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REVIEWS

Crystallographic Approach to the [2 + 2] Photocycloaddition Topochemical Reactions of Unsaturated Compounds with Single Crystal Retention

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Abstract—Based on the results of authors' studies, an approach to the analysis of [2 + 2] photocycloaddition (PCA) topochemical reactions of unsaturated compounds, occurring in a single crystal with either its retention or decomposition under exposure to visible light, has been developed. The main crystal packings, favorable for photoreaction in crystal, are revealed. Conditions for PCA reaction with single crystal retention are established. The factors increasing the probability of implementing crystal packing motifs that are favorable for this reaction (by chemical modification of structural units) are analyzed. The fact of extraordinary implementation of both direct and back (under UV irradiation) photoreactions in the same single crystal is explained.

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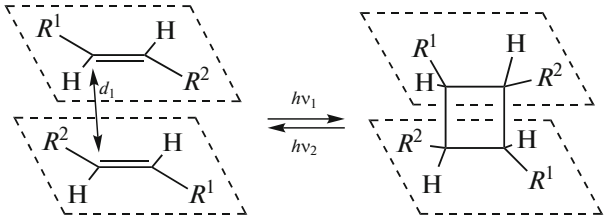
INTRODUCTION

Many ethylene compounds, being exposed to UV or visible light, can undergo a [2 + 2] photocycloaddition (PCA) reaction, which implies simultaneous formation of two C–C σ bonds and gives rise to cyclobutane derivatives:



The PCA reaction, which has been intensively studied since the time of its discovery at the beginning of the last century [1], remains to be of great interest for researchers [1–34].

This is one of the most important photochemical reactions, because it allows one to obtain substituted cyclobutane derivatives, which can hardly be obtained in some other way. The study of the PCA reaction is important for advancing in synthetic chemistry, as well as for understanding the chemical processes occurring in living nature and lying in the basis of such phenomena as photosynthesis, phototaxis, and eyesight. The PCA reaction can also be applied in materials science when developing new optical data recording and stor-

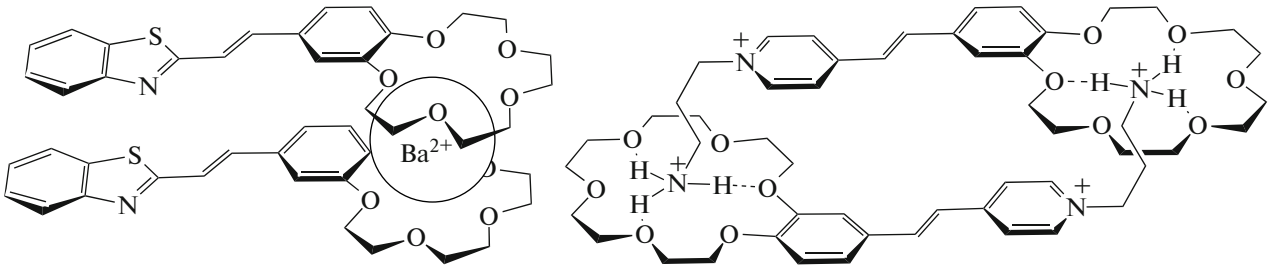


Fig. 1. Structure of two complexes of unsaturated molecules preorganized for PCA.

age systems. Some natural compounds with a cyclobutane fragment, which manifest pharmaceutical properties, can be synthesized using the PCA reaction [35].

The PCA reaction has a number of characteristic features. It belongs to thermally forbidden processes and is photochemically reversible: irradiation of a cyclobutane product by shorter wavelength radiation leads to its decomposition into initial components. Generally the PCA reaction is initiated by visible or near-UV light (340–430 nm), while the back reaction (*retro*-PCA) is initiated by shorter wavelength radiation (220–270 nm). The PCA reaction in solutions is generally neither regio- nor stereoselective.

It was found previously that a necessary condition for implementing a PCA reaction is a certain prearrangement of structural units, in which the C=C fragments of two molecules should be located parallel and spaced by a distance d no longer than ~4.2 Å in the solid phase (Schmidt criterion [1]) and up to 10 Å in a solution.

The PCA reaction may occur both in solutions and the solid phase, including single crystals. Therefore, it can be investigated using NMR ^{1}H-spectroscopy (in solutions) and X-ray diffraction (XRD) analysis (in single crystals). In many cases a single crystal is destroyed during PCA, being transformed into either an amorphous powder or the glassy state. However, in some cases this reaction occurs with single crystal retention. The factors determining the single crystal destruction or retention are not always clear, but in some cases they become evident from the analysis of the specific features of crystal packing in the initial compound.

The study of PCA ↔ *retro*-PCA processes in a single crystal that are not accompanied by its destruction are of particular interest, because a crystal makes it possible to perform the "direct and back" process a crystallographically unlimited number of times, which is important for developing optical data recording and storage systems.

In this review, we generalize the results of our X-ray diffraction studies of the PCA reaction occurring in a single crystal and analyze the possibility of its occurrence without crystal destruction.

1. CRYSTALLOCHEMICAL ANALYSIS OF THE STRUCTURES OF ETHYLENE COMPOUNDS CAPABLE OF PCA REACTION IN SINGLE CRYSTALS

1.1. Two Approaches to Studying the PCA Reaction

A task of top priority for implementing the PCA reaction is to form a priori a "preorganized dimer." There are two approaches for doing this.

The essence of the first is supramolecular design, i.e., the formation of conditions for the occurrence of a "preorganized dimer" in solution due to the ability of unsaturated molecules to be dimerized as a result of various interactions: ion-dipole interactions, formation of hydrogen bonds, etc. [36–41]. Examples of this approach are the systems shown in Fig. 1.

Supramolecular design implies introduction of either only a crown-ether fragment (on the left) or, additionally, a short alkyl chain, having a functional group on its end, such as, e.g., ammonioalkyl substituent at the N atom of the heterocyclic residue (on the right), into the initial molecule of unsaturated compound. Then either a dimer complex is formed in the solution due to the existence of two sets of hydrogen bonds (on the right) or a sandwich complex arises, when a large metal cation M^{2+} is introduced into solution, due to the ion-dipole interactions of M^{2+} with two crown-ether fragments (on the left). In these two cases the PCA reaction leads to the formation of different isomers of cyclobutane derivatives, because the dimer has different ("head-to-head" or "head-to-tail") organizations.

Another version of this approach is incorporation of a pair of ethylene molecules into the cavity of cavitand: cucurbituril, cyclodextrin, or calixarene [32–34, 42–47].

The second approach is *crystal engineering*. It is based on the suggestion that it is the crystal packing that preorganizes the initial unsaturated molecules in a way favorable for PCA. This approach can be used to study the solid-state PCA. In this context, one must answer the following questions:

(i) How many packing motifs in total can there be for planar unsaturated molecular systems and what type of crystal packing motifs is favorable for PCA?

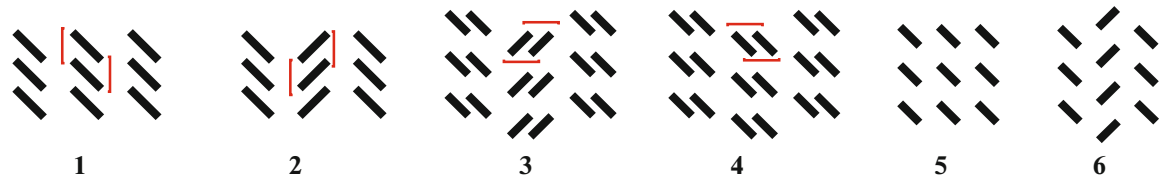


Fig. 2. Canonical types of crystal packings of planar conjugate unsaturated molecules; segments are lateral projections of these molecules, and parentheses indicate parallel dimer pairs.

(ii) Can one control the choice of a desired packing?

(iii) Can one control a prearrangement of molecules that would lead to different isomers of cyclobutane derivatives as a result of the PCA reaction?

(iv) What symmetry operations create different prearrangement versions?

Successful implementation of the second approach allows one to exclude the complex multistage synthesis, and thus investigate a much larger number of readily synthesized compounds; perform a systematic study of the topochemical processes; and, based on the knowledge obtained, try to carry out both the PCA reaction in a single crystal of cyclobutane derivative (under exposure to visible light) and the reverse reaction (*retro*-PCA) in the same crystal under UV irradiation. Note that the occurrence of both reactions in a single crystal has never been observed previously. Single crystals are favorable for carrying out successively direct and reverse photochemical reactions, because (1) crystal lattice keeps the components of both reactions in certain positions, as a result of which both reactions can occur in a crystal a crystallographically unlimited number of times and (2) any (even very small) single crystal can play a role of a finished device.

The idea of implementing topochemical control of PCA reaction in crystal and possibility of forming a cyclobutane derivative by arranging ethylene structural units in crystal in different ways was formulated even in 1984 [48]. Further development of this idea became possible only after 1995, because specifically that period is characterized by rapid development of the XRD method with simultaneous creation of an extensive structural database.

1.2. Possible Crystal Packings of Planar Conjugate Unsaturated Molecular Systems

In the first stage, we analyzed a large number of crystal packings of planar unsaturated molecules according to the Cambridge Structural Database (CSD) data [49]. As a result, six canonical structures characteristic of these compounds were established; they are presented in Fig. 2.

Here, **1** and **2** are, respectively, parallel-stacking and herringbone-stacking packings; **3** and **4** are packings of herringbone-dimer and parallel-dimer types; and **5** and **6** are of staircase and herringbone types. Packings **1**, **4**, **5** (as well as **2**, **3**, **6**) are genetically interrelated. Packing **5** (**6**) can be obtained from **1** (**2**) by shifting molecules in stacks in parallel planes until they cease to be mutually projected, and packing **4** (**3**) can be obtained from packing **1** (**2**) via a similar shift of not one molecule but a molecular pair.

Only packings of types **1**, **2**, **3**, and **4** can maintain a preorganized dimer pair. Packings **5** and **6** are inconsistent with the PCA reaction in crystal. The formation of packings **1**–**4** is controlled by weak directional π···π (stacking) interactions between conjugate unsaturated molecules, whereas the formation of packings **5** and **6** is due to the weak directional interactions of the C–H···π-system type [50]. The former interaction calls for a parallel or parallel-shifted molecular arrangement, whereas the necessary condition for the latter interaction is the T-shaped molecular arrangement or a parallel-shifted arrangement (up to the absence of mutual projecting of planar conjugate unsaturated molecules) (Fig. 3).

The use of molecules with dominating stacking interactions leads to the occurrence of stacking architecture, whereas the molecules with dominance of C–H···π-system interactions give rise to herringbone and staircase architectures. Since these two interactions have close energies, an insignificant modification of molecules with dominance of C–H···π-system interactions in a crystal, for example, introduction of a heterocycle instead of a benzene ring, or π substituents, may result in another crystal packing of modified molecules, in which stacking interactions begin to

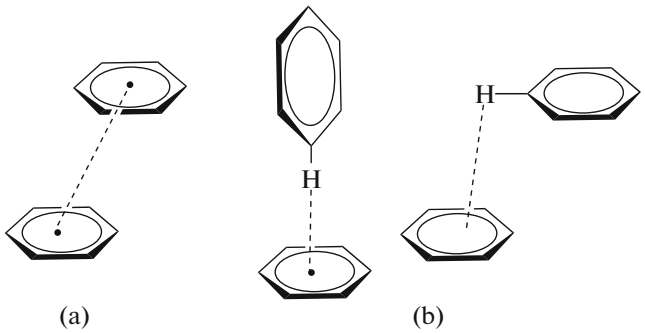


Fig. 3. (a) Geometry of weak directed stacking interactions and (b) the C–H···π-system.

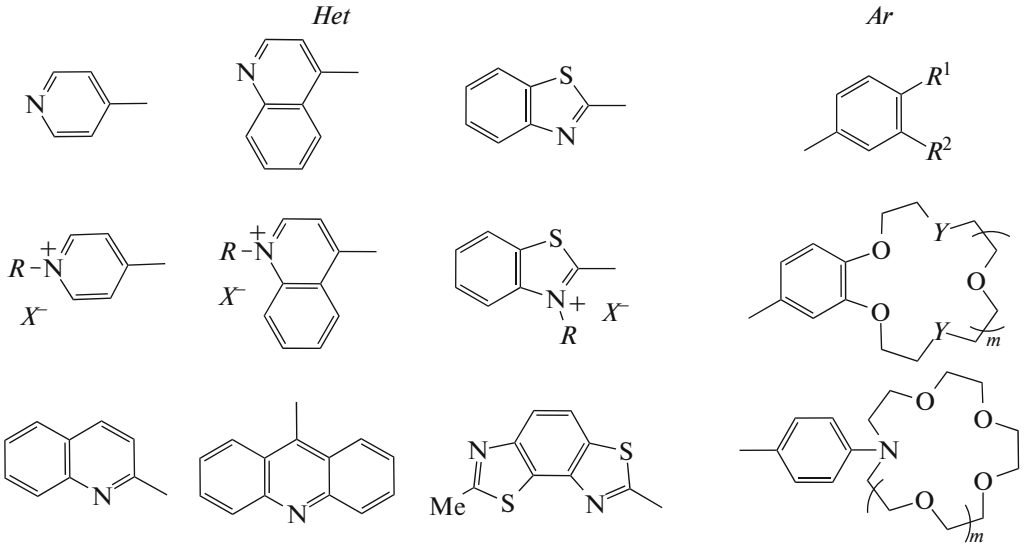


Fig. 4. Formulas of structural fragments of styryl dyes, styrylheterocycles, and counter ions of styryl dyes: $X = ClO_4$, I, Br, BF_4, PF_6, BPh_4, *Ts*O, *Pic*; $R = Alk$, $(CH_2)_nNH_3^+$, $(CH_2)_nSO_3^-$ (n = 2, 3, 6); R^1 and R^2 are different combinations of substituents H, OMe, SMe, NMe_2, Cl, NO_2, N^+Me_2Et; Y = O, S; m = 0–2.

dominate. Stacking-dimer architectures may arise when these two interactions have equal energies. Thus, the second approach may also include molecular design elements.

1.3. Choice of Molecular Systems for Carrying out a PCA Reaction in Crystal

A necessary condition for obtaining dimer pairs preorganized to PCA, with close position of ethylene fragments, is as follows: the geometric center of the conjugate fragment of unsaturated molecules should be approximately within the ethylene fragment. Then the maximum overlap of the π-systems of two molecules located in parallel planes (a circumstance important for PCA) will be implemented at a close arrangement of their ethylene fragments. This condition is satisfied by molecules of stilbenes *Ar*–CH=CH–*Ar* (ST), viologen vinylogues *R*–*Het*$^+$–CH=CH–*Het*$^+$–*R* 2X^- (VV), styryl dyes *R*–*Het*$^+$–CH=CH–*Ar* X^- (SD), neutral styrylheterocycles *Het*–CH=CH–*Ar* (SH), and butadienyl dyes *R*–*Het*$^+$–CH=CH–CH=CH–*Ar* X^- (**БК**) (*Het* is a nitrogen-containing heteroaromatic residue, *Ar* is an aryl residue, and *X* is a counter ion). The aforementioned compounds were investigated with various combinations of structural fragments (Fig. 4).

These compounds are relatively easy to synthesize in a wide assortment, and their spectral characteristics can easily be varied by changing the type of heterocyclic residue and the nature of substituents in the aryl residue. The chromophore of unsaturated compound decomposes during PCA, as a result of which the spectral characteristics of the material, including its color, significantly change; this is one of necessary properties of photoswitchable materials.

Unsaturated ST and VV compounds turned out to be unpromising from the point of view of PCA reaction feasibility in their crystals, because they are characterized by only staircase or herringbone packing motifs **5** and **6** (Fig. 2), where mutual projection of planar conjugate fragments is absent [51–58]. The situation with SD [42, 59–77], SH [67, 78–88], and BD [89–93] crystals is more favorable.

The crystal structures of non-solvated forms of SD and SH and their solvates with different small molecules were determined by XRD. The single crystals whose structures exhibited packings with mutual arrangement of structural units favorable for PCA were exposed to visible light, after which the PCA products (cyclobutane derivatives) formed in the same single crystals were analyzed using X-ray diffraction.

Practically only stacking packings (Fig. 2; **1**, **2**), which are mainly favorable for implementing PCA, manifest themselves in SD and BD crystals, whereas SH crystals exhibit other four packings; however, only two out of them (**3** and **4**) are favorable for PCA. Thus, the general problem of unpredictability of crystal packings of organic compounds in the case of SD, SH, and BD compounds is solved by choosing correctly the objects of study.

1.4. Possible Symmetry of Stacks of Conjugate Unsaturated Molecules

In most cases (~80%), centrosymmetric stack packing motifs with a mutual head-to-tail arrangement of asymmetrically substituted unsaturated mole-

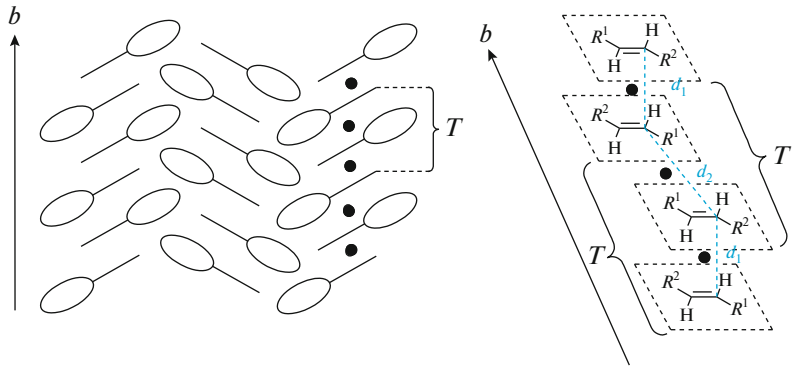


Fig. 5. Two ways to present the arrangement of molecular SD cations in crystals with a stacking architecture; cations in SD are shown as lines and ovals, *T* is the translation along the crystal axis, and the filled circles between cation planes are centers of symmetry.

cules (Fig. 5) are implemented in SD crystals with packings **1** and **2** (Fig. 2) [68, 69]. The double bonds of any two neighboring molecules are strictly antiparallel in this arrangement, a circumstance favorable for implementing PCA.

In the general case, the distances obey the relation $d_1 \neq d_2$ because two neighboring centers of symmetry belong to different crystallographic systems. Thus, the stack is initially divided into dimer pairs. If the condition $d_1 < 4.2$ Å $< d_2$ is satisfied, a PCA reaction may occur in a single crystal with its retention. If both distances are below 4.2 Å, the PCA reaction in a stack occurs most often statistically; i.e., not only between crystallographically equivalent pairs of structural units. This leads to breaking the general symmetry of crystal and its degradation, which manifests itself in either strong cracking of crystal or preservation of its shape and blaze but disappearance of the diffraction pattern and "extinction" in microscope polarized light.

Along with the centrosymmetric stacking packing motif, translationally related stacking packing motifs, in which unsaturated fragments are head-to-head arranged (Fig. 6), are formed in SD in approximately 15% cases [68–70].

Here, ethylene fragments of any two neighboring molecules have strictly parallel orientations, and all distances *d* are identical. Realization of one PCA event will lead to local symmetry breaking and formation of a defect. The propagation of PCA reaction throughout the crystal should be accompanied by breaking its general symmetry for one more reason: the pairs in which PCA may occur arise statistically over stack, which should inevitably lead to the occurrence of "superfluous" unpaired structural units. Therefore, the PCA reaction with single crystal retention in structures with translationally related stacks cannot be implemented in principle. Another forbidding factor is that the distances *d* generally exceed 5 Å, because unsaturated fragments are significantly shifted in parallel planes, which is unfavorable for PCA. These single crystals are stable against irradiation.

The existence of stacking structural motifs in crystal does not contradict to other symmetry operations. One must consider them in order to determine possible cyclobutane isomers formed as a result of PCA reaction.

Possible operations of this type are the twofold symmetry axis *2* and mirror reflection plane *m*. Note that both symmetry elements do not require strict parallelity of structural units; however, implementation of the PCA reaction may require violation of ethylene fragment parallelity up to ~25°. The action of both these symmetry elements, as well as the center of symmetry, leads to partition of stacks into dimer pairs.

Let us consider the stacks formed by the action of mirror-reflection plane (Fig. 7).

Identically charged fragments of structural units are closely spaced in these stacks. This arrangement cannot be implemented during nucleation and crystal growth because of the electrostatic repulsion of similarly charged fragments of molecules. However, the symmetry *m* of dimer pairs may occur in compounds

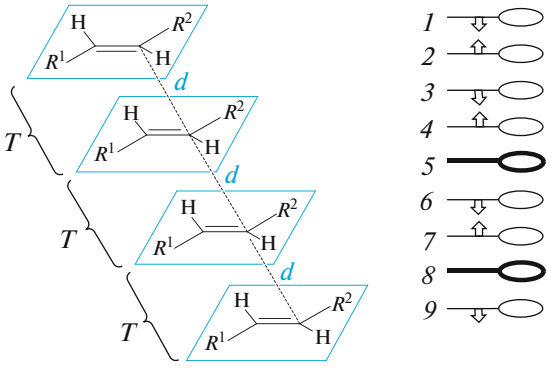


Fig. 6. Translationally linked packing motif; the "superfluous" structural units arising during PCA in a stack are shown by bold lines (on the right).

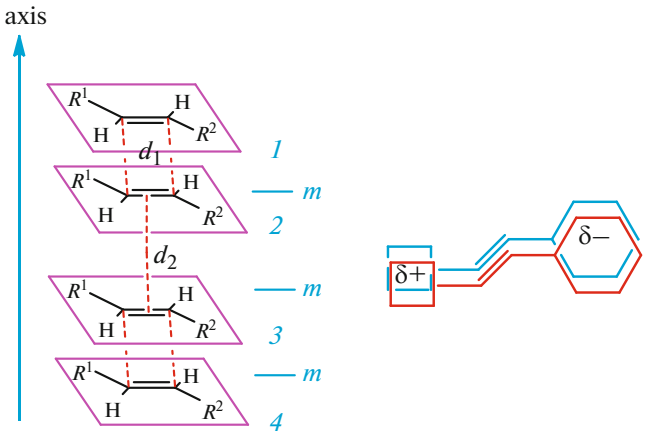


Fig. 7. Schematic diagram of a stack formed via mirror-reflection planes *m*; mutual projecting of pair of structural units is presented on the right.

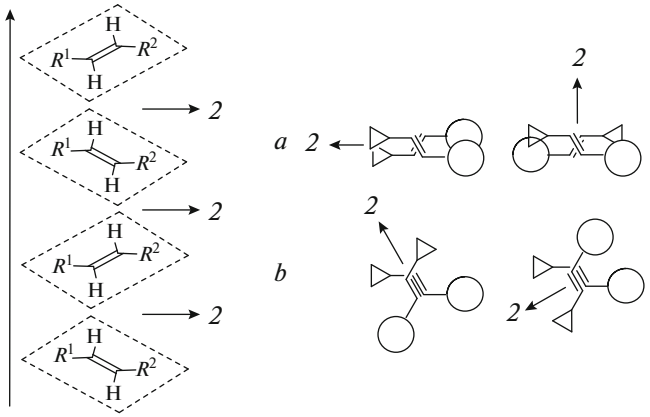


Fig. 8. Stacks of structural units formed by the action of a twofold axis; mutual projecting of structural units in pairs differently oriented with respect to axis *2* is shown on the right.

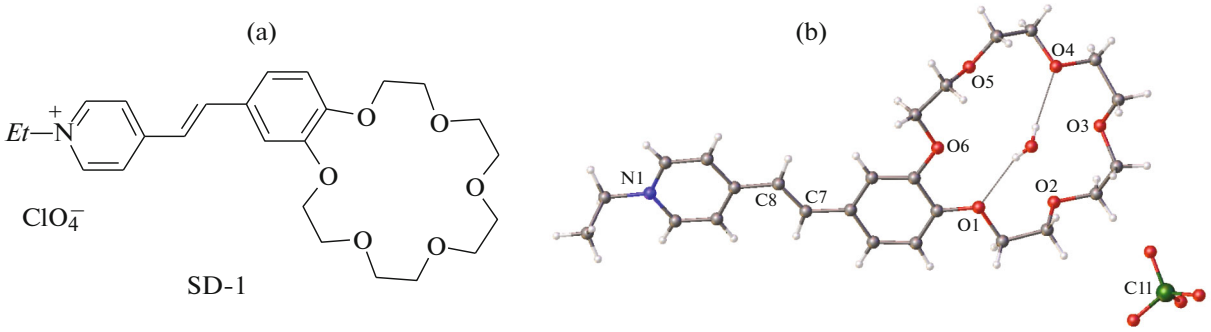


Fig. 9. (a) Structural formula and (b) structure of independent formula units of **SD-1**.

obtained as a result of molecular design due to the interactions of different kinds that link structural units into dimers: argentophilic interactions, hydrogen bonds, and C–H···π interactions [94–98].

Let us consider the stacks in which structural units are linked by twofold axes (Fig. 8).

In the general case, this symmetry is indicative of either crossed (case *a* in Fig. 8) or parallel (case *b*) arrangement of ethylene fragments. The crossed arrangement is not optimal for the PCA occurrence, despite the fact that this arrangement provides good overlap of the π systems of structural units. However, since the symmetry axis *2* does not restrict the mutual twist of two neighboring ethylene fragments in approximately parallel planes, it may be almost completely absent (case *b*). However, under these conditions, the π overlap of conjugate fragments of structural units is reduced to overlap of only their ethylene fragments.

1.5. Factors Affecting the PCA Feasibility in Crystals

The following approaches were used to determine the factors affecting the feasibility of PCA reaction in crystal without its destruction: (1) variation in the dye anion; (2) cocrystallization of SD and SH with small organic molecules, whose conformational and positional mobility compensates for the internal stress arising in the crystal as a result of large atomic displacements during PCA; and (3) introduction of a conformationally flexible fragment into the composition of unsaturated molecule.

The crystal structure of bright yellow crown-containing **SD-1** (Fig. 9) has a stacking packing motif (Fig. 10) of type **2** (see scheme in Fig. 2) [65].

The organic cations in a stack, related by centers of symmetry, are head-to-tail arranged. Cations *A* and *B* (as well as *C* and *D*) of the central stack are projected onto each other along the entire conjugate chain, and the distance d_1 between their ethylene fragments is 3.55 Å; i.e., it satisfies the PCA feasibility condition.

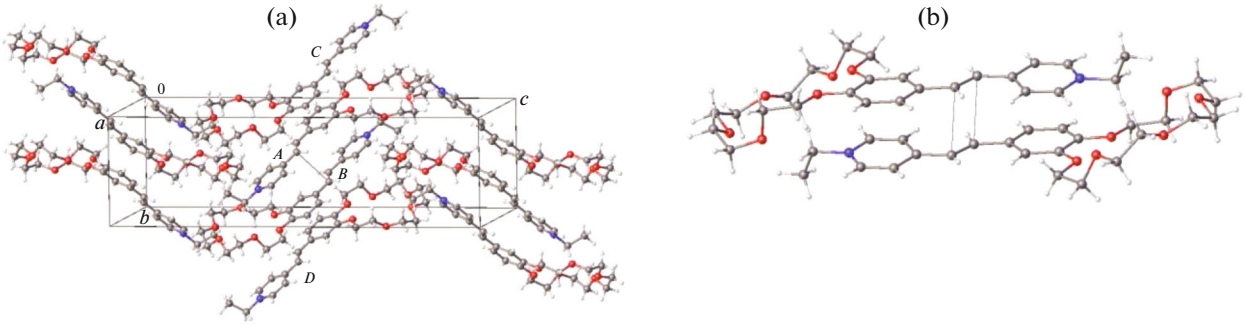


Fig. 10. (a) Stacking crystal packing of **SD-1** and (b) and a dimer pair of *A* and *B* cations.

Neighboring cation pairs *A*–*C* and *B*–*D* are projected onto each other only along the aryl residues, and the distance d_2 between ethylene fragments in them is 6.61 Å (cation sequence in the *C*–*A*–*B*–*D* stack). Thus, the cation stack is divided into dimer pairs, preorganized for PCA.

A 24-h exposure of a **SD-1** single crystal (analyzed previously on a diffractometer) to visible light is accompanied by a change in its color (from bright to pale yellow) and transformation of **SD-1** into a cyclobutane derivative (Fig. 11) [65].

A stacking dimer pair of the initial compound (Fig. 12) is surrounded directly by rotationally mobile perchlorate anions and flexible crown-ether fragments, which form a mobile shell, capable of compensating for large atomic displacements in crystal during PCA, thus preventing the crystal from destruction.

A superposition of the independent part of the unit cell of the crystal under study before and after irradiation shows (Fig. 13) the absence of any significant changes in the crystal space volume per structural unit due to the PCA.

During the photoreaction the central parts of **SD-1** molecular cations approach each other to form two σ bonds between the carbon atoms of ethylene groups. This approach is not impeded by crystal packing, because it is directed into the dimer pair volume. The PCA gives rise to changes in the conformation of flexible crown-ether fragment, as well as in the position and orientation of perchlorate anions, caused by the "adjustment" of mobile structural elements to the changes in the shape of newly formed dication of cyclobutane derivative.

Thus, a necessary condition for implementing a PCA reaction in a crystal without its destruction is the presence of a soft mobile shell around the "preorganized" dimer.

A PCA reaction of the single crystal–single crystal type was also observed for the SD crystals having no crown-ether fragments but containing additional solvate molecules, which can play the role of a mobile shell. Cocrystallization of a styryl dye of the 4-pyridine series *Et*–Py^+–CH=CH–C_6H_4–OMe ClO_4^- (**SD-2**) with small aromatic molecules (Fig. 14) led to the corresponding crystal solvates in eight cases and to nonsolvated forms of **SD-2** (in two crystalline modifications: monoclinic and triclinic) in other cases [70].

Irradiation of non-solvated modifications, which form a stacking crystal packing of type **2** (Fig. 2), is accompanied by cracking of the initial crystal into powder. The reason is the violation of the condition $d_1 < 4.2$ Å $< d_2$ or the "rigidity" of the crystalline environment of dimer pairs, which impedes the mutual adjustment of molecular shapes in order to reduce the internal stress in crystal during PCA.

The thus obtained solvated crystals were subjected to X-ray diffraction analysis and subsequent exposure to visible light. Crystal solvates are characterized by alternating closely packed layers, formed by stacks of molecular cations, and loose layers, formed by anions and solvate molecules. The cation stacks are head-to-tail arranged. The role of the "loose" layers is as follows: due to the mobility of the components forming them, they act as a "soft" mobile shell.

SD-2 crystal solvates with pyrocatechol, resorcin, 1,4-hydroquinone, and 4-aminophenol are characterized by the formation of centrosymmetrically linked stacks, in which both distances *d* are smaller than 4.2 Å. The PCA reaction occurs in them, but it is accompanied by single crystal degradation. In all these

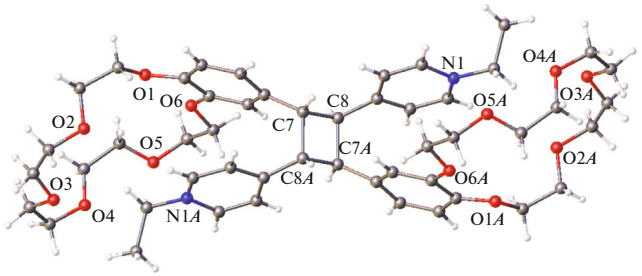


Fig. 11. Cyclobutane dication formed in an **SD-1** single crystal upon its illumination.

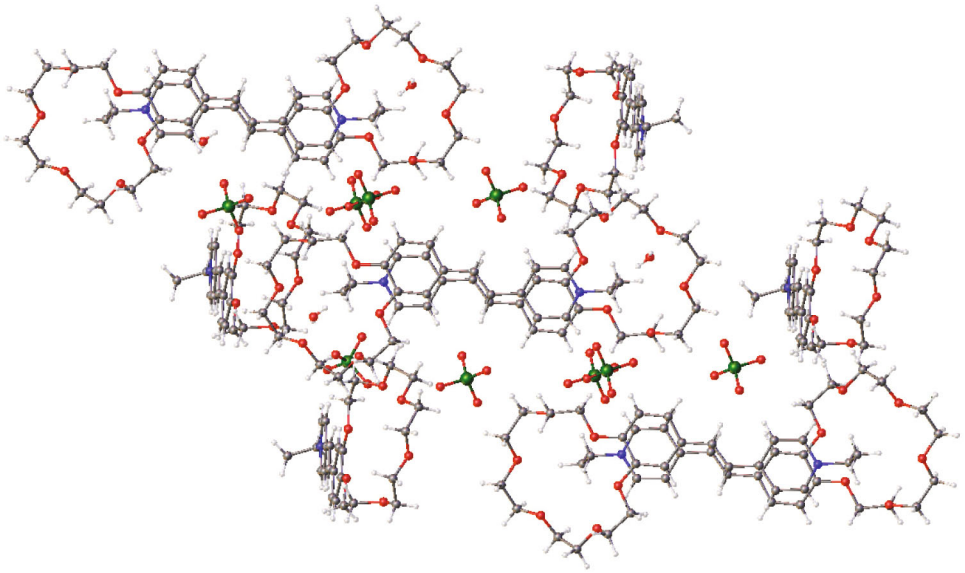


Fig. 12. Crystalline environment of a stacking dimer pair in an **SD-1** crystal.

cases a sample under study was significantly bleached, but its external shape and blaze retained. However, the sample lost its diffraction pattern, having transformed from crystal into glass [70].

In the **SD-2** crystal solvate with 1,5-dihydroxynaphthalene and acetonitrile, where centrosymmetrically linked stacks also are formed and the condition $d_1 < 4.2$ Å $< d_2$ is satisfied, the PCA reaction occurs with single crystal retention [70].

Translationally linked stacks are formed in the **SD-2** crystal solvate with benzene (Fig. 6); therefore, this solvate is stable against irradiation.

In **SD-2** crystal solvates with 2,6- and 2,7-dihydroxynaphthalenes [70], the PCA reaction occurs without single crystal destruction, although both neighboring distances in a stack are smaller than 4.2 Å. The rule $d_1 < 4.2$ Å $< d_2$ is violated because crystallographically independent molecules alternate in a stack. Therefore, the PCA reaction in these solvates does not break the general symmetry of crystal, and, for this reason, is not accompanied by its degradation, although leads to the formation of a significantly disordered crystal. In particular, the latter crystal solvate contains three crystallographically independent dye formula units (*A*1, *A*2, *A*3), which are laid into a pseudo-centrosymmetric stack (...–*A*1–*A*2–*A*3–*A*1–*A*2–*A*3–...) with distances d_1, d_2, and d_3 (3.40, 3.38, and 3.39 Å, respectively) smaller than 4.2 Å; in other words, they all satisfy the geometric condition for PCA. In this context, the PCA reaction gives rise to a significantly disordered structure (Fig. 15).

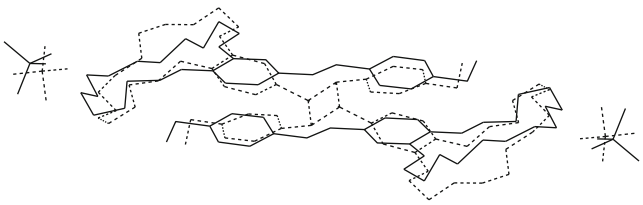


Fig. 13. Superposition of structural units in crystals of **SD-1** and its photoproduct (solid and dashed lines show, respectively, a dimer of the initial compound and the PCA reaction product).

The central **SD-2** molecule in a stack is involved in a PCA reaction with both the "upper" and "lower" molecules. As a result, disorder arises due to the (i) presence of the initial components and reaction products in the same crystal and (ii) statistical realization of the reaction for the central cation in a triad. The PCA reactions between the *A*1–*A*2–*A*3 triads in a stack (i.e., between the structural units *A*3–*A*1) is absent because their ethylene bonds are crossed.

We investigated the PCA reaction in crystalline forms of styryl dye **SD-3** of the 2-benzothiazole series (Fig. 16): its co-crystallizates with 1,4-hydroquinone (**HQ**) of the **SD-3** · 0.5HQ · H_2O or **SD-3** · HQ composition [99].

The tosylate-anion in a crystal of non-solvated form of **SD-3** exhibits a rotational disorder of the SO_3^- substituent over three main positions and a number of intermediate ones, whose existence is supported by high thermal parameters of oxygen atoms. **SD-3** cations form centrosymmetrically linked stacks, separated by layers of tosylate anions, whose planes are oriented almost perpendicular to the cation planes (Fig. 17). The distances d_1 and d_2 in a stack satisfy the PCA feasibility condition (Fig. 18).

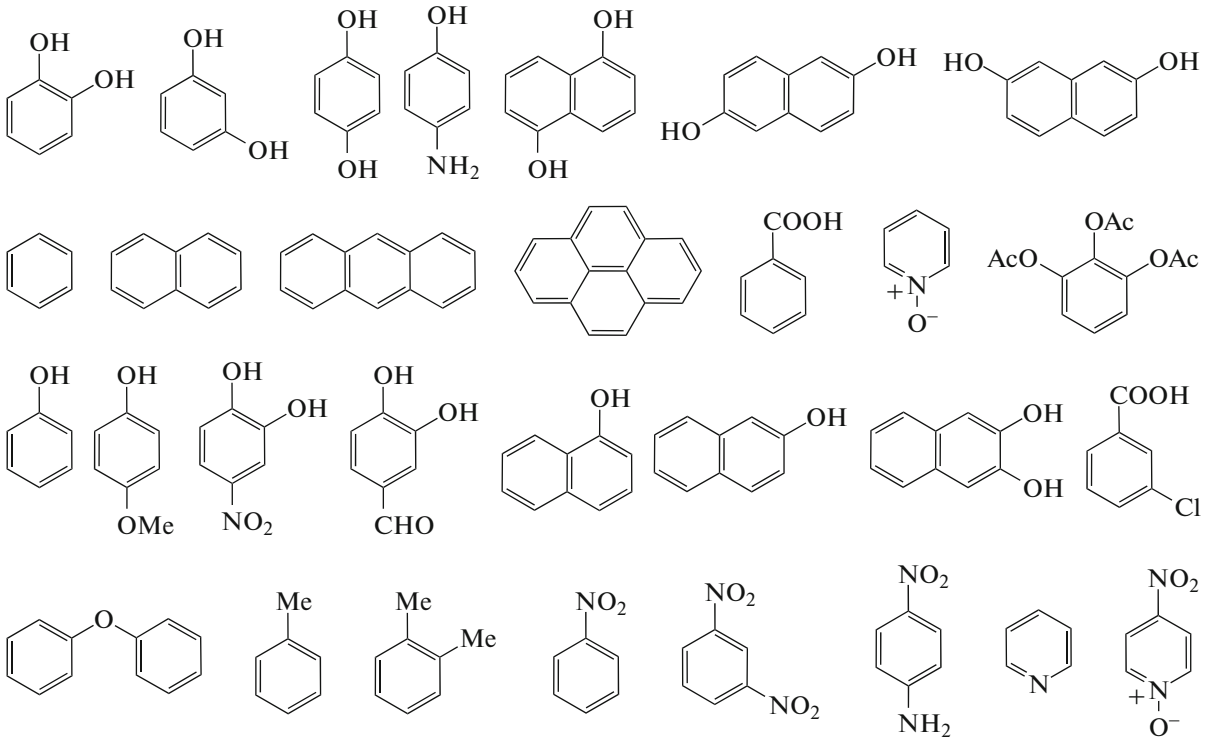


Fig. 14. Aromatic molecules used to crystallize **SD-2**.

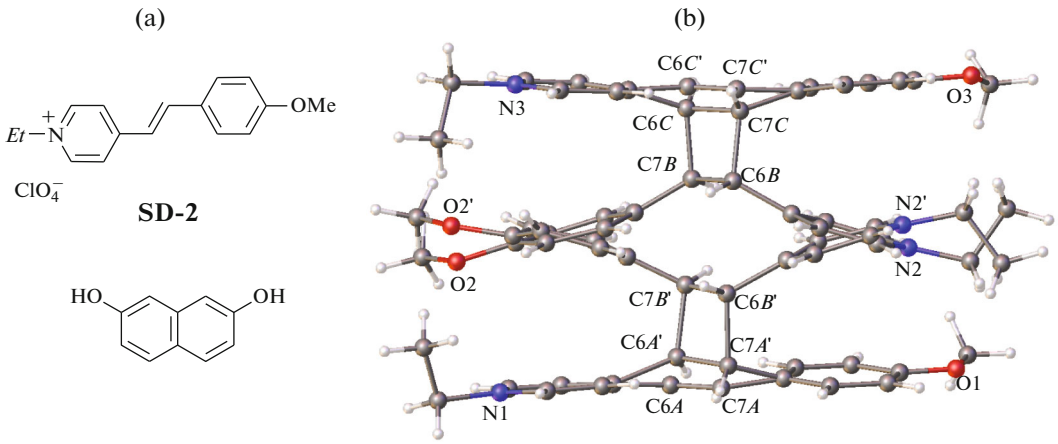


Fig. 15. (a) Formula of **SD-2** and (b) the disordered structure of the cyclobutane dication formed as a result of illumination of **SD-2** crystal solvate with 2,7-dihydroxynaphthalene.

However, the distance d_1 = 3.53 Å in one pair of cations is much shorter than the distance d_2 = 4.05 Å in the other cation pair. In addition, the geometric conditions for projecting ethylene fragments onto each other, i.e., the overlap of their π systems and, correspondingly, the efficiency of the π···π-interaction in nonequivalent cation pairs, are different (Fig. 19).

The mutual projecting is fairly efficient in the left cation pair, where the distance d_1 = 3.53 Å is shorter, but is much worse in the right pair. In addition, the ethyl

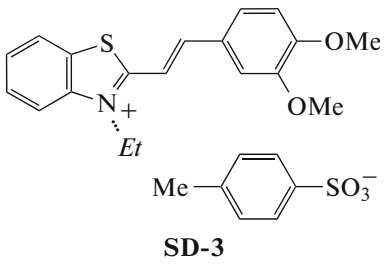


Fig. 16. Formula of **SD-3.**

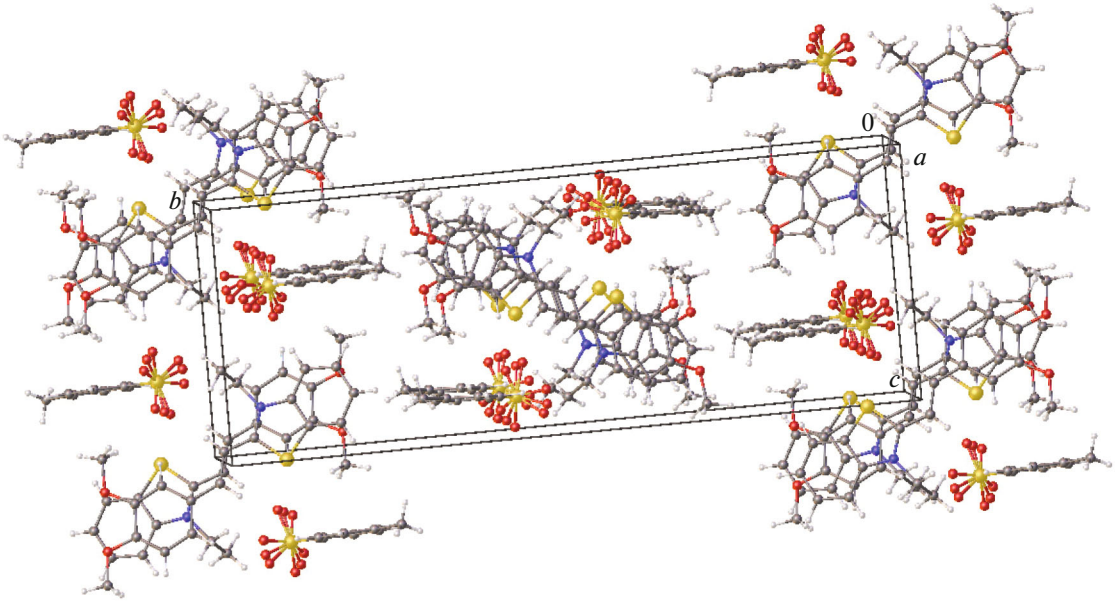


Fig. 17. Fragment of crystal packing of **SD-3**.

substituents at nitrogen atoms in the cation pair with a larger distance d_2 (on the right) are directed inwards the pair, a circumstance that should hinder the cation approach during PCA, whereas in the second pair these substituents are oriented outwards (Fig. 18).

Irradiation of this single crystal induces a PCA reaction in it with preservation of crystallinity (Fig. 20).

Thus, the two latter structures demonstrate different cases of implementing PCA with single crystal retention when the condition $d_1 < 4.2$ Å $< d_2$ is not satisfied.

The crystal solvate **SD-3** · 0.5HQ · H_2O, which contains a water molecule as an additional packing block, has similar structural features. It exhibits centrosymmetrically related stacks of cations, separated by layers filled with tosylate anions, as well as with HQ and water molecules. A radical difference between the packings of **SD-3** and its solvate is that the solvate molecules of HQ and water that are present in the **SD-3** · 0.5HQ · H_2O crystal form OH···OS hydrogen bonds with neighboring tosylate anions. Therefore, the rotational motion of the SO_3^- anion group in the crystal is hindered: no disorder was found for it.

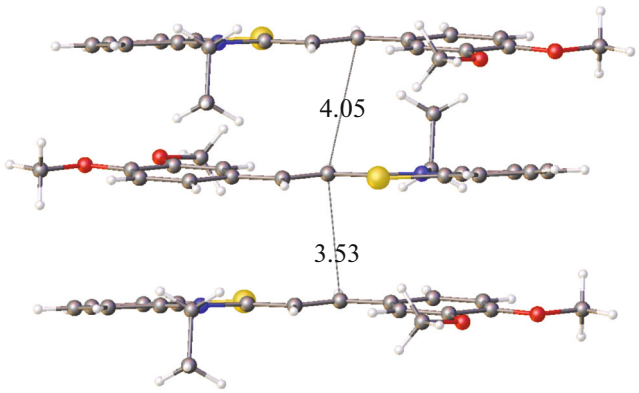


Fig. 18. Fragment of a cation stack in **SD-3** · HQ (distances are indicated in Å).

To initiate a PCA reaction in this crystal, it was necessary to irradiate it for a week, although the formation of cyclobutane product in crystals of non-solvated form of **SD-3** occurred 5 h after the irradiation. Moreover, the reaction was incomplete (only 80%) even under long-term (1 month) subsequent irradiation. Thus, an increase in the structural "rigidity" of the stack environment due to the system of weak directional interactions leads to retardation of the PCA reaction in the single crystal.

Until now, we have considered the cases of formation of centrosymmetrically linked stacks of ethylene structural units. It was mentioned that translationally linked stacks are implemented fairly rarely in crystals and that the PCA reaction in these stacks cannot occur without single crystal destruction. Indeed, all investigated styryl compounds with this type stack organization were found to be stable against illumination. The stacks organized due to the action of twofold axis are also rare. One such case was observed in **SD-4** crystals [69] (Fig. 21).

The substituent of the benzene ring is highly disordered. The introduction of a bulky substituent into the benzene ring made impossible realization of way *a* of mutual projecting, and, therefore, way *b* was implemented (Fig. 8). The structure of the "preorganized dimer" of **SD-4** is shown in Fig. 22.

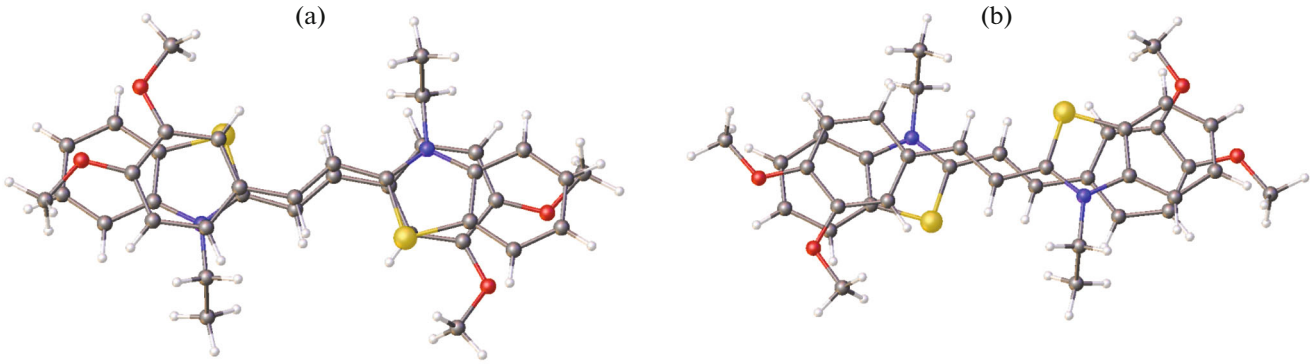


Fig. 19. Mutual projecting of pairs of neighboring cations in a stack in **SD-3**; projections with (a) a short distance d_1 and (b) a long distance d_2.

The ethylene fragments of the "preorganized dimer" are almost parallel, and they are twisted by 24°. The absence of strict parallelity of ethylene fragments does not impede the implementation of PCA in single crystal, which was fulfilled by 34% and led to the formation of another cyclobutane isomer (Fig. 23).

1.6. Influence of the Anion Nature on the PCA Feasibility for Styryl Dyes

The influence of the anion nature on the feasibility of PCA reaction in non-solvated single crystals was investigated for a series of **SD-5** dyes (Fig. 24) [73].

Large organic anions turned out to be of little use for PCA because of the implementation of **SD-5** crystal motifs different from types **1** and **2** (Fig. 2). A centrosymmetric stacking packing motif was established for the **SD-5** crystals with rotational or translational mobile anions ClO_4^-, I^-, PF_6^-, and BF_4^-. The ClO_4^-, PF_6^-, and BF_4^- anions exhibit rotational disorder. The PCA reaction occurs in all these compounds. However, its occurrence with single crystal retention turned out to be possible in only the crystals containing BF_4^- anions (Fig. 25).

The BF_4^- anion in the reaction products, as well as in the initial compound, is disordered over three sites; however, the site occupancy ratios in the initial **SD-5** and in the photoproduct are different: 0.5 : 0.3 : 0.2 and 0.6 : 0.2 : 0.2, respectively. This difference is indicative of rotational dynamics of anion during PCA. Note that, in the **SD-5** crystal with BF_4^- anion, the mobility of only anion turned out to be sufficient for implementing the reaction with single crystal retention; in this case, it was not necessary to include an additional building block in the form of a solvate molecule into the packing.

Note that the PCA reaction in **SD-5** with tetrafluoroborate anion turned out to be the most rapid among the investigated reactions. The transformation of the initial compound into a cyclobutane product manifests itself even 20 min after the onset of crystal observation under a microscope as very rapid crystal bleaching (changing from bright yellow to colorless). A complete transformation into the PCA product occurred after 2-h illumination.

1.7. Polymorphism of Styryl Dyes and PCA Reactions

A study of the PCA reaction in polycrystalline films of **SD-6** dye (Fig. 26) by ^{1}H NMR spectroscopy showed the absence of PCA reaction [77].

Crystallization of this compound provided single crystals of different habits (*a*, *b*, and *c*) with different unit cells. The *a* modification is most widespread, and only few crystals are presented by types *b* and *c*. First, crystals of type *a* arose in the form of shapeless plates, and only long-term exposure yielded (in small numbers) well-faceted crystals of types *b* and *c*.

Crystals of type *a*, as well as polycrystalline films of **SD-6** dye, are stable against irradiation, whereas the PCA reaction in *b* and *c* crystals exposed to light occurs completely. An X-ray diffraction analysis revealed that centrosymmetrically linked stacks, favorable for PCA, are formed in all three crystals. The distances d_1 and d_2 in them (3.54–3.75 and 4.61–4.68 Å, respectively) satisfy the rule $d_1 < 4.2$ Å $< d_2$. However, the ethyl substituents in "preorganized

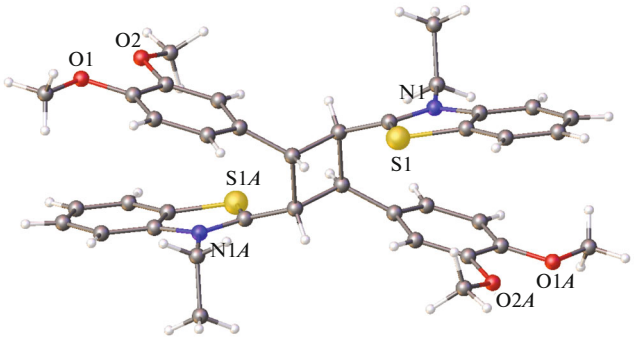


Fig. 20. Structure of cyclobutane obtained upon illumination of **SD-3**.

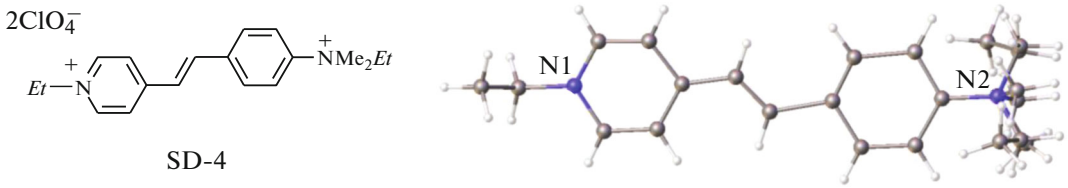


Fig. 21. Structural formula of **SD-4** and the structure of its dication.

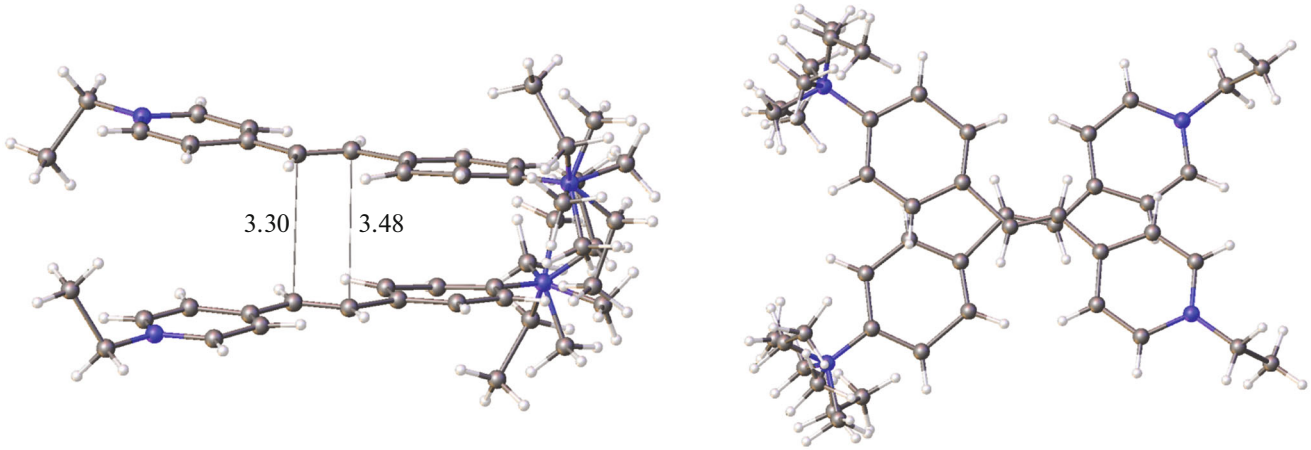


Fig. 22. Structure of the preorganized cation pair of **SD-4** in two projections; distance are indicated in Å.

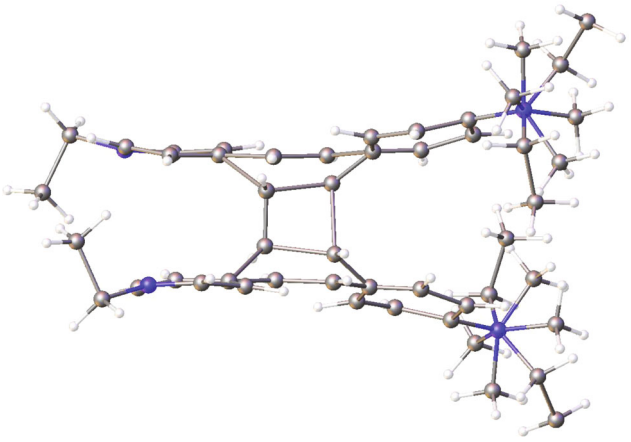


Fig. 23. Structure of the product of incomplete PCA reaction in an **SD-4** crystal, formed from stacks of dications linked by twofold axes.

dimers" crystals *a* are oriented inwards the dimer, whereas in crystals *b* and *c* they are oriented outwards (Fig. 27).

Thus, in the **SD-6** dye, as well as in the above-described **SD-3** dye with a similar cation, the hindrance for implementing the PCA reaction in a preorganized dimer was the that the ethyl substituents were directed inwards the dimer; this directionality impedes the approach of the ethylene fragments of formula units of dimer pair, which is necessary for the PCA reaction to occur.

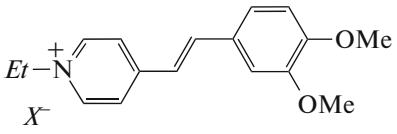
The PCA reaction in **SD-6** crystals (*b* and *c*) occurs as a single crystal–single crystal process. The newly formed doubly charged cation has the same structure as in the photoproduct obtained from **SD-3** (Fig. 20).

The absence of PCA in polycrystalline films of **SD-6** dye is explained by presence of only modification *a* in them, which is formed during fast crystallization.

1.8. Influence of the Enhancement of π···π-Stacking Interaction on PCA

In the **SD-7** dyes (Fig. 28), which are selenium analogues of **SD-3** and **SD-6**, one would expect occurrence of new effects leading to new specific features of crystal packing, for example, enhancement of π···π-stacking interactions or formation of I^{-}···Se secondary bonds.

Crystallization of **SD-7a** from mixtures of different solvents was used to obtain three crystalline forms: co-crystallizate with benzene (**SD-7a** · $0.5C_6H_6$), with hydroquinone (**SD-7a** · 0.5HQ), and with ethyl acetate and water (**SD-7a** · 0.5*Ac*O*Et* · $0.3H_2O$). **SD-7b** was synthesized in the solvate-free form. **SD-7c** was isolated both in the solvate-free form and as a solvate



SD-5

$X = ClO_4$, I, TsO, BF_4, PF_6, *Pic*, BPh_4

Fig. 24. Structural formula of **SD-5** dyes and anions in them.

containing HQ and water (**SD-7c** · 0.5HQ · H_2O). An XRD analysis was performed for all synthesized crystals, and the samples analyzed were exposed to visible light [100].

The results obtained for **SD-7c** crystals were the same as for the sulfuric analog **SD-3**; i.e., the PCA reaction occurs completely with single crystal retention and formation of a photocycloaddition product. The photoreaction in **SD-7c** · 0.5HQ · H_2O crystals is completed by only 25% (Fig. 29).

The subsequent 1-month crystal illumination did not lead to an increase in the content of cyclobutane component, which is due to the hindered rotational dynamics of the SO_3^- group of tosylate anion as a result of its participation in the formation of hydrogen bonds with HQ solvate molecules. A similar effect was described above for the **SD-3** · 0.5HQ · H_2O dye.

It is of interest that, apparently, the PCA reaction occurs also in **SD-7a** · 0.5*Ac*O*Et* · 0.3H_2O crystals. They satisfy the rule $d_1 < 4.2$ Å $< d_2$, and the ethyl substituents in the "preorganized dimer" are oriented outwards. However, destruction of single crystals (due to the evaporation of solvate ethyl acetate) occurs simultaneously with the PCA reaction. As a result, an X-ray amorphous powder is obtained. According to the NMR ^1H spectroscopy data, this is a cyclobutane product.

SD-7b crystals turned out to be stable against irradiation, although the conditions necessary for PCA were provided in them. This is due to the formation of secondary bonds between selenium and iodine atoms (Fig. 30).

Apparently, the participation of selenium atom in this interaction fixes its position in crystal, thus impeding its shift into the dimer, which is necessary for implementing the PCA reaction.

The **SD-7a** · 0.5C_6H_6 **SD-7a** · 0.5HQ crystals exhibited the same packing motif, which differs from that of canonical structures **1**–**6** (Fig. 2) and generally is not characteristic of planar conjugate systems. Figure 31 shows a fragment of this packing for **SD-7a** · 0.5C_6H_6 crystals.

There are no isolated stacks in this packing: each structural unit is π···π-overlapped with neighboring structural units in the stacks developing both along the *ii* and *jj* directions. Thus, a very close packing is formed in the crystal. Despite the fact that the d_1 in these structures is very short (3.36–3.50 Å), the participation of structural units of the stacks developing along the *jj* direction in strong π···π-interactions with the neighboring structural units developing along the *ii* direction impedes implementation of PCA.

Thus, incorporation of selenium into the styryl heterocycle composition may lead to unexpected crystal packings, which were not observed previously in planar conjugate systems.

1.9. Increase in the Probability of Forming Styrylheterocycles of Favorable Packings in Crystals

As was mentioned above, four types of packing motifs (Fig. 2, **3**–**6**) can be implemented in SH crystals, but a dimer pair favorable for PCA may exist in only two of them (**3** and **4**).

The probability of forming packings favorable for PCA in SH crystals can be increased in two ways: by (a) modification of molecules that expands the π-conjugation region, due to which the probability of forming associates with stacking interactions, i.e., stacks

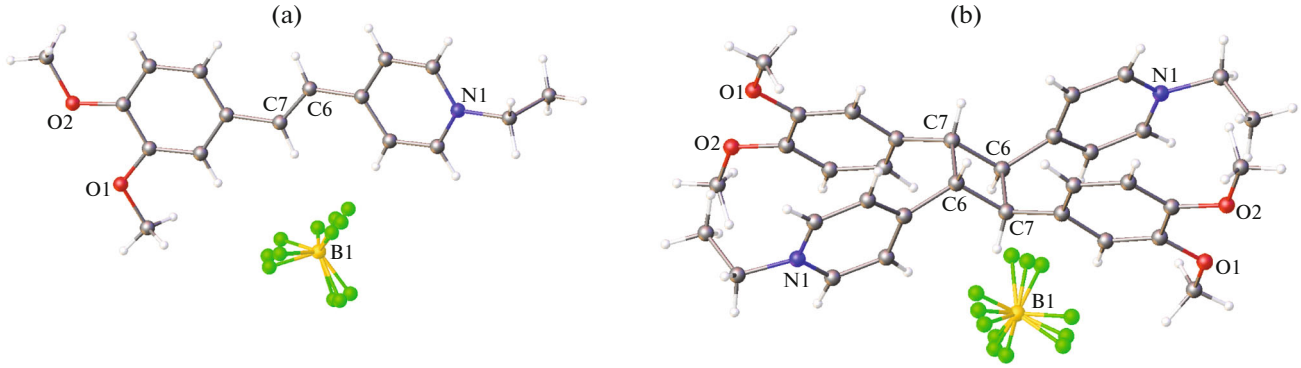
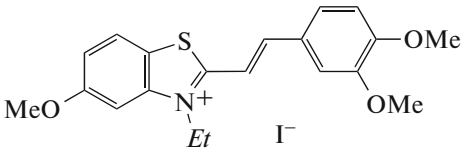


Fig. 25. (a) Structure of **SD-5** ($X = BF_4$) and (b) cyclobutane formed from it during PCA.



SD-6

Fig. 26. Structural formula of **SD-6**.

(packings **1** or **2**) or dimers (packing **3** or **4**), increases during crystallization and (b) protonation of molecules over the nitrogen atom, i.e., transformation of neutral SH molecules into electron analogues of SDs, for which the formation of crystal packings similar to those typical of SDs (packings **1** or **2**) should be expected.

The tendency to form stacking packing elements increases in the series of **SH-1**–**SH-4** compounds (Fig. 32) with a successively expanding conjugation region [83].

There is a herringbone packing in the **SH-1** crystal (Fig. 2, packing **6**), which excludes implementation of the PCA reaction. The **SH-2** compound with a more extensive conjugation region is crystallized with a herringbone-dimer packing (Fig. 2, packing **3**), which is favorable for PCA (Fig. 33).

The photoreaction in an **SH-2** single crystal exposed to light occurs by 70% after 6-h irradiation and is completed for 30 h (Fig. 34) [67].

Similar behavior was demonstrated by the pair of **SH-3** and **SH-4** compounds. Indeed, **SH-3** crystals provided a herringbone molecular packing, which is not fit for PCA, whereas **SH-4** was crystallized with a herringbone-dimer packing characterized by a distance d of 3.80 Å in centrosymmetric dimer pairs, which is favorable for PCA [83].

Thus, expanding the conjugation region in planar SH molecules, one can increase the probability of forming packing motifs favorable for PCA in a crystal.

Protonated forms HSH^+X^- (X = ClO_4) were obtained for the series of 4-styryl-pyridines (Fig. 35) [84]. Since HSH^+X^- and the corresponding SDs have similar shape and electronic structure, similarity of their crystal packings, i.e., preferred primary formation of stacking packing motifs, was expected.

Preliminary NMR ^1H spectroscopy of HSH^+X^- polycrystalline films after their illumination showed that approximately a half of investigated samples are involved in the PCA reaction; the reaction rate for them is much lower than that for the related SDs.

Stacking architectures similar to those of related SDs are mainly formed in HSH^+X^- crystal packings. Many of them, especially the centrosymmetrically related ones, are favorable for the solid-phase PCA reaction. However, in contrast to **SDs**, no more rare architectures in protonated SHs are translationally linked stacking ones, in which the PCA reaction is impossible. This feature differs the protonated SHs from both neutral SHs (Fig. 2, packings **3**–**6**) and the corresponding **SDs**, for which centrosymmetrically related stacks (Fig. 2, packings **1**, **2**) with head-to-tail molecular packing are dominant. This difference is due to the formation of hydrogen bonds between the N^+–H fragment of molecular cation and the perchlorate anion. The occurrence of hydrogen bonds in crystal packing also increases the general rigidity of crystal structure and leads to retardation of the PCA reaction in it.

Despite the aforementioned increase in the rigidity of HSH^+X^- structures, the PCA reaction occurs in practically all crystals with centrosymmetrically linked stacking packings. However, this process in HSH^+X^- crystals is accompanied more often (than for similar dyes) by their destruction, because the condition $d_1 \le 4.2$ Å $\le d_2$ is not satisfied in this case.

The proposed approach within the crystalline design of specified **SH** packings turned out to be correct. Despite the fact that **SHs** and their protonated forms are somewhat less favorable objects for studying the solid-state PCA reaction in single crystals than SDs, they are promising because make it possible to expand significantly the range of objects under study due to the use of **SHs** as ligands in coordination compounds [94–98].

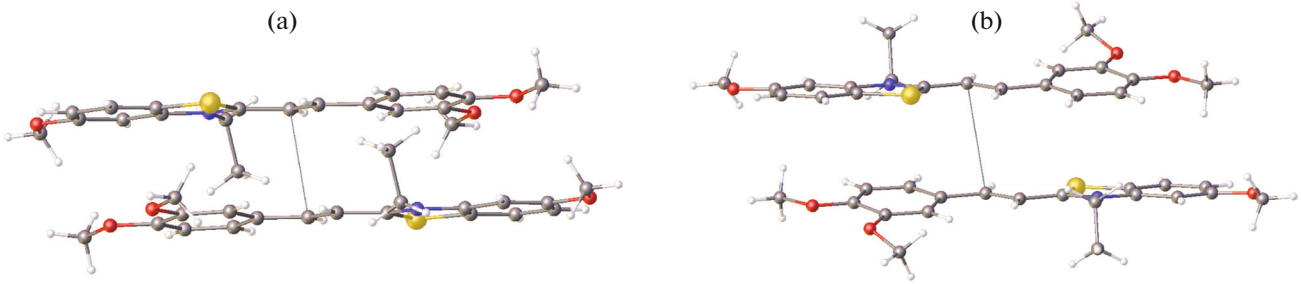


Fig. 27. Structure of preorganized dimer pair in crystals (a) *a* and (b) *b* and *c* of **SD-6**.

1.10. "Pedal" Disorder of Ethylene Compounds and Its Influence on PCA

The so-called "pedal" disorder of azastilbene fragments, corresponding to their rotation by 180° around the long axis, was revealed in most of **HSH**$^+X^-$ structures and, somewhat more rarely, in SD and SH structures. This disorder is a consequence of the dynamic process of solid-phase pedal isomerization in crystal, when an ethylene fragment rotates around its single bonds, while aromatic substituents are only slightly displaced in their intrinsic planes [101–103].

The pedal isomerization in XRD manifests itself as a structural disorder [68, 84] (Fig. 36). An especially interesting case is presented on the right (protonated styrylpyridine with an NMe_2 substituent) [84]. There are two crystallographically independent structural units in the crystal, and only one of them is subjected to pedal isomerization. Their crystalline environments are qualitatively identical. This means that, due to the small difference in the crystal fields around these two cations, one of them exhibits dynamic behavior, whereas the other does not.

The dynamic process of pedal isomerization inevitably reduces the probability of PCA reaction, i.e., leads to its retardation. Indeed, when implementing a temperature-dependent pedal isomerization in crystal, one can select four versions of mutual arrangement of molecules in dimer pairs at each instant (Fig. 37).

Only two of them (*a* and *b* in Fig. 37) satisfy the condition for the reaction onset, because they contain ethylene fragments with antiparallel orientations, whereas the mutual arrangement of these fragments in the two other versions (*c* and *d*) is crossed.

Note that pedal isomerization is observed in not only **SHs** and their protonated forms, but also in other ethylene compounds, in particular, in **SDs**. Monitoring of the PCA reaction (i.e., analysis of the reaction products 5 and 20 h after the crystal irradiation onset) was performed for the **SD** 4-pyridine series, which is characterized by the presence of ethyl substituent at the nitrogen atom (**SD-8** in Fig. 38,) and a pedal isomer ratio of 0.7 : 0.3 [69].

A disordered structure, in which both the initial pedal components and cyclobutane coexist in a ratio of 0.4 : 0.3 : 0.3, was obtained in **SD-8** after 5-h irradiation (Fig. 39a). The largest contribution is from the cyclobutane component that was formed from the major pedal component. The PCA reaction is completed 20 h after the irradiation onset, yielding a product in the form of two cyclobutane "isomers" (Fig. 39b).

When a crystal is exposed to visible light, the second dynamic process—pedal isomerization—occurs in it along with the PCA. Since the probability of implementing the versions of arrangement of structural units that are favorable for PCA (*a* and *b* in Fig. 37) in a "preorganized dimer" is higher for the major component than for the minor one, practically only the major component starts reacting in the first stage.

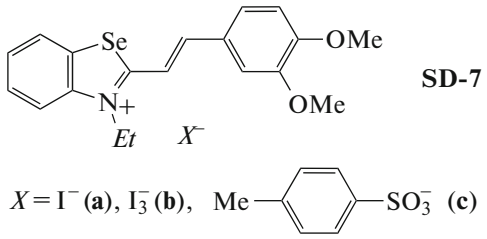


Fig. 28. Structural formula of **SD-7** dyes.

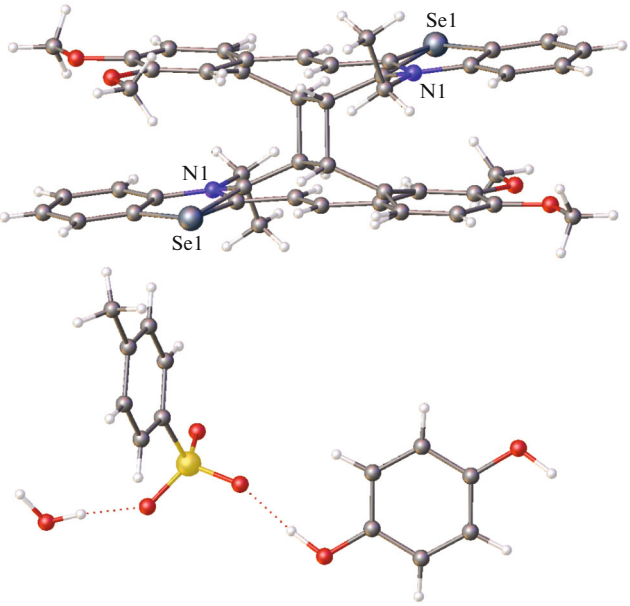


Fig. 29. Components of **SD-7c** · 0.5HQ · H_2O crystal after illumination.

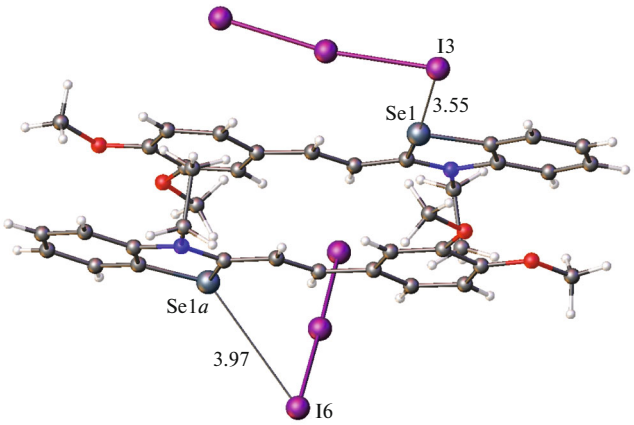


Fig. 30. Structure of the formula units of **SD-7c** crystal (distances are given in Å).

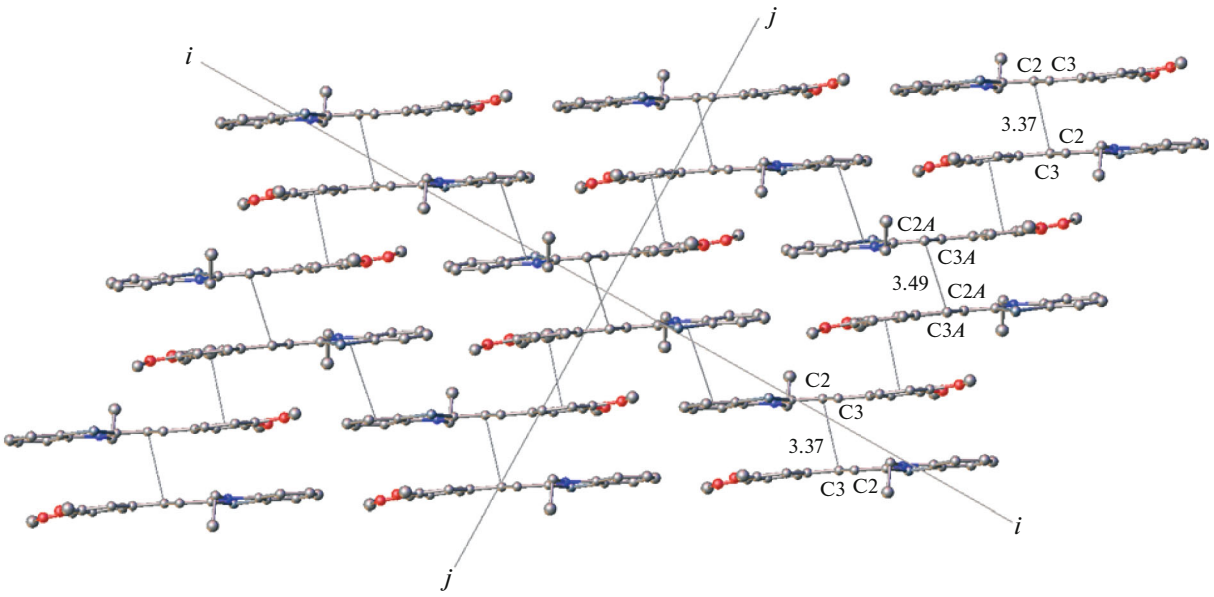


Fig. 31. Fragment of **SD-7a** · $0.5C_6H_6$ crystal packing.

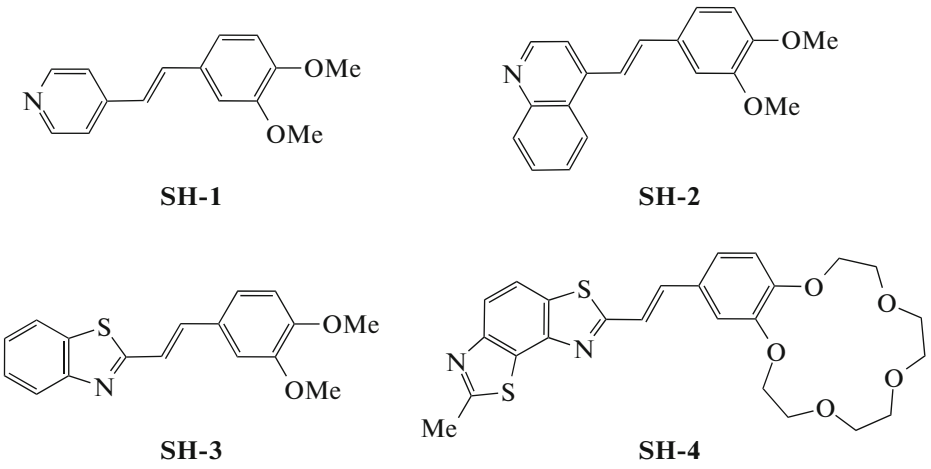


Fig. 32. Structural formulas of **SH-1**–**SH-4** styrylheterocycles.

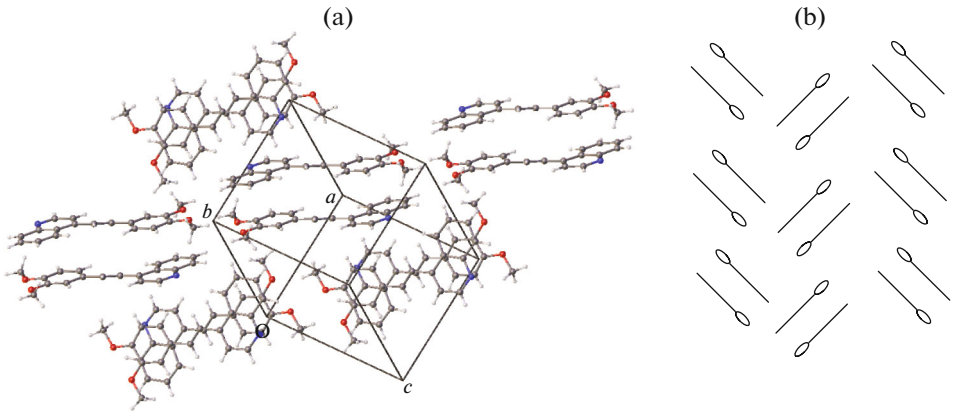


Fig. 33. (a) Fragment of **SH-2** crystal packing and (b) graph of this packing.

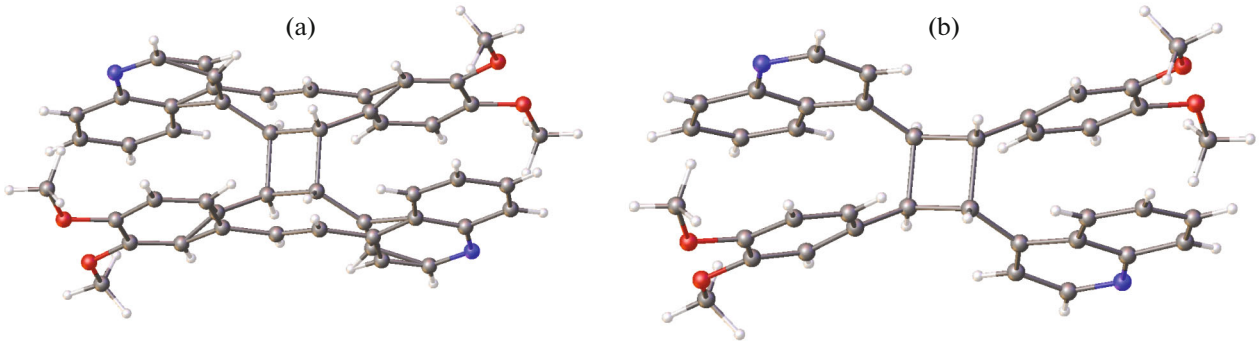


Fig. 34. Structure of an **SH-2** crystal exposed to visible light for (a) 6 and (b) 30 h.

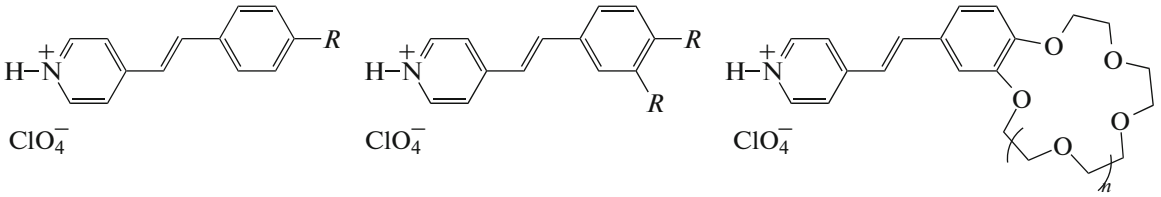


Fig. 35. Structural formulas of protonated styrylheterocycles $HSH^{+}ClO_4^{-}$ (R = H, OMe, SMe, NMe_2, Cl, NO_2; n = 1, 2).

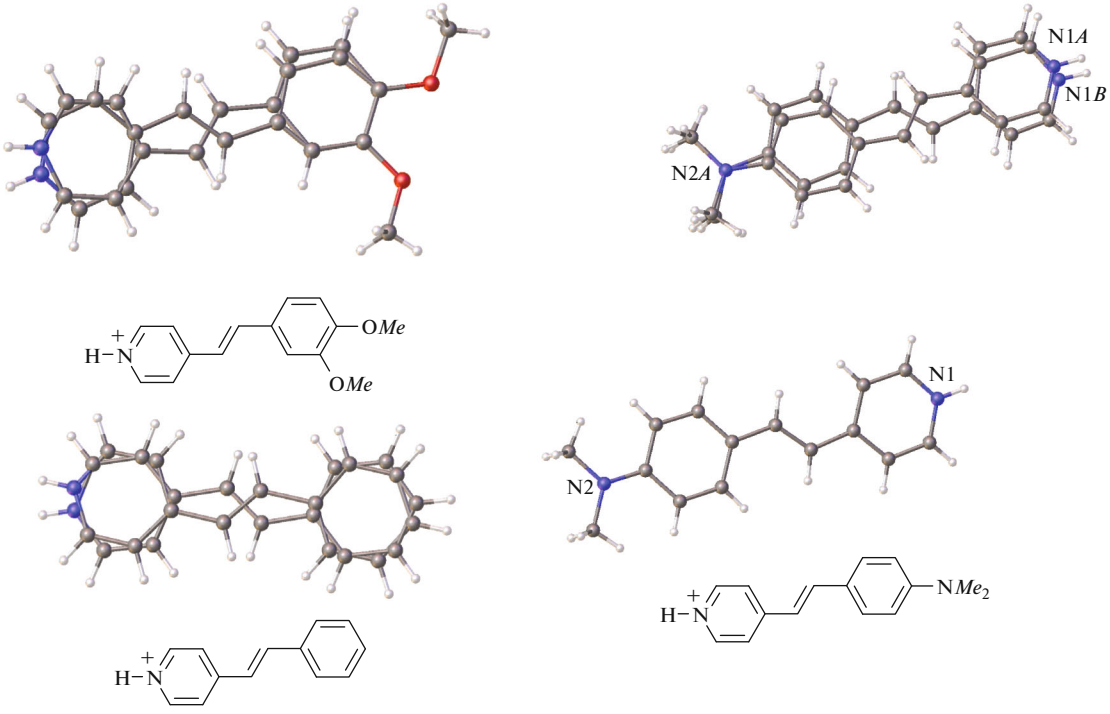


Fig. 36. Examples of structures of protonated **SH**s with pedal disorder; the anion is ClO_4^{-} in all cases.

The ratio of disordered cyclobutane components amounts to 0.8 : 0.2, i.e., differs from the ratio of the major and minor components in the initial **SD-8**. Five hours after the irradiation onset, when the ratio of the initial pedal isomers is equalized, pedal isomerization started affecting significantly the PCA process. The initially minor **SD-8** component was only partially transformed into the minor cyclobutane "isomer". The rest, being influenced by the pedal isomerization, was transformed into the initially major pedal compo-

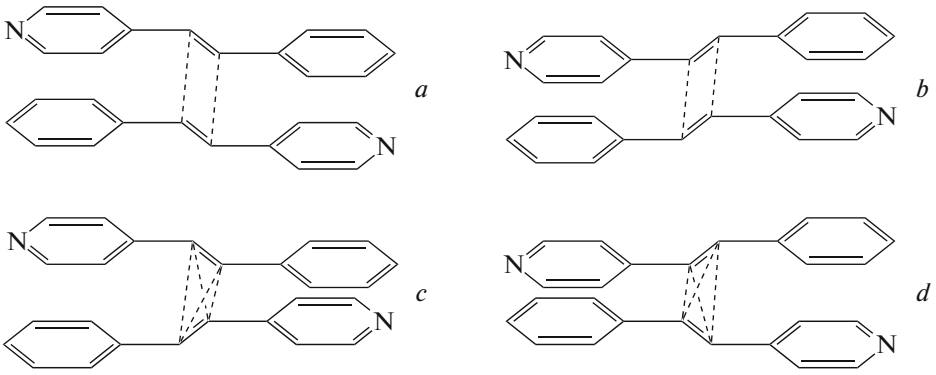


Fig. 37. Arrangement versions for pedal isomers in a dimer pair.

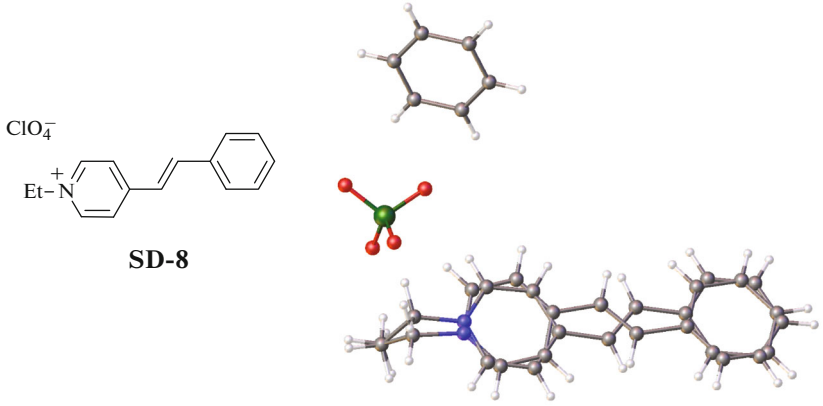


Fig. 38. Structural formula and structure of **SD-8**.

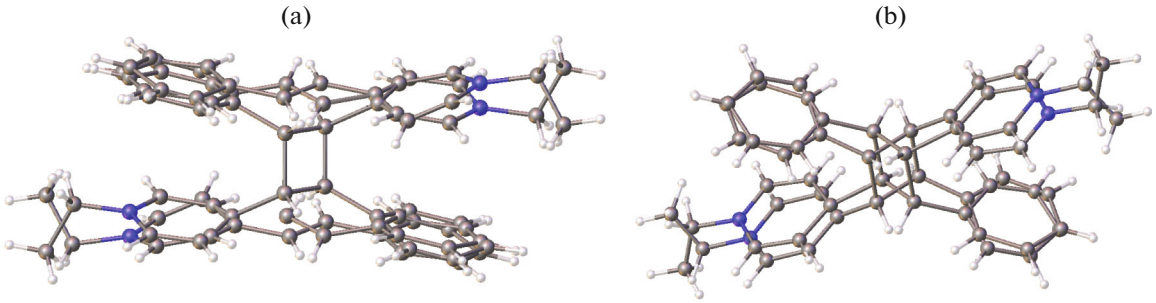
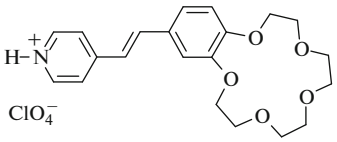


Fig. 39. Structure of **SD-8** exposed to visible light for (a) 5 and (b) 20 h.

nent of **SD-8** and thus increased the probability of forming the major cyclobutane "isomer" from it. As a result, the amount of the latter exceeded the amount of the major component in the initial mixture of pedal isomers.

There are two crystallographically independent formula units in a crystal of protonated 15-crown-5-containing H**SH-5**$^{+}$$ClO_4^-$ [84]. They form a pseudo-centrosymmetric dimer (Fig. 40), in which only one of the cations exhibits pedal disorder with a ratio of pedal isomers of 0.53 : 0.47, while the second molecule is in a more "rigid" crystalline environment, which does not allow for pedal isomerization.

It is of interest that almost parallel arrangements of ethylene fragments are exhibited by the "lower" cation and the minor pedal component of the upper cation; this circumstance should lead to significant retardation of the PCA reaction. Indeed, no changes were observed in the initial crystal after 9-day irradiation. However, the crystal changed significantly its color



HSH-5^{+}ClO$_4^{-}$

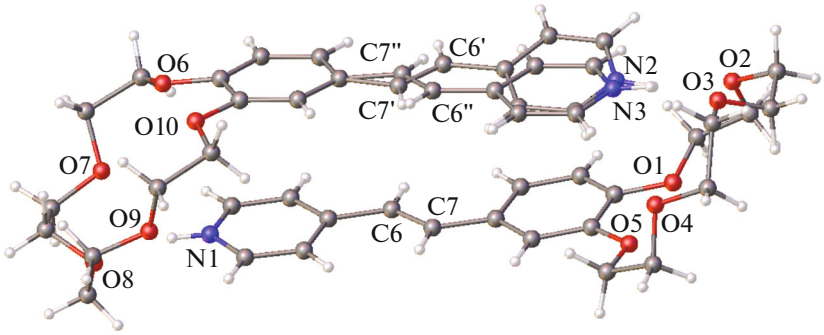


Fig. 40. Structure of the dimer pair in HSH-5^{+}ClO$_4^{-}$; the distances C6...C7" and C7...C6" are 3.62 and 3.43 Å, respectively.

(from bright to pale yellow) on the tenth day, an indication of PCA reaction occurring in it. The structure of the newly formed product was determined from X-ray diffraction data (Fig. 41).

The initial cation HSH-5^{+} coexist in the strongly disordered structure in the form of both pedal isomers and a photoproduct.

The irradiation of this crystal was continued, and it became completely colorless on the next day. An XRD analysis revealed completeness of the PCA reaction in the compound under study (Fig. 42).

This fact confirms again the dynamic character of pedal disorder, as a result of which the fraction of the minor component of the initial compound that is spent during PCA is constantly made up due to the pedal isomerization.

Thus, the pedal isomerization slows down the PCA process, but in some cases makes it complete. In addition, one would expect the pedal isomerization to allow for PCA in stacks organized via axes *2* in case *a* (Fig. 8), where the ethylene fragments of the dimer are crossed. However, such examples have not been found yet.

1.11. Feasibility of retro-PCA Reaction in Crystal

An attempt to carry out a *retro*-PCA reaction in crystal was made for the above-described dyes **SD-3** [99] and **SD-5** (anion BF_4^-, Fig. 24 [73]), in which the direct PCA reaction was found to have a high rate. For the **SD-5** dye, PCA is characterized by high color contrast between the initial compound and the reaction product, due to which both reactions can be traced visually.

A single crystal of each cyclobutane product (yellow-orange for the cyclobutane from **SD-3** and colorless for the cyclobutane from **SD-5**) was exposed to unfiltered UV light (xenon mercury lamp). The spectrum of this radiation included both a long-wavelength component, inducing the direct PCA reaction, and a short-wavelength component, which should initiate the back reaction (*retro*-PCA). Therefore, the product

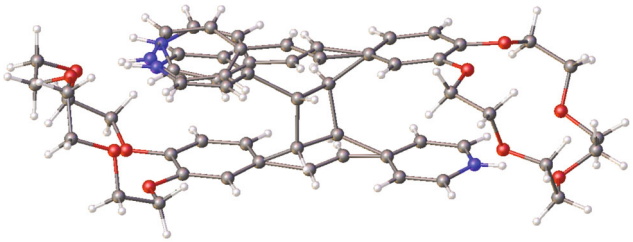


Fig. 41. Structure of the PCA product in HSH-5^{+}ClO$_4^{-}$ exposed to visible light for 10 days.

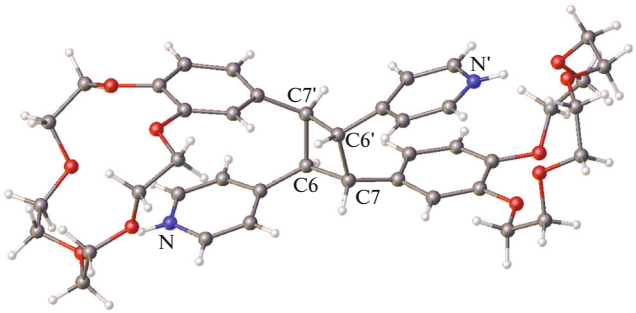


Fig. 42. Structure of the PCA product in HSH-5^{+}ClO$_4^{-}$ exposed to visible light for 11 days.

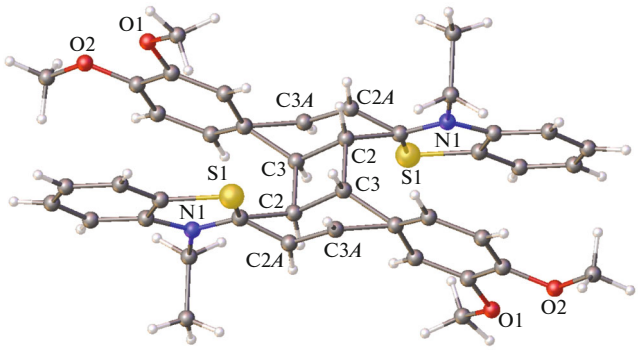


Fig. 43. Disordered structure obtained as a result of UV illumination of cyclobutane from **SD-3**.

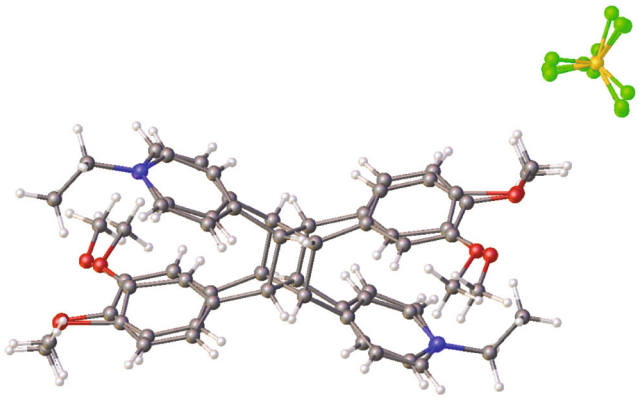


Fig. 44. Structure of the product of UV illumination of cyclobutane crystal from **SD-5**.

of *retro*-PCA reaction in each of these cases was expected to be a disordered structure containing both the cyclobutane component and the initial dye, similarly to the previously described cases of incomplete transformation of the initial compound into a cyclobutane derivative, which are presented in Figs. 23, 29, and 34. Moreover, one would not expect a significant contribution of the initial dye component to the general disordered structure, because only 10% of UV-lamp power falls on the short-wavelength spectral region. However, it appeared important to establish the fundamental possibility of implementing both reactions (PCA and *retro*-PCA) in the same single crystal.

The existence of a disordered system, including both a cyclobutane product and the initial dye, was revealed for a UV-irradiated crystal of cyclobutane from **SD-3** (Fig. 43).

Despite the fact that the contribution ratio of the cyclobutane and initial dye was only 0.93 : 0.07, the occurrence of *retro*-PCA reaction was established reliably.

After 4-h UV illumination, the crystal from **SD-5** acquired the same yellow color as the initial compound. Then this crystal was mounted again on a diffractometer, and a new X-ray experiment was performed. The result turned out to be unexpected (Fig. 44).

The pattern obtained resembles that shown in Fig. 39 for two orientations of cyclobutane from **SD-8**, corresponding to pedal **SD-8** isomers. However, the object of UV-irradiation was a crystal containing the only cyclobutane "isomer" that was formed as a result of exposure of **SD-5** to visible light and did not exhibit pedal isomerization. In this case, one cyclobutane "isomer" cannot be transformed into another without breaking two σ bonds. Therefore, the *retro*-PCA reaction occurs indeed (in the form of a single crystal–single crystal process). Note that cyclobutane "isomer" ratio is 0.9 : 0.1 in this case. Apparently, the back reaction is accompanied by changes in the crystalline environment of structural units, due to which pedal dynamics can be implemented in the newly formed structural units of **SD-5**. In turn, the newly formed pedal isomers are transformed into two cyclobutane "isomers" under exposure to visible light. Two features indicate a change in the crystalline environment of structural units during both reactions. First, the change in the unit-cell parameters reaches 7% during the PCA and *retro*-PCA reactions. Second, the rotamer ratio for the disordered anion BF_4^- changes significantly: it amounts to 0.5 : 0.3 : 0.2 in the dye, 0.6 : 0.2 : 0.2 in cyclobutane, and 0.4 : 0.4 : 0.2 after the UV-irradiation.

Therefore, both (direct and back) reactions may occur as a single crystal–single crystal process in this case.

CONCLUSIONS

A crystallochemical description of the topochemical [2 + 2] photocycloaddition reaction was developed for planar unsaturated compounds, the absence of this reaction for some packing motifs was explained, and the conditions for implementing this reaction without single crystal destruction were determined. Several approaches were proposed to form crystals with desired packing motifs; they imply structural modification of molecules of unsaturated compounds, their cocrystallization with small solvate molecules, and variation in the anion nature. The possibility of implementing both the direct and reverse photochemical reactions in one single crystal was proven.

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