1H, H(3)), 8.53 (d, J = 8.6 Hz, 1H, H(8)), 9.07 (d, J = 8.2 Hz, 1H, H(5)), 9.33 (d, J=6.6 Hz, 1H, H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 14.98 (Me), 51.90 (CH_2N), 68.17 (4′-OCH_2), 68.35 (3′-OCH_2), 68.46 (4′-OCH_2CH_2), 68.60 (3′-OCH_2CH_2), 69.61 (OCH_2), 69.71 (3 OCH_2), 69.83 (OCH_2), 69.86 (OCH_2), 111.62 (C(2′)), 112.54 (C(5′)), 115.73 (C(3)), 117.11 (C(a)), 118.81 (C(8)), 124.38 (C(6′)), 126.45 (C(10)), 126.75 (C(5)), 128.30 (C(1′)), 128.82 (C(6)), 134.96 (C(7)), 137.54 (C(9)), 143.46 (C(b)), 146.70 (C(2)), 148.36 (C(3′)), 150.90 (C(4′)), 152.98 (C(4)). UV-Vis ($c = 5 \times 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 434 nm (ε = 33 900 M^{-1} cm^{-1}). Anal. calcd for $C_{29}H_{36}ClNO_{10} \times H_2O$: C, 56.91; H, 6.26; N, 2.29; found: C, 56.79; H, 6.11; N, 2.13%.

***r*-4-[*c*-2,*t*-4-Bis(3,4-dimethoxyphenyl)-*t*-3-(4-quinolyl)cyclobutyl]quinoline (*rctt*-6).** A solution of compound (*E*)-**1** (9.4 mg) in acetonitrile (0.5 mL) was evaporated in a Petri dish (d = 10 cm) with formation of a thin polycrystalline film of the compound. This film was then irradiated with light from a 60 W incandescent lamp (35 h; distance from the light source = 15 cm) to give *rctt*-**6** as colourless solid (>98%), mp 67–70 °C. ^{1}H NMR (DMSO-d_6, 25 °C) δ: 3.35 (s, 6H, 2 3′-MeO), 3.52 (s, 6H, 2 4′-MeO), 5.09 (dd, J = 10.5 Hz, J = 5.6 Hz, 2H, 2 H(b)), 5.14 (dd, J = 10.5 Hz, J = 5.6 Hz, 2H, 2 H(a)), 6.57 (d, J = 8.4 Hz, 2H, 2 H(5′)), 6.70 (d, J = 1.9 Hz, 2H, 2 H(2′)), 6.92 (dd, J = 8.4 Hz, J = 1.9 Hz, 2H, 2 H(6′)), 7.58 (m, 2H, 2 H(6)), 7.68 (m, 2H, 2 H(7)), 7.77 (d, J = 4.6 Hz, 2H, 2 H(3)), 7.90 (d, J = 7.9 Hz, 2H, 2 H(8)), 8.41 (d, J = 8.2 Hz, 2H, 2 H(5)), 8.82 (d, J = 4.6 Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 43.59 (2 C(a)), 44.62 (2 C(b)), 54.89 (2 3′-MeO), 55.04 (2 4′-MeO), 110.78 (2 C(5′)), 112.48 (2 C(2′)), 119.27 (2 C(3)),

119.67 (2 C(6′)), 125.07 (2 C(5)), 125.73 (2 C(6)), 127.17 (2 C(10)), 128.75 (2 C(7)), 129.09 (2 C(8)), 131.88 (2 C(1′)), 146.15 (2 C(4)), 146.97 (2 C(4′)), 147.38 (2 C(9)), 147.47 (2 C(3′)), 149.84 (2 C(2)). UV-Vis ($c = 2.5 \times 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 282 nm ($\varepsilon = 8600$ M^{-1} cm^{-1}), 226 nm ($\varepsilon = 41\,500$ M^{-1} cm^{-1}). MS (I_{rel} (%)) m/z: 582 $[M]^+$ (0.8), 292 (12), 291 (69), 101 (18), 82 (22), 69 (15), 59 (44), 58 (100), 57 (17), 55 (27). Anal. calcd for $C_{38}H_{34}N_2O_4 \cdot 0.67H_2O$: C, 76.74; H, 5.99; N, 4.71; found: C, 76.88; H, 5.56; N, 4.83%.

***r*-4-[*c*-2,*t*-4-Bis(3,4-dimethoxyphenyl)-*t*-3-(1-ethyl-4-quinoliniumyl)cyclobutyl]-1-ethylquinolinium diperchlorate (*rctt*-7).** A solution of compound (*E*)-**2** (14.3 mg) in a mixture of acetonitrile (0.5 mL) and benzene (0.3 mL) was evaporated in a Petri dish ($d = 10$ cm) with formation of a thin polycrystalline film of the compound. This film was irradiated with light from a 60 W incandescent lamp (80 h; distance from the light source = 15 cm) to give a mixture of (*E*)-**2** and *rctt*-**7**. Compound *rctt*-**7** was separated by crystallization from a MeCN–benzene solution; orangey crystals (9.2 mg, yield 64%), mp 235–236 °C (decomp.). ^{1}H NMR (DMSO-d_6, 25 °C) δ: 1.48 (t, $J = 7.1$ Hz, 6H, 2 $MeCH_2$), 3.46 (s, 6H, 2 3′-MeO), 3.52 (s, 6H, 2 4′-MeO), 5.02 (m, 4H, 2 CH_2), 5.44 (dd, $J = 10.3$ Hz, $J = 6.7$ Hz, 2H, 2 H(b)), 5.50 (dd, $J = 10.3$ Hz, $J = 6.7$ Hz, 2H, 2 H(a)), 6.57 (d, $J = 8.3$ Hz, 2H, 2 H(5′)), 6.79 (d, $J = 1.7$ Hz, 2H, 2 H(2′)), 6.95 (dd, $J = 8.3$ Hz, $J = 1.7$ Hz, 2H, 2 H(6′)), 8.01 (m, 2H, 2 H(6)), 8.19 (m, 2H, 2 H(7)), 8.42 (d, $J = 6.2$ Hz, 2H, 2 H(3)), 8.46 (d, $J = 8.8$ Hz, 2H, 2 H(8)), 8.85 (d, $J = 8.4$ Hz, 2H, 2 H(5)), 9.45 (d, $J = 6.2$ Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 15.14 (2 $MeCH_2$), 44.90 (2 C(a)), 45.32 (2 C(b)), 52.42 (2 CH_2Me), 55.22 (4 MeO), 110.96 (2 C(5′)), 112.58 (2 C(2′)), 118.73 (2 C(8)), 120.18 (2 C(6′)), 120.44 (2 C(3)), 127.94 (2 C(5)), 128.33 (2 C(10)), 128.95 (2 C(6)), 130.07 (2 C(1′)), 134.85 (2 C(7)), 136.11 (2 C(9)), 147.54 (2 C(4′)), 147.70 (2 C(3′)), 147.75 (2 C(2)), 159.19 (2 C(4)). UV-Vis ($c = 2.5 \times 10^{-5}$ M, MeCN, 22 °C) λ_{max}: 310 nm ($\varepsilon = 7900$ M^{-1} cm^{-1}), 229 nm ($\varepsilon = 45\,000$ M^{-1} cm^{-1}). Anal. calcd for $C_{42}H_{44}Cl_2N_2O_{12}$: C, 60.07; H, 5.28; N, 3.34; found: C, 60.12; H, 5.16; N, 3.27%.

4-[(*Z*)-2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-1-ethenyl]quinoline ((*Z*)-3) and *r*-4-[*c*-2,*t*-4-bis(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-*t*-3-(4-quinolyl)cyclobutyl]quinoline (*rctt*-8). A solution of compound (*E*)-**3** (10 mg) in acetonitrile (0.5 mL) was evaporated in a Petri dish ($d = 10$ cm) with formation of a thin polycrystalline film of the compound. This film was irradiated with light from a 60 W incandescent lamp (distance from the light source = 15 cm) to give a mixture of (*E*)-**3**, (*Z*)-**3**, and *rctt*-**8** in a 5.7 : 3.7 : 1 molar ratio (from ^{1}H NMR) after 10 h and in a 1.2 : 1 : 2.4 molar ratio after 150 h of light exposure. (*Z*)-**3**: ^{1}H NMR (DMSO-d_6, 30 °C) δ: 3.43 (m, 2H, 3′-OCH_2), 3.48–3.60 (m, 12H, 6 CH_2O), 3.66 (m, 4H, 3′-OCH_2CH_2, 4′-OCH_2CH_2), 3.98 (m, 2H, 4′-OCH_2), 6.49 (d, $J = 1.9$ Hz, 1H, H(2′)), 6.64 (dd, $J = 8.5$ Hz, $J = 1.9$ Hz, 1H, H(6′)), 6.75 (d, $J = 8.5$ Hz, 1H, H(5′)), 6.93 (s, 2H, H(a), H(b)), 7.35 (d, $J = 4.4$ Hz, 1H, H(3)), 7.58 (m, 1H, H(6)), 7.77 (m, 1H, H(7)), 8.03 (d, $J = 8.4$ Hz, 1H, H(5)), 8.06 (d, $J = 8.2$ Hz, 1H, H(8)), 8.83 (d, $J = 4.4$ Hz, 1H, H(2)). *rctt*-**8**: ^{1}H NMR (DMSO-d_6, 30 °C) δ: 3.46–3.55 (m, 24H, 12 CH_2O), 3.58 (m, 8H, 4 CH_2O), 3.71 (m, 4H, 2 CH_2O), 3.77 (m, 4H, 2 CH_2O), 5.05 (dd, $J = 10.0$ Hz, $J = 6.3$ Hz, 2H, 2 H(b)), 5.14 (dd, $J = 10.0$ Hz, $J = 6.3$ Hz, 2H, 2 H(a)), 6.55 (d, $J = 8.4$ Hz, 2H, 2 H(5′)), 6.73 (d, $J = 1.9$ Hz, 2H, 2 H(2′)), 6.86 (dd, $J = 8.4$ Hz, $J = 1.9$ Hz, 2H, 2 H(6′)), 7.57 (m, 2H, 2 H(6)), 7.66 (m, 2H, 2 H(7)), 7.74 (d, $J = 4.5$ Hz, 2H, 2 H(3)), 7.89 (d, $J = 8.1$ Hz, 2H, 2 H(8)), 8.37 (d, $J = 8.6$ Hz, 2H, 2 H(5)), 8.81 (d, $J = 4.5$ Hz, 2H, 2 H(2)). ^{13}C NMR (DMSO-d_6, 30 °C) δ: 43.63 (2 C(a)), 44.58 (2 C(b)).

***r*-4-[*c*-2,*t*-4-Bis(2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)-*t*-3-(1-ethyl-4-quinoliniumyl)cyclobutyl]-1-ethylquinolinium diperchlorate (*rctt*-9).** This was obtained in a similar way to *rctt*-**6**, namely, by the irradiation for 20 h of a thin polycrystalline film of compound (*E*)-**5**. ^{1}H NMR (DMSO-d_6, 30 °C) δ: 1.50 (t, $J = 7.2$ Hz, 6H, 2 $MeCH_2$), 3.48 (s, 8H, 4 CH_2O), 3.52 (m, 16H, 8 CH_2O), 3.59 (m, 8H, 4 CH_2O), 3.74 (m, 4H, 2, 4′-OCH_2), 3.82 (m, 4H, 2 3′-OCH_2), 4.95–5.11 (m, 4H, 2 MeCH_2), 5.41 (dd, $J = 9.1$ Hz, $J = 7.0$ Hz, 2H, 2 H(b)), 5.48 (dd, $J = 9.1$ Hz, $J = 7.0$ Hz, 2H, 2 H(a)), 6.58 (d, $J = 8.4$ Hz, 2H, 2 H(5′)), 6.82 (d, $J = 1.9$ Hz, 2H, 2 H(2′)), 6.93 (dd, $J = 8.4$ Hz, $J = 1.9$ Hz, 2H, 2 H(6′)), 8.00 (m, 2H, 2 H(6)), 8.19 (m, 2H, 2 H(7)), 8.40 (d, $J = 6.3$ Hz, 2H, 2 H(3)), 8.47 (d, $J = 9.0$ Hz, 2H, 2 H(8)), 8.82 (d, $J = 8.3$ Hz, 2H, 2 H(5)), 9.45 (d, $J = 6.3$ Hz, 2H, 2 H(2)).

X-Ray crystallography

Crystals of **1** and **3** were obtained by the slow evaporation of CH_2Cl_2–hexane solutions in darkness. Crystals of **2**, **6** · 2$HClO_4$, and **7a** were obtained by the slow saturation of MeCN solutions with benzene by vapour diffusion methods (in darkness for **2**). Single crystals of all compounds were coated with perfluorinated oil and mounted on a Bruker SMART-CCD diffractometer (graphite monochromatized Mo-Kα radiation, $\lambda = 0.71073$ Å, ω scan mode).

A set of experimental reflections for **1** were measured using a light yellow single crystal of dimensions 0.38 × 0.34 × 0.26 mm^3. The structure was solved by direct methods and refined with anisotropic thermal parameters. All hydrogen atoms were located in the difference Fourier synthesis, but for further refinement their geometrically calculated positions were used. All hydrogen atoms were refined with an isotropic approximation.

Crystallographic data for **1**. $C_{19}H_{17}NO_2$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.6020(3)$, $b = 10.9717(3)$, $c = 12.6859(4)$ Å, $\beta = 99.022(2)°$, $V = 1457.39(7)$ $Å^3$, $Z = 4$, $d = 1.328$ g cm^{-3}, 11 822 reflections measured, 3839 unique reflections [R(int) = 0.0319], $R_1 = 0.0434$, $wR_2 = 0.1209$ for 3181 reflections with $I > 2\sigma(I)$, $R_1 = 0.0538$, $wR_2 = 0.1262$ for all reflections.

A single crystal of **1** was subjected to irradiation with visible light from a standard incandescent lamp (60 W, distance from the light source was ~15 cm) over a period of 6 h to form **1**/**6**. The single crystal of **1**/**6** was lighter in colour with respect to the initial crystal. A set of experimental reflections for **1**/**6** was measured with the same diffractometer. The structure was solved by direct methods. The structure simultaneously contains the initial compound and the cyclobutane product in a 0.66 : 0.34 ratio. The refinement of all non-hydrogen atoms

was performed with an anisotropic approximation. The positions of the hydrogen atoms were calculated, and their refinement was carried out with an isotropic approximation, excluding the hydrogen atoms of the cyclobutane fragment which were refined using a riding model.

Crystallographic data for **1**/**6**. $C_{38}H_{34}N_2O_4$, monoclinic, space group $P2_1/c$ (no. 14), a = 10.7020(7), b = 10.9624(7), c = 12.5151(8) Å, β = 98.443(3)°, V = 1452.35(16) Å^3, Z = 2, d = 1.332 g cm^{-3}, 11 419 reflections measured, 3798 unique reflections [R(int) = 0.0324], R_1 = 0.0648, wR_2 = 0.1466 for 2903 reflections with $I > 2\sigma(I)$, R_1 = 0.0864, wR_2 = 0.1558 for all reflections.

The single crystal of **1**/**6** transforms into colourless **6** after its further irradiation under the same conditions for 24 h. A set of experimental reflections for **6** was measured with the same diffractometer. The structure was solved by direct method and refined with an anisotropic approximation. All hydrogen atoms were refined with an isotropic approximation.

Crystallographic data for **6**. $C_{38}H_{34}N_2O_4$, monoclinic, space group $P2_1/c$ (no. 14), a = 10.9855(12), b = 10.8828(12), c = 12.2120(13) Å, β = 98.282(5)°, V = 1444.8(3) Å^3, Z = 2, d = 1.339 g cm^{-3}, 11 297 reflections measured, 3752 unique reflections [R(int) = 0.0681], R_1 = 0.0690, wR_2 = 0.1333 for 2535 reflections with $I > 2\sigma(I)$, R_1 = 0.1123, wR_2 = 0.1472 for all reflections.

A set of experimental reflections for **6** · 2HClO$_4$ was measured using a very small single crystal of dimensions 0.16 × 0.08 × 0.04 mm^3. The structure was solved by direct methods and refined with an anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were calculated geometrically and refined with an isotropic approximation.

Crystallographic data for **6** · *2HClO*$_4$. $C_{38}H_{36}Cl_2N_2O_{12}$, triclinic, space group $P\bar{1}$ (no. 2), a = 11.4976(5), b = 12.2916(6), c = 13.5348(6) Å, α = 93.589(2), β = 110.545(2), γ = 92.542(2)°, V = 1783.11(14) Å^3, Z = 2, d = 1.459 g cm^{-3}, 12 884 reflections measured, 8721 unique reflections [R(int) = 0.0403], R_1 = 0.0614, wR_2 = 0.1350 for 5052 reflections with $I > 2\sigma(I)$, R_1 = 0.1263, wR_2 = 0.1547 for all reflections.

A set of experimental reflections for **2** was measured using an orange single crystal of dimensions 0.48 × 0.40 × 0.36 mm^3. The structure was solved by direct methods. A benzene solvate molecule situated at the symmetry center was found from the Fourier synthesis. The structure was refined with an anisotropic approximation for all non-hydrogen atoms, and an isotropic approximation was applied to all hydrogen atoms.

Crystallographic data for **2**. $C_{24}H_{25}ClNO_6$, monoclinic, space group $P2_1/n$ (no. 14), a = 7.0340(5), b = 21.0718(14), c = 14.6964(10) Å, β = 94.3050(10)°, V = 2172.1(3) Å^3, Z = 4, d = 1.403 g cm^{-3}, 14 637 reflections measured, 5628 unique reflections [R(int) = 0.0265], R_1 = 0.0443, wR_2 = 0.1220 for 4185 reflections with $I > 2\sigma(I)$, R_1 = 0.0662, wR_2 = 0.1311 for all reflections.

After irradiation of the single crystal of **2** with visible light from a standard incandescent lamp (60 W, distance from the light source was ~15 cm) for 30 h, a yellow single crystal **7** formed. A set of experimental reflections for **7** was measured with the same diffractometer. The structure was solved by direct methods. The structure was refined with an anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were refined using a riding model, or isotropically with fixed values for the thermal parameters. All peaks of electron density in the difference Fourier map are located in the vicinity of the perchlorate anion, which point out somewhat rotational disorder of the perchlorate anion over several positions. However, a refinement of these peaks as new oxygen atoms with partial occupation factors did not result in essential improvement of structure accuracy and change of geometrical parameters of the organic skeleton.

Crystallographic data for **7**. $C_{48}H_{50}Cl_2N_2O_{12}$, monoclinic, space group $P2_1/n$ (no. 14), a = 7.7053(9), b = 20.304(2), c = 14.3081(15) Å, β = 99.737(5)°, V = 2206.2(4) Å^3, Z = 2, d = 1.382 g cm^{-3}, 11 384 reflections measured, 5204 unique reflections [R(int) = 0.1426], R_1 = 0.1495, wR_2 = 0.3078 for 2180 reflections with $I > 2\sigma(I)$, R_1 = 0.2886, wR_2 = 0.3606 for all reflections.

Orange crystals of **7a** were grown as a benzene solvate from a MeCN–benzene mixture. A set of experimental reflections for **7a** was measured using a single crystal of dimensions 0.50 × 0.44 × 0.20 mm^3. The structure was solved by direct methods and refined with an anisotropic approximation for all non-hydrogen atoms. All the hydrogen atoms were found in the difference Fourier synthesis and refined with an isotropic approximation.

Crystallographic data for **7a**. $C_{60}H_{62}Cl_2N_2O_{12}$, triclinic, space group $P\bar{1}$ (no. 2), a = 11.0230(4), b = 11.2484(4), c = 12.5132(5) Å, α = 82.944(2), β = 76.649(2), γ = 61.394(2)°, V = 1325.19(9) Å^3, Z = 1, d = 1.346 g cm^{-3}, 9388 reflections measured, 6577 unique reflections [R(int) = 0.0270], R_1 = 0.0523, wR_2 = 0.1156 for 4164 reflections with $I > 2\sigma(I)$, R_1 = 0.0977, wR_2 = 0.1283 for all reflections.

Yellowish crystals of **3** were grown as a water and dichloromethane solvate. A set of experimental reflections for **3** was measured using a plate-like crystal of dimensions 0.60 × 0.50 × 0.08 mm^3. The structure was solved by direct methods and refined with an anisotropic approximation for all non-hydrogen atoms. Almost all of the hydrogen atoms were located in difference Fourier synthesis. However, for further refinement, the hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Two hydrogen atoms of the water molecule present an exception. One of them was objectively located and its positional and thermal parameters were fixed. The second hydrogen atom was not located in the final difference Fourier synthesis, apparently, because of its disorder over several positions. These positions may correspond to hydrogen bonding of this hydrogen atom to the O(4) atom or the Cl(1) atom related to the basis one through the b translation. The corresponding distances O···O and O···Cl (2.909 and 3.343 Å, respectively) fit well with this assumption. Apparently, a combination of poor quality of the single crystal and lacking of one H atom in the structure resulted in a relatively high value of residual electron density.

Crystallographic data for **3**. $C_{28}H_{35}Cl_2NO_7$, monoclinic, space group $P2_1/c$ (no. 14), a = 14.135(4), b = 7.983(2), c = 25.020(7) Å, β = 100.855(10)°, V = 2772.7(14) Å^3, Z = 4, d = 1.362 g cm^{-3}, 18 483 reflections measured, 7330 unique reflections [R(int) = 0.2731], R_1 = 0.1576, wR_2 = 0.4168 for 2222 reflections with $I > 2\sigma(I)$, R_1 = 0.3390, wR_2 = 0.4553 for all reflections.

All crystallographic data, data collection, solution and refinement parameters for **1**, **1**/**6**, **6**, **2**, **3**, **6** · 2$HClO_4$, **7**, and **7a** are listed in Tables 1S–3S (ESI†). Selected bond lengths and angles are given in Tables 4S–11S (ESI).

All the calculations were performed using the SHELXTL-Plus software.[9] CCDC reference numbers 630151 (**1**), 630152 (**1**/**6**), 630153 (**2**), 630154 (**3**), 630155 (**6**), 630156 (**6** · 2$HClO_4$), 630157 (**7**), and 630158 (**7a**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615056j

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