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Influence of the anion nature on styryl dye crystal packing and feasibility of the direct and back [2+2] photocycloaddition reactions without single crystal degradation

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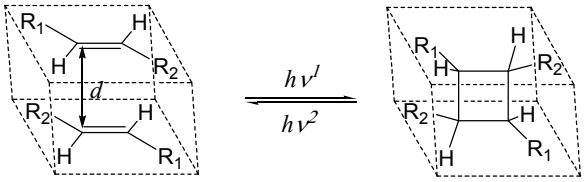
A family of styryl dyes of the 4-pyridine series, Et–Py^+–CH=CH–$C_6H_3(OMe)_2$ X^-, with different anions X^-, was synthesized. Their ability to undergo [2+2] photocycloaddition (PCA) in polycrystalline state with the formation of 1,2,3,4-tetrasubstituted *rctt* cyclobutanes under irradiation with visible light was investigated by ^{1}H NMR spectroscopy. Crystal packing of the dyes and feasibility for the PCA reaction in single crystals were investigated by X-ray structural analysis. Small inorganic anions such as ClO_4^-, BF_4^-, PF_6^- that do not form secondary interactions with the organic cation, aid formation of cation stacking motifs of the "head-to-tail" type. In these stacks, any adjacent cations are arranged in antiparallel fashion and approach one another at distances shorter than 4.2 Å, which corresponds to the Schmidt's rule for feasibility of PCA reaction in the solid state. As a result of PCA, *rctt* isomers of cyclobutane derivatives are formed. Success of the PCA reaction without single crystal degradation was only found for the dye containing BF_4^- anion. On irradiation with UV light of the cyclobutane product formed in crystal, back phototransformation without single crystal degradation was observed. A number of weak interactions I^-…H–C in the dye with I^- anion prevents significant atomic displacements that accompany the PCA transformation from being achived. Occurence of the bulky tosylate anion forming a set of hydrogen bonds with solvate acetonitrile and water molecules aids to formation of "head-to-head" type stacks, with a large separation between the adjacent ethylene bonds. In the dye containing bulky BPh_4^- anion, the main structure-forming role belongs to anions, which suppress the cation trend to form stacking packing motif. The dye with picrate anion forms two types of crystals. Crystal packing of one of them excludes any PCA transformation, whereas, the other one permits it, but with single crystal degradation.

Introduction

The solid phase reaction of [2+2] photocycloaddition (PCA) of unsaturated compounds resulting in cyclobutane derivatives has created great interest since the 1960's. On the one hand this reaction is the best way for obtaining substituted cyclobutanes[1–20] and on the other hand, it may be used in systems for optical data recording due to considerable change in physico-chemical properties of the compounds.[21,22] The PCA reaction in these compounds is accomplished upon their irradiation with visible or near UV-range light in both solid and liquid phases. The PCA reaction without single crystal degradation presents a special case.[3–5,7,9,12–14,20,23–29] However, more frequently the reaction leads to crystal degradation to amorphous glass-like state or powder. The reasons why single crystal retains or decomposes in the course of PCA are not always evident. Although in individual cases they become evident from the analysis of X-ray structural data.[23–29]

For the PCA reaction to occur, a particular spatial preorganization of two starting unsaturated molecules is required (Scheme 1). The molecules should be arranged in parallel planes in such a way that their ethylene groups are located one above another and are oriented parallel (or antiparallel) to each other with the distance *d* between the carbon atoms varying in the range 3.4–4.2 Å (Schmidt's rule).[1]



Scheme 1. View of preorganization of two ethylene units for PCA reaction.

This preorganization can be achieved as a result of a molecular design. In styryl dyes of general formula R–Het^+–CH=CH–Ar X^-, or their precursors – neutral styrylheterocycles Het–CH=CH–Ar – the actual geometry of the initial preorganized dimer can be controlled by involving different functional fragments in ethylene-containing systems. For instance, one of these fragments may be a benzocrown-ether group forming sandwich dimers in the presence of big metal cations in solutions.[30] Whereas, an addition of *N*-sulfonatoalkyl or *N*-ammonioalkyl group in the opposite position of this molecular system aids formation of another

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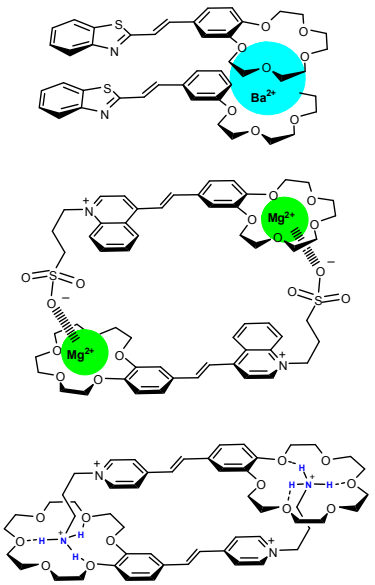
geometry of the preorganized dimers in the solid state and in solution (Scheme 2).[31–34]



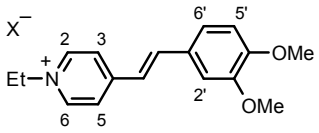
Scheme 2. Structure of dimers with different types of preorganization for PCA.

The creation of other type of sandwich dimers via binding to a metal cation, or hydrogen bonds forming between the components[3,5–7,9,10,12–16,18–20,35] or due to an assistance by macroheterocyclic compounds (crown ethers, cucurbit[8]uril, γ-cyclodextrin, calix[*n*]arenes, *etc*.)[8,28,36–44] is also described for unsaturated compounds.

In this work, we used another approach for creating sandwich dimers, taking into account that the crystal lattice may perform a topochemical control over the PCA reaction. Namely, the requirement for PCA preorganized dimers are enhanced by their crystal environment.[23–27,29,45] Then the investigation of PCA reactions is based on crystal engineering.[46] The investigation involves analyzing crystal packing for the group of compounds related to those to be chosen for study and searching for ways to construct the optimal crystal packing.

Previously, we have investigated the influence of the cation and the occurrence of additional building blocks in crystal packing of the related styryl dyes, on the formation of a particular crystal packing favourable for the PCA reaction without single crystal degradation.[23–27,29,45] In the last case, relatively small aromatic solvent molecules were used as additional building blocks.[27] The aim of this work was to explore possibilities for controlling crystal packing motifs by the anion variation. Dyes of the 4-pyridine series **1a-g** chosen as objects of this study are shown at Scheme 3.

These anions have the same charge but different shape, spatial behavior and ability to form weak interactions with surrounding functional groups in the crystal. These are spherical shape anion (I^-), pseudo-spharical shape anions revealing fluxional behavior resulting in rotational disorder in crystals (ClO_4^-, BF_4^-, PF_6^-), non-symmetrical anion having conformational freedoms (TsO^-), big planar anion prone to form a charge-transfer complex (CTC) with aromatic species (Pic^-), and bulky nonplanar anion BPh_4^-. The two last anions are capable of influencing the crystal packing formation significantly.



1a-g

Scheme 3. Structure formula of dyes **1**: $X^- = ClO_4^-$ (**a**), I^- (**b**), TsO^- (**c**), BF_4^- (**d**), PF_6^- (**e**), Pic^- (picrate anion) (**f**), BPh_4^- (**g**).

Here we describe the synthesis and X-ray structure determination of dyes **1c-g** and analyze the crystal packing for series **1c-g**, as well as the previously investigated dyes **1a** and **1b**.[25,26] After the X-ray study of the compounds was carried out, their single crystals were subjected to irradiation with visible light. For the crystals, that are saved unchanged, the second X-ray structural study was performed. For compound **1d** that was found to transform into cyclobutane derivative without single crystal degradation, we attempted to record a back (retro) photochemical reaction, without single crystal degradation by irradiating the cyclobutane product of the direct photochemical reaction with UV light. For comparison, we also performed a visible light irradiation of thin polycrystalline films of dyes **1a-g** and analyzed a composition of products and a degree of photoconversion using ^{1}H NMR.

Results and discussion

Synthesis and photochemical investigation in polycrystalline films

Synthesis of dyes **1a**,**b** has been described earlier.[25] Synthesis of dye **1c** containing tosylate anion was performed by quaternization of neutral dimethoxystyrylpyridine with ethyl 4-methylbenzenesulfonate. Dyes **1d-g** were obtained by anion exchange in **1c** on treatment with appropriate salt ($NaBF_4$, NH_4PF_6, NaPic, $NaBPh_4$) in methanol (Scheme 4). All new compounds were characterized by ^{1}H NMR spectroscopy data and elemental analysis.

Yellow dyes **1a-g** in the form of polycrystalline films on glass substrates were irradiated with visible light under comparable conditions. The compositions of the samples thus obtained were analyzed by ^{1}H NMR spectroscopy. The results are given in Table 1.

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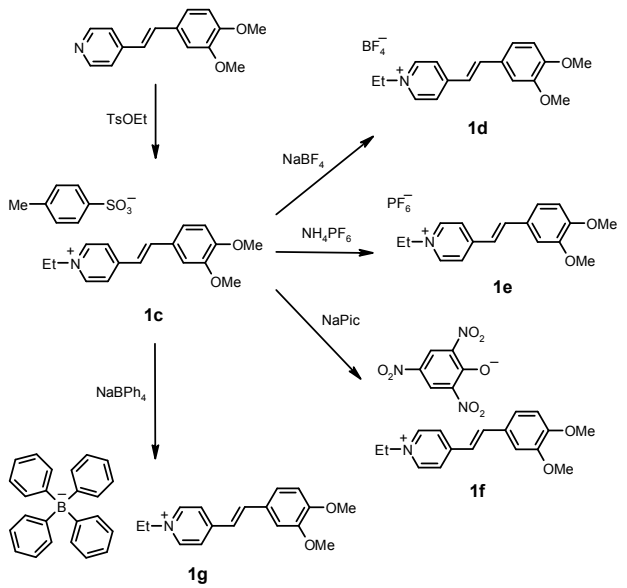


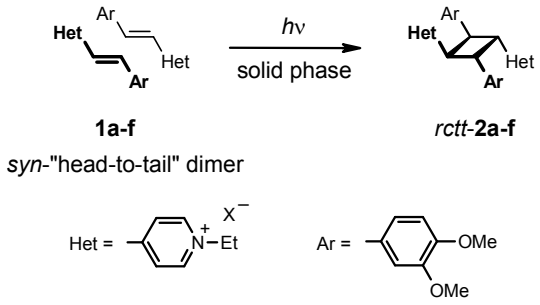
Scheme 4. Synthesis of dyes **1c-g**.

Table 1. The starting dye **1**-to-cyclobutane derivative *rctt*-**2** ratio and the degree of conversion (χ) in polycrystalline films of dyes **1a-g** irradiated with visible light.

Compound	*t* / h [a]	dye : cyclobutane (mol/mol) [b]	χ (%) [b]
1a [c]	10	1 : 5.8	92
1b [c]	10	5.4 : 1	27
1c	10	1 : 18.5	97
1d	10	0 : 1	100
1e	10	1 : 3.3	87
	26	1 : 10.4	95
1f	10	2.77 : 1	42
	50	1.13 : 1	64
	240	1 : 1.34	73
1g	10	1 : 0	0

[a] The duration of irradiation. [b] Based on the ^{1}H NMR spectroscopic data. [c] Data from Ref.[25]

Dye **1g** proved to be insensitive to light. By contrast, the irradiation of the other compounds resulted in the formation of centrosymmetric *rctt* isomers of cyclobutane derivatives **2a-f** (Scheme 5). The ^{1}H NMR spectra of **2a-f** show characteristic[23–25,28,29] signals of cyclobutane protons at δ 4.8–4.9: two symmetric doublets of doublets and the AA'BB'-type spin system. This is indicative of the existence of *syn*-"head-to-tail" stacked dimers in the solid state, which should precede the formation of cyclobutanes with this stereochemistry. The rates of the PCA reactions are substantially different. The phototransformation proceeds most rapidly in dyes **1a**,**c-e** (the degree of conversion 87–100% for 10 h), whereas the complete conversion of picrate **1f** was not achieved even within >240 h. The phototransformation of iodide **1b** was also found to be much slower.[25]



Scheme 5. Synthesis of cyclobutane derivatives *rctt*-**2a-f**.

In order to check a possibility for the solid state *retro*-PCA reaction in the compounds obtained, we performed the following experiment. At first, polycrystalline film of dye **1d** was irradiated with visible light (λ > 390 nm) until full transformation to cyclobutane derivative *rctt*-**2d** (monitored by ^{1}H NMR). Then this film was subjected to short-wave irradiation (λ in the range of 280–340 nm). Fragments of the ^{1}H NMR spectra of dye **1d** and photolyzates of its film are shown at Fig. 1.

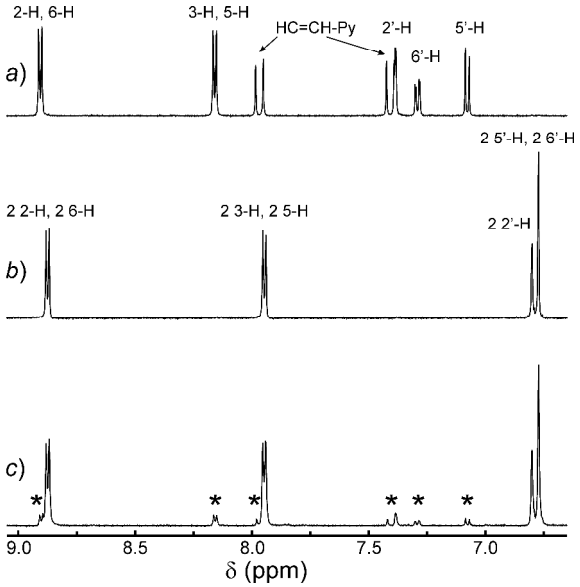


Figure 1. ^{1}H NMR spectra (aromatic protons region, DMSO-d_6) of (*a*) dye **1d**, (*b*) dye **1d** irradiated with visible light in thin film (cyclobutane *rctt*-**2d**), and (*c*) *rctt*-**2d** irradiated with UV light in thin film (a 4.3:1 mixture of **2d** and **1d**; the proton signals of minor dye **1d** are marked with asterisk).

It is observed that on irradiation of the initial compound its proton signals in spectrum have disappeared completely, whereas, subsequent UV irradiation results in their reappearance again: the *rctt*-**2d**/**1d** molar ratio is equal to 4.3:1 (degree of back transformation equals to 10%). Thus, we proved that both direct and back PCA reactions in the solid state of dyes **1** are feasible in principle.

X-Ray structural investigations

For all synthesized compounds, the X-ray structural study was performed. Single crystals of the dyes were grown by slow saturation of their acetonitrile solutions by benzene or benzene–hexane vapors in darkness. Another crystal

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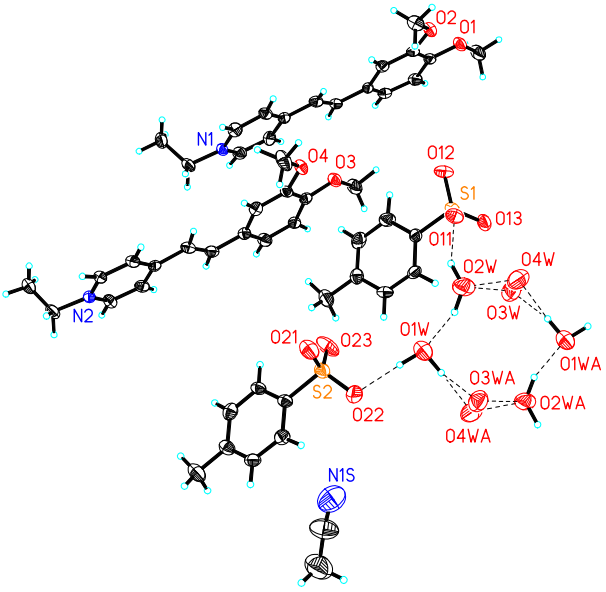
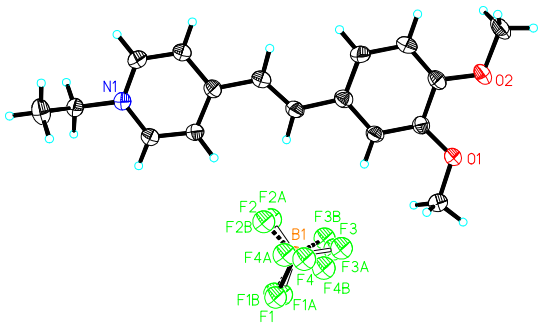
modification of dye **1f** was prepared by slow evaporation of its solution in a water–MeCN mixture.

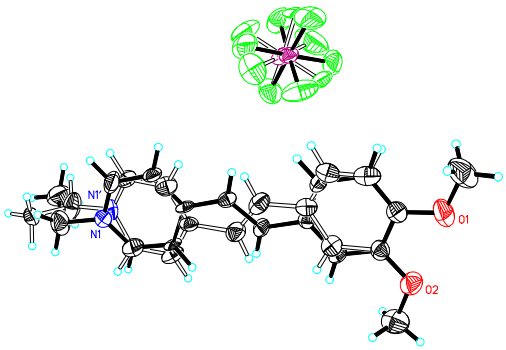
Structures of formula units for compounds **1c-g** are shown in Fig. 2. For dyes **1a** and **1b**, structural determination have been performed earlier.[25,26]



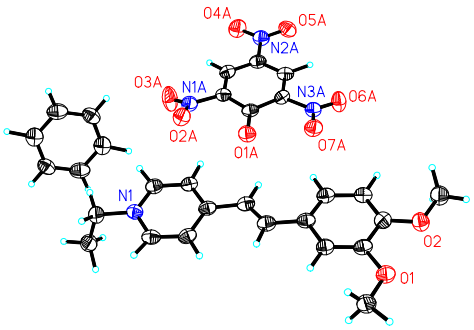
1c·0.5MeCN·1.5H_2O



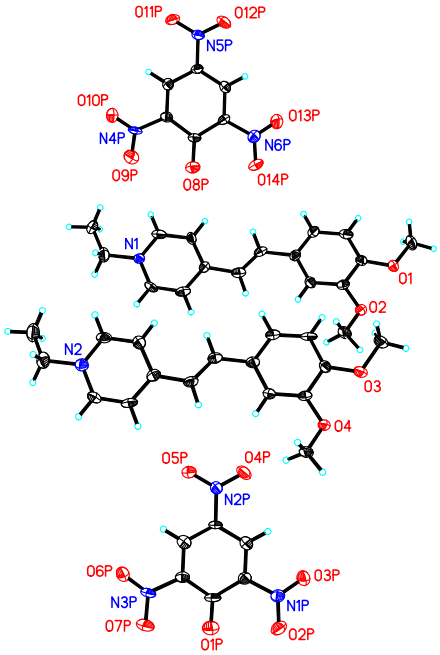
1d



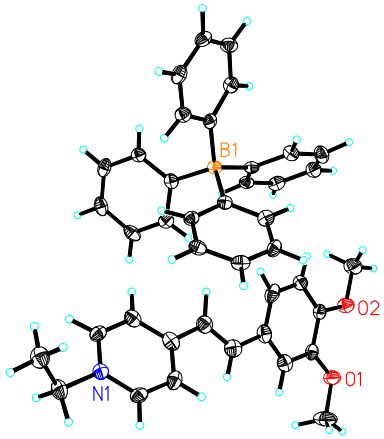
1e



1f·0.5C_6H_6



1f



1g

Figure 2. Independent molecular moieties of crystal structures **1c-g**. Displacement ellipsoid are drawn at the 50% probability level.

The independent moieties of crystal unit cells of **1a,b,d,e,g** and **1f**·0.5C_6H_6 includes one organic cation and one anion, whereas crystal unit cells of **1c**·0.5MeCN·1.5H_2O and **1f**

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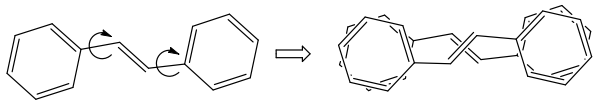
contain two independent cations and two independent anions. Independent crystallographic unit for **1c** also contains one acetonitrile solvate molecule and three water molecules, one of which is disordered over two positions close to each other with nearly equal occupancies. Assymetric unit of **1f**·0.5C_6H_6 contains half a benzene solvate molecule situated at a symmetry centre.

The cation in structure **1e** reveals a "pedal" disorder. This disorder is a consequence of a temperature-dependent dynamic process of "pedal" isomerisation in the crystal,[18,47–49] when the ethylene fragment is subjected to a rotation about its single bonds (Scheme 6). Rather often this phenomenon is observed in styryl dyes[25–27,29] and neutral styrylheterocycles[45]. The ratio of "pedal" isomers in **1e** corresponds to 0.64:0.36.

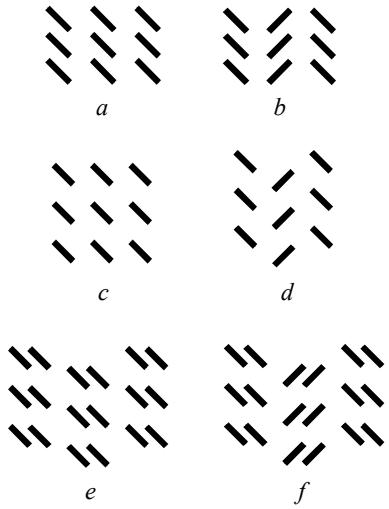


Scheme 6. Mechanism of "pedal" motion in crystals of ethylene compounds.

In crystal **1e** the PF_6^- anion is also disordered over two close positions. Rotational disorder of the BF_4^- anion over at least three positions was also observed for **1d**, with the ratio of occupancies 0.51:0.33:0.16. In reality, many residual peaks of electron density are observed in the vicinity of boron atom. However, their inclusion as partial atoms shows no improvement in the least square refinement of the structure.

Crystal packings and feasibility of PCA transformation

An analysis of the CSD data[50] made it possible to select six canonical packing forms for planar molecules (organic cations) of unsaturated compounds (Scheme 7).



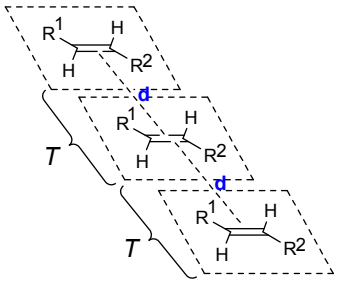
Scheme 7. Canonical packing motifs for planar structural units, molecules or cations; solid lines denote planar structure units in profile.

Packings *a* and *b* are parallel-stacking and parquet-stacking, packings *c* and *d* are staircase and parquet, packings *e* and *f* are dimeric-parallel and dimeric-parquet. In packings *c* and *d* there is no overlapping of the conjugated fragments. These packings can be deduced from packings *a* and *b*, respectively, by an equal slide to the same side of any moiety with respect to previous one. In packings *e* and *f*, any dimeric π–conjugated moiety does not overlap in projection with neighbouring ones. These packings may also be deduced from packings *a* and *b*, respectively, by analogous slide of pairs of molecules.

These types of crystal packing are typical for styryl dyes, protonated styrylheterocycles R–Het^+–CH=CH–Ar X^- (Het – nitrogen-containing heterocycle, X^- – anion), and neutral styrylheterocycles Het–CH=CH–Ar. Packings *a*, *b*, *e*, and *f* may contain dimers preorganized for PCA reaction, whereas, packings *c* and *d* cannot contain such dimers. Our previous work shows that styryl dyes and protonated styrylheterocycles almost exclusively form crystal packing of *a* and *b* types, whereas, packings *c*, *d*, *f*, and *e* are typical for neutral styrylheterocycles.[23-27,29]

For ethylene derivetives prone to participate in PCA transformation, stacking packing motifs may be of different types depending on the symmetry operation combining structural units in a stack. Centrosymmetrically related stacks with *syn*-"head-to-tail" organization of structural units form most frequently, whereas, translation-related stacks of the syn-"head-to-head" structure unit organization occur rather rare[25-27,51-52] Only one case of 2-fold-axis-related stacks is known for styryl dyes.[26]

In the case of translation-related stacks (Scheme 8), the PCA reaction in the crystal without its decomposition is impossible.



Scheme 8. Translation-related stack of *syn*-"head-to-head" type; *T* – translation, d – distance between adjacent ethylene fragments.

In this stack, one event of PCA would result in loss of its local symmetry and defect formation. If the number of the events increases, the defect region rises. This eventually results in crystal degradation. In reality the formation of this type stacks in styryl dyes is associated with significant slide of adjacent cations with respect to one another in order to reduce the Coulomb interaction between similarly charged fragments of adjacent cations. Therefore, the distance between the ethylene fragments of adjacent cations, d, is much longer than 4.2 Å and this also makes PCA transformation impossible in crystals of this type packing.

In centrosymmetrically related stacks of the *syn*-"head-to-tail" type, the mutual organization of structural units is favorable for PCA. In this case, the PCA reaction is feasible, sometimes without single crystal degradation. A set of additional conditions is required for this.[23–27,29] The relationships $d_1 < 4.2$ Å and $d_2 > 4.2$ Å, where d_1 and d_2 are alternating distances between adjacent ethylene fragments in a stack, is often beneficial to PCA (Scheme 9).

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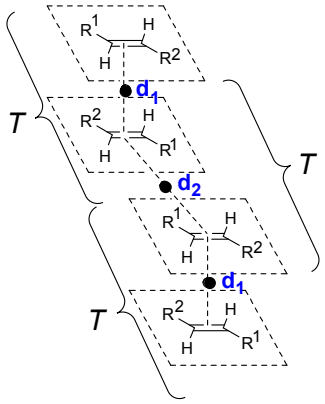

Scheme 9. Centrosymmetrically related stack of *syn*-"head-to-tail" type; *T* – translation, • – symmetry centre, d_1 and d_2 – distances between ethylene fragments in dimers and between the dimers, respectively.

In the case when both distances satisfy the condition of the PCA feasibility (d_1 and $d_2 < 4.2$ Å) the PCA process should go statistically between crystallographically independent pairs of structural units related by symmetry centres belonging to different crystallographic systems. This inevitably results in general crystal symmetry violation, that is, crystal degradation.

The second additional condition is an occurrence of soft flexible shell about the dimers, capable of reducing internal stresses in the crystal that arise due to rather significant atomic displacements in the course of PCA.[23–29] This shell may be created by positionally or rotationally flexible anions, solvate molecules, and fragments of molecular cations or molecules, such as crown-ether fragments or bulky alkyl substituents.

In the crystal packing of **1f**·0.5C_6H_6, isolated alternating layers formed by stacks of cations and anions occur (Fig. 3).

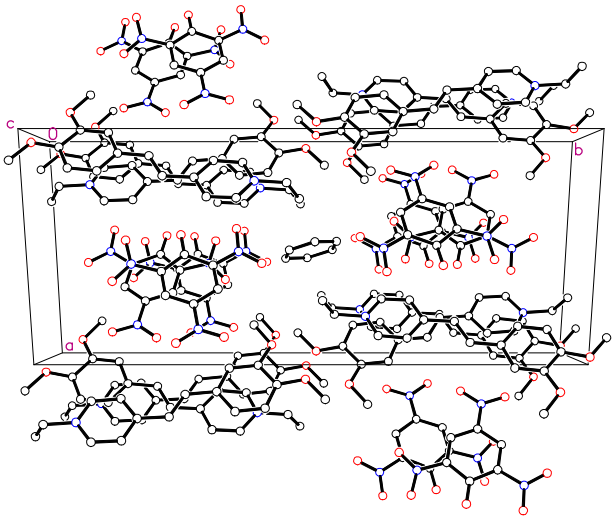

Figure 3. Crystal packing of **1f**·0.5C_6H_6.

The layers of anions also involve benzene solvate molecules. The inclusion of large anions that are prone to form CTCs, does not prevent the formation of stacks of the cations.

The mutual arrangement of cations in a stack (Fig. 4) is unfavorable for the PCA reaction to be accomplished in this crystal. Actually, ethylene fragments of the adjacent cations are not parallel. Moreover, they do not overlap in projection (Fig. 4, (b)). First of these unfavorable circumstances might be overcome due to aforementioned "pedal" motion, and the second, because of mutual translation of molecules. Examples of a PCA reaction in the solid state going in spite of long distances (> 5 Å) between ethylene compounds were described earlier.[47,53] However, crystals **1f**·0.5C_6H_6 manifest high stability to irradiation with visible light.

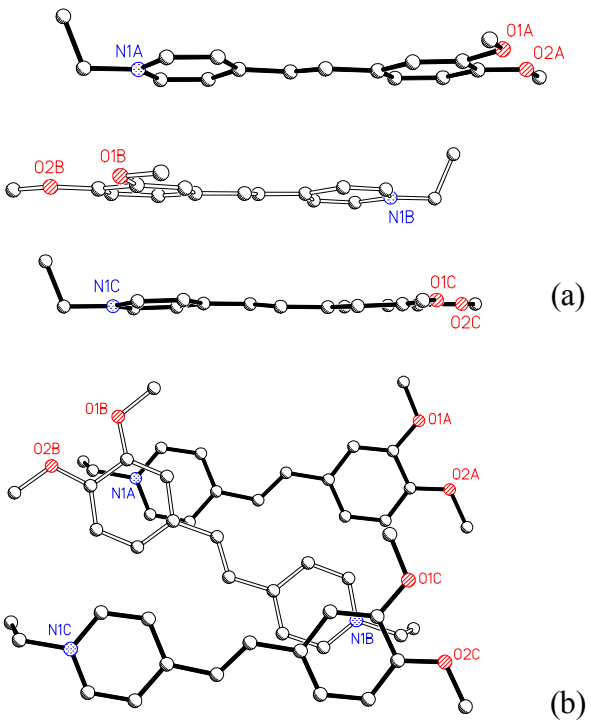

Figure 4. Structure of a cation stack in **1f**·0.5C_6H_6 in two projections.

In the layer formed by picrate anions and benzene solvate molecules (Fig. 3), there are no π-stacking interactions between anions, since they do not overlap in projection. This layer does not contain conformationally flexible elements. Apparently, the structural rigidity of this layer explains high stability of crystals **1f**·0.5C_6H_6 to irradiation.

The second crystal form of **1f** does not contain solvent molecules. Its crystal packing is different. It is constructed of mixed stacks that involve both cations and anions. In a stack four cations alternate with four anions (Fig. 5). Two central cations form centrosymmetrically related couple with the *syn*-"head-to-tail" arrangement and C6…C7A / C6A…C7 intermolecular distance equial to 3.79 Å, which is favorable for the PCA reaction that should result in cyclobutane *rctt*-**2f**. Two other cations in the stack present crystallographically independent species. They are arranged in pseudocentrosymmetric mode with respect to the cations that form the central centrosymmetric couple. The intermolecular distance C6…C7' and C6'…C7 in the adjacent couple of cations (both 6.09 Å) is too long, which prevents the PCA transformation between these cations.

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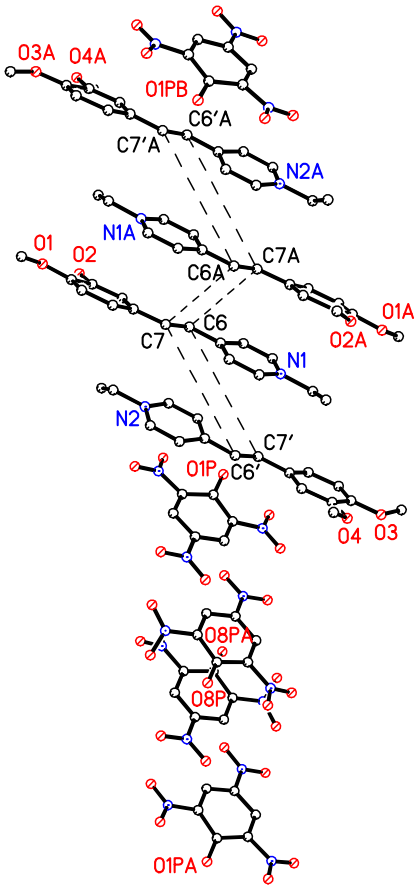

Figure 5. Stack of cations and anions in crystal **1f**.

In the quaternion of anions, only two central ones are involved in a rather strong π-stacking interaction. The neighboring cation and anion overlap in projection thus to form CTC. This packing appears to predominate in a polycrystalline film of **1f**, because it allows the PCA transformation that actually takes place, although relatively slowly (see Table 1).

Crystals **1c**·0.5MeCN·1.5H_2O are built of alternating layers of cations and anions. The anion layers also involve water and acetonitrile solvate molecules. The sulfonate groups of the tosylate anions and water molecules are involved in a network of hydrogen bonds (see Fig. 2).

Stacks of cations are arranged in the *syn*-"head-to-head" pattern (Fig. 6). According to aforementioned consideration, this type of stack organization excludes a feasibility of PCA in single crystal. Actually, the distances between neighboring ethylene fragments are in the range of 7.62–8.22 Å that exceeds greatly the longest distance when the PCA reaction can proceed. Indeed, crystals **1c**·0.5MeCN·1.5H_2O are stable to irradiation with visible light. However the PCA reaction occurs in polycrystalline film of dye **1c** very efficiently to give centrosymmetric isomer of cyclobutane derivative *rctt*-**2c**. This means that the predominant packing motif in fine-grained crystals of polycrystalline film of **1c** differs from that found in single crystals.

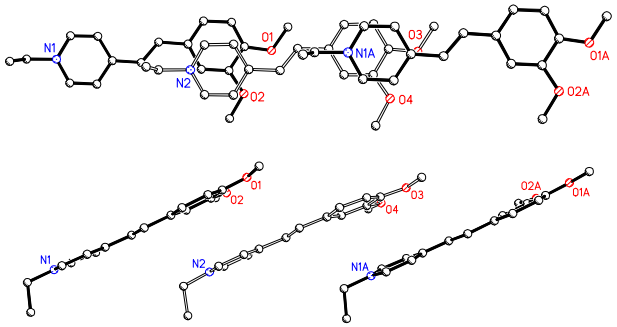

Figure 6. Stack of cations in structure **1c**·0.5MeCN·1.5H_2O in two projections.

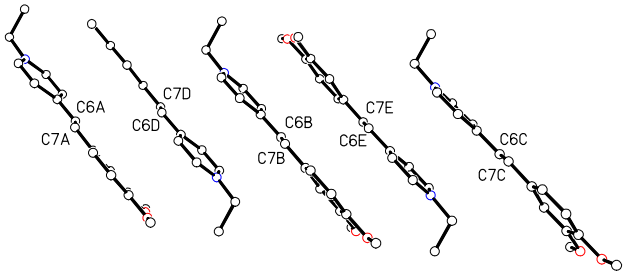

Figure 7. Mutual arrangement of cations of **1b** in a stack.

In the crystal packing of dye **1b**[25,26] cations are arranged in stacks of the *syn*-"head-to-tail" type (Fig. 7). Any two adjacent cations are related via a symmetry centre. The distance between the ethylene fragments of cations A and D (C6A…C7D and C7A…C6D) is equal to 4.18 Å and lies in the vicinity of the upper limit of PCA reaction feasibility. While the distance between the ethylene fragments of the adjacent cation pair, D and B (C6D…C7B and C7D…C6B) is too long, 6.89 Å, for the PCA reaction to proceed.

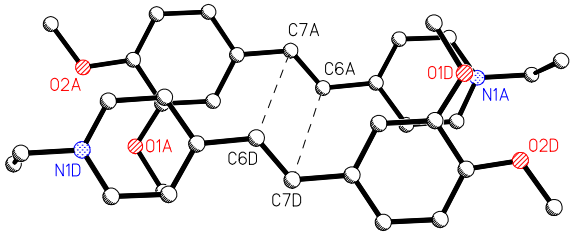

Figure 8. Projection of a cation onto plane of another cation in **1b**.

The mutual arrangement of cation pair A and D is not the best one for the feasibility of the PCA reaction (Fig. 8). The region of the π-overlap of the two cations covers only periphery of their conjugated systems, which is not optimal for the PCA reaction in single crystal. Apparently, this is defined in most degree by the influence of the I^- anion on the crystal packing. This anion tends to form secondary bonds of the C–H…I^- type (Fig. 9), which results in shifts of the cations from the positions corresponding to optimal geometry of preorganized dimers with efficient π…π overlap between the cations of the A and D type. Distances I1…H1, I1…H4, I1…H5 are equal to 2.90, 3.24, 3.10 Å, which are shorter or equal to minimum value of van der Waals distance (~3.2 Å) and correspond to usual distances for the interactions of this type.[54,55] Involvement of cations in these weak interactions,

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apparently deteriorates preorganization of the A…D type cations for PCA.

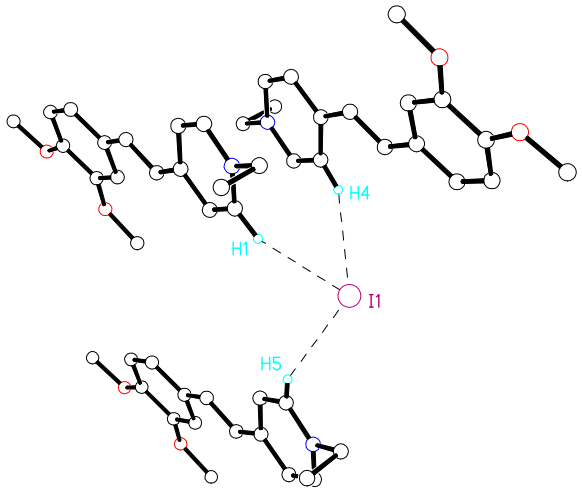


Figure 9. Environment of I^- anion in crystal **1b**.

However, taking into account a high trend of ethylene groups to parallel displacement in the course of PCA, one may expect accomplishing this reaction in crystals **1b**, but only with crystal degradation. Indeed, the PCA process is very slowly developing in crystals of **1b**. During two weeks these crystals are stable to irradiation with visible light, but then they begin to slowly decompose. In a polycrystalline film this compound behaves analogously.

In crystals **1a**, **1d**, **1e** with rotationally flexible anions (ClO_4^-, BF_4^-, and PF_6^-, respectively), crystal packings qualitatively similar to that observed in **1b** are realized. All these packings are described by motif *b* in Scheme 7. As an example, packing of **1a** is shown in Fig. 10. It is composed of centrosymmetric stacks with *syn*-"head-to-tail" mutual organization of cations. This organization involves dimers favorable for PCA.

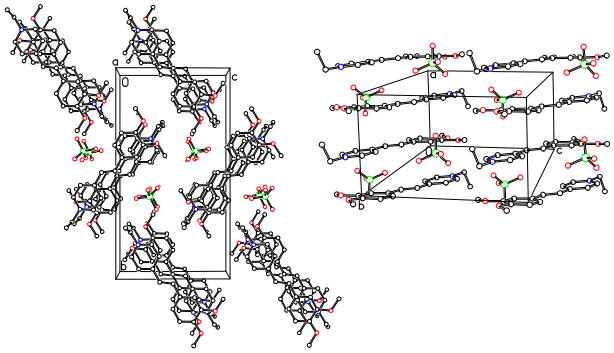


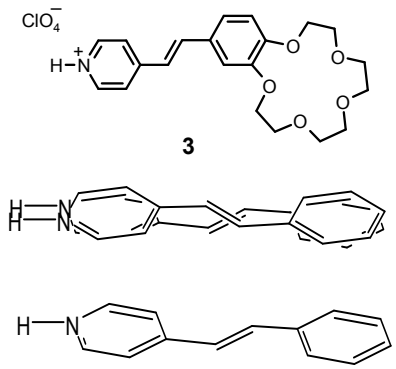
Figure 10. Crystal packing of **1a** in two projections.

Although differences in crystal packings of **1a**, **1d**, and **1e** are quantitative, they determine different behavior of the compounds with respect to PCA in single crystals.

In crystal packing of **1a**, both distances d_1 and d_2 (3.74 and 3.66 Å) satisfy conditions d_1 and $d_2 < 4.2$ Å. Therefore, PCA reaction is possible in this case, but with crystal decomposition. Indeed, upon irradiation with visible light, crystals decompose to an amorphous powder and the compound becomes lighter in colour. The result of this reaction is the formation of centrosymmetric *rctt* isomer of cyclobutane derivative **2a**, from both crystallographically independent pairs of cations.

In crystals **1e**, analogous *syn*-"head-to-tail" stacks of cations occur, in which different "pedal" isomers are statistically distributed. Therefore, pairs of adjacent cations with major–major, minor–minor, and major–minor mutual arrangement may exist simultaneously. In two first cases the adjacent ethylene fragments are antiparallel, which is favourable for PCA. In the third case, the mutual arrangement of these fragments is near perpendicular, which is unfavourable for PCA. However, the aforementioned dynamic "pedal" process may change the mutual orientation of the ethylene fragments in the third type pair to make the photoreaction possible.

Earlier,[29] we have established that dynamic process of "pedal" isomerization in crystal of protonated styrylpyridine **3** actually takes place. This crystal contains two crystallographically independent cations that are situated in parallel one above another. One of these cations reveals "pedal" disorder (Scheme 10). Only the ethylene bond of the minor component of this disordered system is parallel with the ethylene bond of another ordered cation.



Scheme 10. Structure formula of compound **3** and its dimer formed by two independent cations in crystal.

Nevertheless the full PCA transformation without crystal decomposition has been observed in the crystal, which is only possible if the "pedal" motion actually takes place in the crystal.

Figs 11 and 12 show stacks with participation of cations of the major–major and minor–minor types in **1e**.

In both cases, distances d_1 and d_2 are shorter than 4.2 Å, which should evidence that the PCA transformation in this crystal is only possible with crystal decomposition. Indeed, crystals **1e** decompose under irradiation with visible light to give an amorphous powder. Under the same conditions, a polycrystalline film of **1e** almost completely transforms into cyclobutane derivative *rctt*-**2e**.

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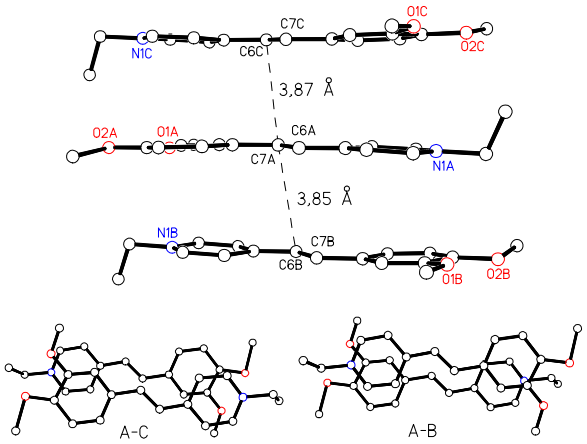


Figure 11. Stacks formed by major "pedal" isomers (top) and mutual projecting of adjacent pairs of cations (bottom) in **1e**.

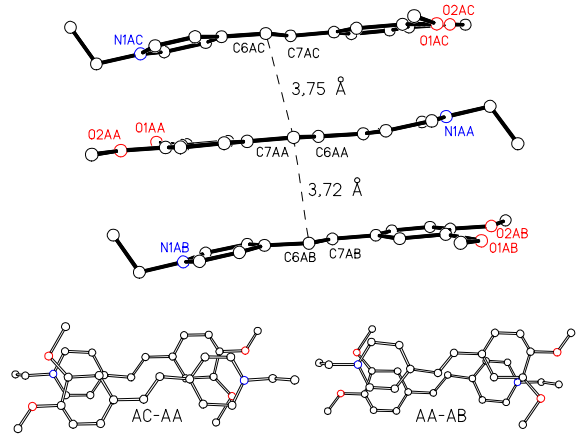


Figure 12. Stacks formed by minor "pedal" isomers (top) and mutual projecting of adjacent pairs of cations (bottom) in **1e**.

Kept under visible light, crystals **1d** become colourless very quickly (Fig. 13). Big crystals crack into smaller ones, but small crystals are mechanically stable, their shape stays unchanged.

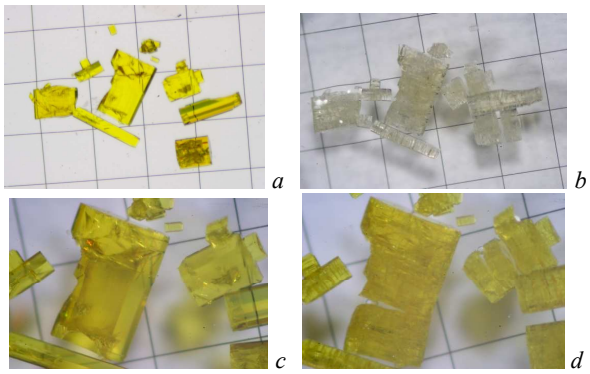
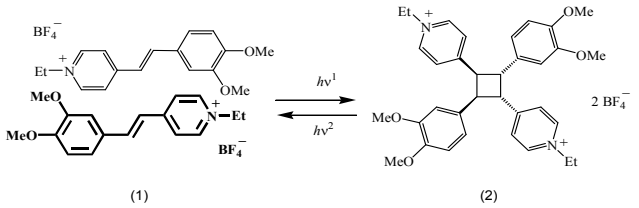


Figure 13. Crystals of **1d** in perfluorinated oil on a glass support with 2D millimeter scale: *a* and *c* before irradiation; *b* and *d* after irradiation with unfiltered light of Fiber Optical Light Source (200 W, Meiji Techno) during 10 min (*d*) and 2 h (*b*). Photographs are made using a EMZ-13RT microscope (Meiji Techno).

These results indicate a PCA transformation without single crystal degradation in **1d** (Scheme 11).



Scheme 11. Direct and back PCA reactions in single crystal **1d**.

The change in colour turned out to be distinct after approximately 20 minutes – the time required for manipulation with crystals at microscope before X-ray diffraction experiment start. Because of high rate of the PCA transformation in a single crystal, we failed to obtain very precise experiment for single crystal **1d**. Rotational disorder of the BF_4^- anion also reduces the accuracy of this X-ray study.

In crystal **1d** the cations are arranged in centrosymmetrical stacks of the *syn*-"head-to-tail" type (Fig. 14). Alternating distances d_1 and d_2 are equal to 3.67 and 3.97 Å.

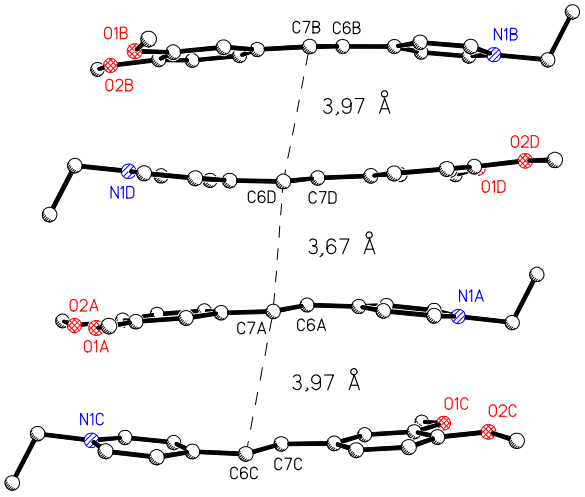


Figure 14. Stack of cations in crystal **1d**.

Although both distances are shorter than 4.2 Å, the A–D pair is better preorganized for PCA than two crystallographically equivalent pairs B–D and A–C. It is seen from Fig. 14 that the ethylene groups at the central pair (A–D) are bent towards one another. Moreover, in pair A–D there are better geometric conditions for conjugated fragments efficient π-overlapping (Fig. 15). This gave basis to the suggestion that in crystal **1d** the PCA reaction will go only in crystallographically equivalent pairs. Therefore this reaction should not be accompanied by crystal decomposition.

Indeed, after 3-h irradiation with visible light of the same crystal of **1d** that had been studied using X-ray diffraction analysis it turned colourless. The X-ray study established that the complete PCA transformation of dye **1d** into cyclobutane derivative *rctt*-**2d** had taken place without crystal decomposition (Fig. 16). The BF_4^- anion remains rotationally disordered over three positions.

It should be noted that in contrast to crystal **1d**, crystal **2d** turned out to be of a rather good quality.

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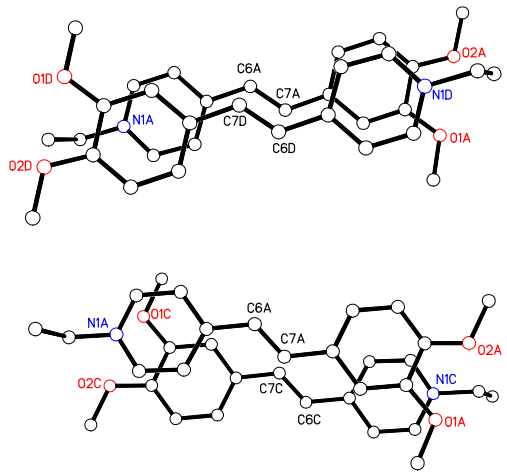

Figure 15. Mutual projection of crystallographically nonequivalent pairs of cations in **1d**.

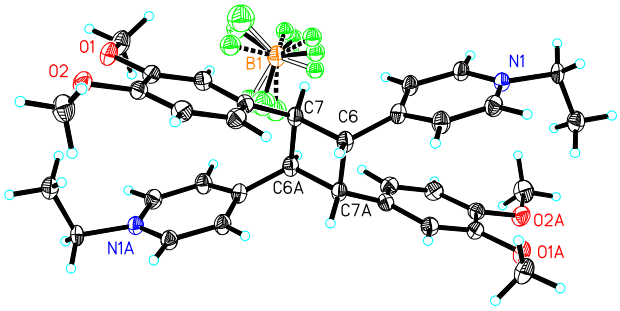

Figure 16. Structure of cyclobutane derivative *rctt*-**2d** formed on irradiation of **1d**.

A superposition of a pair of structure units of the initial compound **1d** and corresponding structural units of the product **2d** is shown in Fig. 17. It is seen that the cyclobutane moiety of **2d** lies inside the pair of the initial cations. A shift of the boron atoms in **2d** from their positions in **1d** is equial to 0.21 Å. The BF_4^- anions in both compounds are slightly rotated with respect to one another and the ratio of their occupancies is slightly changed (0.51:0.33:0.16 in **1d**, 0.60:0.20:0.20 in **2d**). One may conclude that the changes are due to tuning of anions to a slightly changed crystal environment in the course of the PCA reaction.

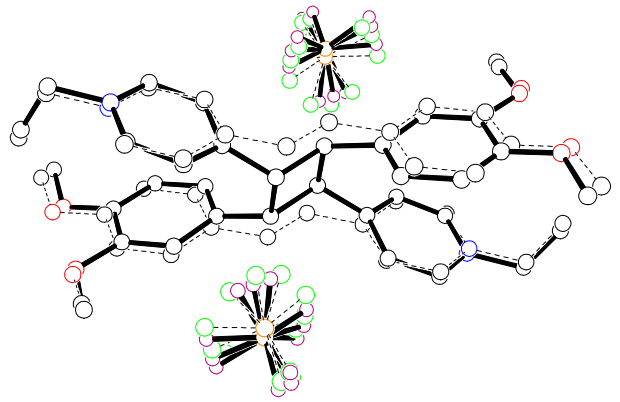

Figure 17. Superposition of structure units of initial compound **1d** (dash lines) and product **2d** (solid lines); the fluorine atoms of anions in **1d** and **2d** are shown with green and violet colours, respectively.

Apparently these results explain why the PCA reaction in **1d** goes so quickly and without crystal decomposition at least in small crystals. For this reason we tried to discover a photochemical reaction of *retro*-PCA, **2d**→**1d**.

The same single crystal of compound **2d** was then subjected to unfiltered UV-vis radiation from a L8252 mercury-xenon lamp (Hamamatsu) at room temperature. Its spectrum contains a set of wavelengths. Among these are the ones initiating both the direct and the back phototransformations. After 4-h irradiation of single crystal **2d** it has turned bright yellow again (crystal **4d**). It should be noted that when UV-vis irradiation of the crystal was stopped, it becomes colourless in approximately 30 minutes of keeping on light at room temperature, but its colour remains unchanged at low temperature (~150 K) for several hours.

In crystal **4d** we expected to observe the coexistence of both compounds, **1d** and **2d** (mixed **1d**/**2d** system), but with *a priori* unknown ratio of their contents. Similar mixed systems were observed earlier many times as the results of incomplete direct PCA reactions (for examples, see Refs[4,24,26,27,29]). Nevertheless this result could be important in this particular case because it might indicate that the back photochemical reaction is also feasible in single crystal in parallel with the direct PCA reaction. Note that in polycrystalline film of *rctt*-**2d**, the *retro*-PCA does take place resulting in the apperance of 10% initial dye **1d** (see Fig. 1 and its discussion).

Meanwhile, the actual result of the irradiation of single crystal **2d** turned out to be unexpected (Fig. 18). Instead of mixed system **1d**/**2d**, the disordered cyclobutane system **4d** has appeared, with differently oriented cyclobutane. The ratio of two components of cyclobutane is 0.89:0.11 and both are centrosymmetric *rctt* isomers. This result might be easily interpreted if molecules of dye **1d** formed *in situ* during irradiation contain the "pedal" disorder. In this case structure **4d** will directly form from the intermediate mixed **1d**/**2d** system. As the "pedal" disorder is lacking in initial crystal **1d**, it is obvious that such a transformation of one cyclobutane moiety into another one requires the back transformation of **2d** into initial compound together with its "pedal" isomerization. New-formed **1d** compound quickly transforms into the cyclobutane derivative again, being in a photostationary equilibrium. However, during the existence, it also transforms into another "pedal" isomer. On light, these two "pedal" isomers further convert in two kinds of cyclobutanes to give the observed disordered crystal **4d**. Although the "pedal" disorder in the initial crystals **1d** is lacking, it could appear in **1d**/**2d** mixed crystal as a result of small displacements in crystal packing due to photochemical transformations.

It should be noted that, in structures **1d**, **2d**, and **4d**, the BF_4^- anion was found to be rotationally disordered over three positions with the ratios of occupancies 0.51:0.33:0.16 in **1d**, 0.60:0.20:0.20 in **2d**, and 0.38:0.38:0.24 in **4d**. The ratios in **1d** and **2d** are rather close, whereas, in **4d** they are significantly different. This fact shows that the nearest environment of the reacting components of UV-irradiated crystal **2d** may differ enough from that in crystals **1d** and **2d** for making feasible the "pedal" motion in the crystal.

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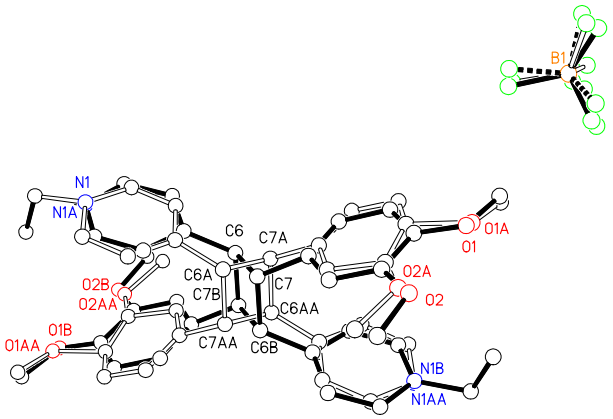

Figure 18. Structure of cyclobutane derivative **4d** obtained after 4-h UV-vis irradiation of crystal **2d**.

Thus, obtained structure **4d** serves as a proof that both photochemical processes – PCA and *retro*-PCA – are feasible in the same crystal without its decomposition.

In crystal of the dye **1g** containing huge BPh_4^- anion, the main structure-forming role belongs to anions, which interrupt the cation's trend to form π-stacking elements in crystal packing. That is, the main packing motifs for planar molecules shown in Scheme 7 are not applied here. This is in good agreement with the absence of PCA products in irradiated polycrystalline films of the dye **1g** (see Table 1).

Conclusions

This investigation made it possible to establish that the nature of the anion in styryl dyes affects significantly the crystal packing motif. Rotationally flexible anions such as ClO_4^-, BF_4^-, PF_6^- present the most favorable type for realization of centrosymmetrically related stacking motif of the organic cations. In most of the structures investigated a trend to form stacking elements of the packing motif for cations is observed. Even the ability of picrate anion to form charge-transfer complexes with aromatic moieties does not violate this trend. Only bulky BPh_4^- anion representing major structure-forming element in the crystal of the corresponding dye, is capable of suppressing this trend.

We have received the first proof that direct and back reactions of [2+2] photocycloaddition can be accomplished in the same single crystal of an ethylene compound with the retention of the single crystal. We believe this process could be accomplished repeatedly in a crystal, which is important on creating switching systems or memory cells.

Experimental section

General

Melting points (uncorrected) were measured in capillaries on a Mel-Temp II apparatus. ^{1}H NMR spectra were recorded on a Bruker DRX500 instrument (500.13 MHz) in DMSO-d_6 at 25–30°C using the solvent as an internal standard (δ_H 2.50 ppm). Elemental analyses were performed in the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Elementoorganic Compounds of the Russian Academy of Sciences (Moscow, Russian Federation). The samples for elemental analyses were dried at 80°C in vacuo.

Preparations

Synthesis of 4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]pyridine, dyes **1a**,**b** and cyclobutanes *rctt*-**2a**,**b** was described earlier.[25,45]

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium tosylate (**1c**). A mixture of 4-[(*E*)-2-(3,4-dimethoxyphenyl)-1-ethenyl]pyridine (0.31 g, 1.27 mmol) and ethyl 4-methylbenzenesulfonate (0.76 g, 3.81 mmol) was heated at 120°C (oil bath) in darkness for 2 h. After cooling to room temperature, the resulting mass was washed with benzene (2 × 10 mL) and the solids was twice extracted with hot benzene (15 mL, for 1 h) in darkness. The insoluble substance was dissolved in abs. EtOH (3 mL) and the solution was diluted with Et_2O (30 mL). The glassy precipitate thus formed was decanted and dried at 70°C *in vacuo* in darkness to give dye **1c** (0.49 g, yield 87%) as a yellow-orange powder, mp 146–148°C. Cacld. for $C_{24}H_{27}NO_5S{\cdot}0.25H_2O$: C 64.63, H 6.21, N 3.14. Found: C 64.65, H 6.64, N 3.05%. ^{1}H NMR: δ = 1.53 (t, J = 7.3 Hz, 3 H, *Me*CH_2), 2.29 (s, 3 H, *Me*Ar), 3.83 (s, 3 H, 4'-MeO), 3.85 (s, 3 H, 3'-MeO), 4.51 (q, J = 7.3 Hz, 2 H, CH_2N), 7.08 (d, J = 8.4 Hz, 1 H, 5'-H), 7.10 (d, J = 8.0 Hz, 2 H, 3"-H, 5"-H), 7.30 (dd, J = 8.4 Hz, J = 1.5 Hz, 1 H, 6'-H), 7.39 (br.s, 1 H, 2'-H), 7.40 (d, J = 16.3 Hz, 1 H, CH=C*H*Py), 7.48 (d, J = 8.0 Hz, 2 H, 2"-H, 6"-H), 7.96 (d, J = 16.3 Hz, 1 H, C*H*=CHPy), 8.16 (d, J = 6.7 Hz, 2 H, 3-H, 5-H), 8.90 (d, J = 6.7 Hz, 2 H, 2-H, 6-H).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium tetrafluoroborate (**1d**). A solution of $NaBF_4$ (20 mg, 0.17 mmol) in MeOH (1 mL) was added to a solution of dye **1c** (64 mg, 0.15 mmol) in MeOH (1 mL) in darkness and the resulting mixture was cooled to 5°C. The precipitate thus formed was filtered, washed with cold MeOH (2 × 1 mL) and dried in air to give dye **1d** (36 mg, yield 73%) as a yellow powder, mp 219–220°C. Calcd. for $C_{17}H_{20}BF_4NO_2$: C 57.17, H 5.64, N 3.92. Found: C 57.24, H 5.67, N 3.88%. ^{1}H NMR: δ = 1.52 (t, J = 7.3 Hz, 3 H, *Me*CH_2), 3.83 (s, 3 H, 4'-MeO), 3.85 (s, 3 H, 3'-MeO), 4.50 (q, J = 7.3 Hz, 2 H, CH_2N), 7.08 (d, J = 8.3 Hz, 1 H, 5'-H), 7.29 (dd, J = 8.3 Hz, J = 1.8 Hz, 1 H, 6'-H), 7.39 (d, J = 1.8 Hz, 1 H, 2'-H), 7.41 (d, J = 16.3 Hz, 1 H, CH=C*H*Py), 7.97 (d, J = 16.3 Hz, 1 H, C*H*=CHPy), 8.16 (d, J = 6.9 Hz, 2 H, 3-H, 5-H), 8.91 (d, J = 6.9 Hz, 2 H, 2-H, 6-H).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium hexafluorophosphate (**1e**). A solution of NH_4PF_6 (45 mg, 0.28 mmol) in MeOH (1 mL) was added to a solution of dye **1c** (102 mg, 0.23 mmol) in MeOH (2 mL) and the resulting mixture was cooled to 5°C in darkness. The precipitate thus formed was filtered, washed with cold MeOH (2 × 1 mL) and dried in air to give dye **1e** (80 mg, yield 84%) as a yellow powder, mp 242–244°C. Calcd. for $C_{17}H_{20}F_6NO_2P$: C 49.16, H 4.85, N 3.37. Found: C 49.06, H 4.84, N 3.29%. ^{1}H NMR: δ = 1.53 (t, J = 7.3 Hz, 3 H, *Me*CH_2), 3.83 (s, 3 H, 4'-MeO), 3.85 (s, 3 H, 3'-MeO), 4.51 (q, J = 7.3 Hz, 2 H, CH_2N), 7.08 (d, J = 8.3 Hz, 1 H, 5'-H), 7.30 (dd, J = 8.3 Hz, J = 1.6 Hz, 1 H, 6'-H), 7.38 (br.s, 1 H,

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2'-H), 7.40 (d, J = 16.3 Hz, 1 H, CH=C*H*Py), 7.96 (d, J = 16.3 Hz, 1 H, C*H*=CHPy), 8.16 (d, J = 6.7 Hz, 2 H, 3-H, 5-H), 8.90 (d, J = 6.7 Hz, 2 H, 2-H, 6-H).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium picrate (**1f**). A solution of sodium picrate (42 mg, 0.17 mmol) in MeOH (1.5 mL) was added to a solution of dye **1c** (67 mg, 0.15 mmol) in MeOH (1 mL) and the resulting mixture was cooled to 5°C in darkness. The precipitate thus formed was filtered, washed with cold MeOH (2 × 1 mL) and dried in air to give dye **1f** (57 mg, yield 75%) as a yellow powder, mp 149–150°C. Calcd. for $C_{23}H_{22}N_4O_9$: C 55.42, H 4.45, N 11.24. Found: C 55.64, H 4.41, N 11.15%. ^{1}H NMR: δ = 1.53 (t, J = 7.3 Hz, 3 H, *Me*CH$_2$), 3.83 (s, 3 H, 4'-MeO), 3.85 (s, 3 H, 3'-MeO), 4.51 (q, J = 7.3 Hz, 2 H, CH$_2$N), 7.08 (d, J = 8.4 Hz, 1 H, 5'-H), 7.30 (dd, J = 8.4 Hz, J = 1.8 Hz, 1 H, 6'-H), 7.38 (br.s, 1 H, 2'-H), 7.40 (d, J = 16.3 Hz, 1 H, CH=C*H*Py), 7.96 (d, J = 16.3 Hz, 1 H, C*H*=CHPy), 8.16 (d, J = 6.8 Hz, 2 H, 3-H, 5-H), 8.58 (s, 2 H, 3"-H, 5"-H), 8.90 (d, J = 6.8 Hz, 2 H, 2-H, 6-H).

4-[(*E*)-2-(3,4-Dimethoxyphenyl)-1-ethenyl]-1-ethylpyridinium tetraphenylborate (**1g**). A solution of sodium tetraphenylborate (146 mg, 0.43 mmol) in MeOH (2.5 mL) was added to a solution of dye **1c** (157 mg, 0.36 mmol) in MeOH (5 mL) and the resulting mixture was cooled to –10 °C in darkness. The precipitate thus formed was filtered, washed with cold MeOH (2 × 2 mL) and dried in air to give dye **1g** (206 mg, yield 98%) as a yellow powder, mp 195–197 °C. Calcd. for $C_{41}H_{40}BNO_2$: C 83.53, H 6.84, N 2.38. Found: C 83.57, H 6.70, N 2.24%. ^{1}H NMR: δ = 1.52 (t, J = 7.3 Hz, 3 H, *Me*CH$_2$), 3.83 (s, 3 H, 4'-MeO), 3.85 (s, 3 H, 3'-MeO), 4.50 (q, J = 7.3 Hz, 2 H, CH$_2$N), 6.78 (t, J = 7.2 Hz, 4 H, 4 4"-H), 6.92 (t, J = 7.4 Hz, 8 H, 4 3"-H, 4 5"-H), 7.08 (d, J = 8.4 Hz, 1 H, 5'-H), 7.17 (m, 8 H, 4 2"-H, 4 6"-H), 7.29 (dd, J = 8.4 Hz, J = 1.8 Hz, 1 H, 6'-H), 7.38 (d, J = 1.8 Hz, 1 H, 2'-H), 7.40 (d, J = 16.3 Hz, 1 H, CH=C*H*Py), 7.96 (d, J = 16.3 Hz, 1 H, C*H*=CHPy), 8.16 (d, J = 6.8 Hz, 2 H, 3-H, 5-H), 8.90 (d, J = 6.8 Hz, 2 H, 2-H, 6-H).

Synthesis of cyclobutane derivatives from dyes 1 (general procedure). A solution of dye **1c-g** (40 μmol) in MeCN (~ 0.5 mL) was concentrated in a 10-cm Petri dish to form a thin polycrystalline film of the corresponding compound. The sample was irradiated with unfiltered light using a 60 W incandescent lamp at a distance of 15 cm for 10–240 h. The resulting compounds were collected mechanically. The compositions of the products and the degree of conversion into cyclobutane derivatives were analyzed based on the ^{1}H NMR spectroscopy data (in DMSO-d$_6$) by comparing the integrated intensities of the signals for protons. The experimental data obtained at different exposure times are given in Table 1. In the cases when the degree of conversion was ≥95%, the characteristics of the resulting cyclobutane derivatives are given.

4,4'-[2-*c*,4-*t*-Bis(3,4-dimethoxyphenyl)cyclobutane-1-*r*,3-*t*-diyl]bis(1-ethylpyridinium) ditosylate (*rctt*-**2c**). Compound *rctt*-**2c** (11.4 mg, yield 65%) was obtained as a yellowish powder, mp 70–75°C. Calcd. for $C_{48}H_{54}N_2O_{10}S_2 \cdot 1.5H_2O$: C 63.35, H 6.31, N 3.08. Found: C 63.49, H 6.27, N 3.13%. ^{1}H NMR: δ = 1.41 (t, J = 7.3 Hz, 6 H, 2 *Me*CH$_2$), 2.29 (s, 6 H, 2 *Me*Ar), 3.65 (s, 6 H, 2 3'-MeO), 3.67 (s, 6 H, 2 4'-MeO), 4.49 (q, J = 7.3 Hz, 4 H, 2 CH$_2$N), 4.81 (dd, J = 9.8 Hz, J = 7.3 Hz, 2 H, 2 C*H*Ar), 4.90 (dd, J = 9.8 Hz, J = 7.3 Hz, 2 H, 2 C*H*Py), 6.77 (s, 4 H, 2 5'-H, 2 6'-H), 6.80 (s, 2 H, 2 2'-H), 7.11 (d, J = 8.0 Hz, 4 H, 2 3"-H, 2 5"-H), 7. 47 (d, J = 8.0 Hz, 4 H, 2 2"-H, 2 6"-H), 7.95 (d, J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.88 (d, J = 6.7 Hz, 4 H, 2 2-H, 2 6-H).

4,4'-[2-*c*,4-*t*-Bis(3,4-dimethoxyphenyl)cyclobutane-1-*r*,3-*t*-diyl]bis(1-ethylpyridinium) di(tetrafluoroborate) (*rctt*-**2d**). Compound *rctt*-**2d** (11.6 mg, yield 85%) was obtained as a slightly yellowish powder, mp 194–196°C. Calcd. for $C_{34}H_{40}B_2F_8N_2O_4$: C 57.17, H 5.64, N 3.92. Found: C 57.31, H 5.69, N 3.98%. ^{1}H NMR: δ = 1.42 (t, J = 7.3 Hz, 6 H, 2 *Me*CH$_2$), 3.65 (s, 6 H, 2 3'-MeO), 3.67 (s, 6 H, 2 4'-MeO), 4.49 (q, J = 7.3 Hz, 4 H, 2 CH$_2$N), 4.81 (dd, J = 9.6 Hz, J = 7.4 Hz, 2 H, 2 C*H*Ar), 4.89 (dd, J = 9.6 Hz, J = 7.4 Hz, 2 H, 2 C*H*Py), 6.77 (s, 4 H, 2 5'-H, 2 6'-H), 6.80 (s, 2 H, 2 2'-H), 7.95 (d, J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.88 (d, J = 6.7 Hz, 4 H, 2 2-H, 2 6-H).

4,4'-[2-*c*,4-*t*-Bis(3,4-dimethoxyphenyl)cyclobutane-1-*r*,3-*t*-diyl]bis(1-ethylpyridinium) di(hexafluorophosphate) (*rctt*-**2e**). Compound *rctt*-**2e** (15.1 mg, yield 90%) was obtained as a yellowish powder, mp 225–230°C. Calcd. for $C_{34}H_{40}F_{12}N_2O_4P_2$: C 49.16, H 4.85, N 3.37. Found: C 49.09, H 4.86, N 3.35%. ^{1}H NMR: δ = 1.42 (t, J = 7.3 Hz, 6 H, 2 *Me*CH$_2$), 3.65 (s, 6 H, 2 3'-MeO), 3.67 (s, 6 H, 2 4'-MeO), 4.49 (q, J = 7.3 Hz, 4 H, 2 CH$_2$N), 4.81 (dd, J = 9.7 Hz, J = 8.3 Hz, 2 H, 2 C*H*Ar), 4.89 (dd, J = 9.7 Hz, J = 8.3 Hz, 2 H, 2 C*H*Py), 6.77 (s, 4 H, 2 5'-H, 2 6'-H), 6.80 (s, 2 H, 2 2'-H), 7.95 (d, J = 6.7 Hz, 4 H, 2 3-H, 2 5-H), 8.88 (d, J = 6.7 Hz, 4 H, 2 2-H, 2 6-H).

Photolysis of thin films of dye 1d and cyclobutane *rctt*-2d. A solution of dye **1d** (1.7 mg, 5 μmol) in MeCN (0.1 mL) was concentrated in a Petri dish to form a thin polycrystalline film of this dye (spot diameter ~ 2 cm). The sample was irradiated with the light from a L8253 xenon lamp (Hamamatsu, maximum power, ZhS10 light filter (transmission > 390 nm), distance to the light source 10 cm) for 1 h. A half of the film was collected mechanically and then analyzed by ^{1}H NMR method (in DMSO-d$_6$), which showed full conversion into cyclobutane derivative *rctt*-**2d**. The residual film consisting of *rctt*-**2d** was irradiated for 2 h in the same conditions but using a set of ZhS3 and UFS5 light filters (transmission 280–340 nm). By comparing the integrated intensities of the signals for protons, analysis of the ^{1}H NMR spectroscopy data of this film (as a solution in DMSO-d$_6$) revealed 10% conversion into initial dye **1d**. Fragments of these ^{1}H NMR spectra are shown in Fig. 1.

X-Ray diffractometry

Single crystals of compounds **1c-g**, **2d**, and **4d** were subjected to X-ray single crystal measurements at a Bruker CCD SMART diffractometer (SMART-6K for **1c-e,g** and **1f**·0.5C$_6$H$_6$, SMART-1K for **2d** and SMART-APEX-II for **4d**) using graphite monochromatized MoK$_\alpha$ radiation (wavelength 0.71073 Å) and ω scan mode, and a Bruker PLATINUM135 CCD area diffractometer for **1f** using CuK$_\alpha$ radiation (wavelength 1.54178 Å) and φ-ω scan mode under a stream of

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cooled nitrogen gas. The reduction of experimental reflections was performed by SAINT program[56].

The structures were solved by direct methods and refined on F^2 by full-matrix least-squares in anisotropic approximation for non-hydrogen atoms using SHELXTL-Plus[57] and Olex-2[58] software. Positions of hydrogen atoms were calculated geometrically. In experiments for **1c**, **1d**, **1e**, **1f**, **1f**·0.5C_6H_6, **1g** and **4d** hydrogen atoms were refined using "riding" model and for **2d** hydrogen atoms were refined in the isotropic approximation. The BF_4^- anion in structures **1d**, **2d**, **4d** reveal a rotational disorder over three positions, with occupancies ratios discussed above. The PF_6^- anion in **1e** is disordered over two positions, with one common fluorine atom and close positions of the P atoms. The ratio of occupancies of two components of the disorder is equal to 0.77:0.23. The cation in **1e** reveals the "pedal" disorder with the ratio of occupancies equal to 0.61:0.39.

For compound **1f** (unsolvated form) only very small single crystals visible in microscope as bright points were obtained. Such single crystals gave only a few very weak X-ray reflections at Mo-radiation and rather weak ones at Cu-radiation. However, we have managed to collect a big number of rather weak experimental reflections in the near area on θ. The structure was successfully solved and refined in the anisotropic approximation, but with a rather high standard deviations in geometric parameters. However, taking into account that only packing motif of this crystal is required for our discussion and also special importance of this particular structure to establish a correlation between its packing motif and photochemical behaviour of the compound in thin polycrystalline films we included these data in this article.

A summary of the crystallographic data and structure determination parameters is provided in Table 2.

The experimental data for all structures are deposited with the Cambridge Crystallographic Data Centre (CCDC registration numbers are 969548 (**1c**·0.5MeCN·1.5H_2O), 859813 (**1d**), 969549 (**1e**), 969551 (**1f**), 969550 (**1f**·0.5C_6H_6), 969552 (**1g**), 859814 (**2d**), 859815 (**4d**)). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2, EZ, UK (fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk.

Table 2. X-ray structure determination summary.

Compound	**1c**·0.5MeCN·1.5 H_2O	**1e**	**1f**·0.5C_6H_6	**1f**	**1g**	**1d**	**2d**	**4d**
Empirical formula	$C_{25}H_{31.5}N_{1.5}O_{6.5}S$	$C_{17}H_{21}F_6NO_2P$	$C_{26}H_{25}N_4O_9$	$C_{23}H_{22}N_4O_9$	$C_{41}H_{40}BNO_2$	$C_{17}H_{20}BF_4NO_2$	$C_{34}H_{40}B_2F_8N_2O_4$	$C_{34}H_{40}B_2F_8N_2O_4$
M	489.08	415.31	537.50	498.45	589.55	357.15	714.30	714.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	15.6904(6)	7.106(2)	11.7370(10)	14.2243(10)	8.9861(4)	7.3589(3)	7.3008(3)	7.319(2)
b/Å	21.8223(8)	22.507(7)	26.623(2)	14.4190(9)	9.0343(4)	20.8300(9)	20.8807(6)	20.852(7)
c/Å	15.8024(6)	11.576(3)	8.2528(7)	22.4404(15)	40.1047(17)	11.2706(5)	11.3281(4)	11.302(4)
α/°	90	90	90	90	90	90	90	90
β/°	113.2560(10)	90.143(8)	109.714(3)	104.933(4)	90	91.727(13)	91.018(2)	91.835(5)
γ/°	90	90	90	90	90	90	90	90
V/Å^3	4971.1(3)	1851.5(10)	2427.6(4)	4447.1(5)	3255.8(2)	1726.84(13)	1725.95(11)	1723.9(9)
Z	8	4	4	8	4	4	2	2
F(000)	2080	860	1124	2080	1256	744	744	744
μ/mm^{-1}	0.174	0.219	0.113	0.991	0.072	0.117	0.117	0.117
T/K	120	120	120	100	120	120	120	150
Data collected	36155	14757	22602	14627	29245	12462	13052	17378
Unique data (R_{int})	10832 (0.1497)	4884 (0.0977)	5846 (0.1896)	4653 (0.0443)	9470 (0.0961)	4142 (0.0792)	4538 (0.0486)	4156 (0.0357)
θ range/°	1.55–27.00	0.90–28.99	1.84–26.5	3.22–53.37	2.03–30.00	1.96–28.00	1.95–29.00	2.05–28.00
No. of variables	634	409	356	649	409	237	318	302
R_1 [I>2σ(I)]	0.0712	0.0632	0.0808	0.0840	0.0732	0.0790	0.0572	0.0601
wR_2 (all data)	0.1754	0.1431	0.1869	0.2049	0.1130	0.1786	0.1336	0.1668
GOF	0.868	1.168	0.914	1.046	0.962	1.042	1.045	1.093
Δρmax, min/ e·Å^{-3}	0.629/-0.427	0.243/-0.302	0.464/-0.372	0.823/-0.363	0.405/-0.237	0.409/-0.323	0.489/-0.451	0.591/-0.372

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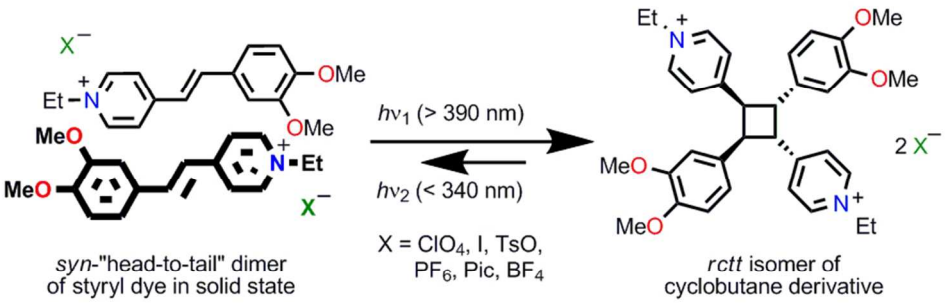

syn-"head-to-tail" dimer of styryl dye in solid state

rctt isomer of cyclobutane derivative

By X-ray diffractometry, [2+2]-photocycloaddition reaction and its back reaction were investigated in same single crystal without its degradation.

78x36mm (300 x 300 DPI)

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