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Photoinduced transformations in single crystals of 1,2-bis(2-[(*E*)-3-oxo-3-phenylprop-1-enyl]phenoxy)ethane and 1,5-bis(2-[(*E*)-3-oxo-3-phenylprop-1-enyl]phenoxy)-3-oxapentane

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Differences in the parameters of pre-organization of chalcone podands to intermolecular photoinduced [2+2] cycloaddition (PCA) in crystals were discovered. As a result of PCA, the chalcone podand with two oxyethylene units forms stereoregular cyclobutane-containing polymer chains over the whole volume of the single crystal. In the case of the chalcone podand with one oxyethylene unit, the PCA reaction in single crystal becomes impossible; however, its mechanical destruction results in the formation of surface layers with stacking dimers. In these layers, photodimerization occurs due to a decrease in topochemical control from the molecular lattice.

Key words: chalcone podand, [2+2] photocycloaddition, topochemical control, photopolymerization, α-truxillic structure.

The use in polymer synthesis of methods and principles of supramolecular chemistry, such as self-assembling of highly ordered structures in single crystals, is one of the promising trends in the production of novel materials capable of demonstrating unique physicochemical properties.[1—4] For instance, polyfunctional compounds with photocontrolled groups (vinyl, styryl, cinnamoyl, anthryl, *etc.*) capable of reacting in stereospecific topochemical reactions of [2π+2π] and [4π+4π] photocycloaddition (PCA) and others are used in the synthesis of linear polymers of stereoregular structure.[5—9] These processes are directly controlled by the crystal lattice providing the maximum approach of parallel photosensitive double bonds to the distance that does not exceed 4.2 Å.[5,10—12] The studies of the photochemical transformations of olefins in crystals showed that photopolymerization is most characteristic of conjugated dienes with the CH=CH groups in the *para*-position of the (hetero)aromatic ring.[5] Photopolymerization in single crystals depends to a considerable extent on the nature of photosensitive terminal groups of the reacting molecules. On going from conjugated dienes with styryl or acrylate terminal groups to cinnamates, the polymerization direction shifts to photodimerization with the side formation of small amounts of oligomers (n = 3, 4).[13,14]

It is rather difficult to attain crystal structure retention during the PCA, *i.e.*, to retain topochemical control of the reaction course until its completion. The solution of this problem was proposed for particular classes of olefins, *e.g.*, styryl dyes.[15—18] The main approach is the creation of loose region in the crystal structure due to the inclusion into the structural units (molecules or molecular ions) of conformationally mobile groups, solvate molecules, or rotationally mobile counterions.

Combination of photosensitive groups with the conformationally mobile polyoxyethylene spacer in one molecule also could result in the appearance of loose regions in crystals. The loose regions surround the dimeric π-stacking fragments preorganized to the PCA. However, attempts to carry out solid-phase PCA reactions in the series of olefinic compounds, such as podands in which pairs of ditopic ligands are separated by polyether chains, were unsuccessful.[19,20] In our X-ray diffraction study of the aryl-containing chalcone podands with the propenone group in the *ortho*-position to the bridging oxyethylene units, we have earlier[21] found two compounds capable of topochemical PCA reactions: 1,2-bis(2-[(*E*)-3-oxo-3-phenylprop-1-enyl]phenoxy)ethane (**1a**) and 1,5-bis(2-[(*E*)-3-oxo-3-phenylprop-1-enyl]phenoxy)-3-oxapentane (**1b**).

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The purpose of the present work is to study photoinitiated transformations in single crystals of the above indicated compounds and to determine the degree of influencing of the oxyethylene substituents in molecules and topochemical control of the molecular lattice on the depth of the PCA occurrence.

Experimental

The IR spectra were recorded on a Spectrum One FT-IR spectrometer (Perkin—Elmer) with a diffuse reflectance sampling accessory (DRA). The Raman spectrum was obtained on a Nicolet 6700 FTIR spectrometer with an NXR Raman module ($\lambda = 976$ nm). The UV spectra were measured on a UV-2401 PC spectrometer (Shimadzu) with an integrating sphere attachment. The ^{1}H NMR spectra in DMSO-d$_6$ were recorded on a Bruker DRX-400 instrument with the working frequency 400 MHz using Me_4Si as the internal standard. Melting points were determined on a Boetius microheating stage. TLC was carried out on Silufol-254 plates eluting with ethyl acetate or benzene. TLC spots were developed with iodine vapors.

Photochemical transformations in chalcone podand 1a single crystals and solid-phase synthesis of 1*r*,3*t*-dibenzoyl-2*c*,4*t*-bis-{2-[2-(2-[(*E*)-3-oxo-3-phenylprop-1-enyl]phenoxy)ethoxy]-phenyl}cyclobutane (2a). *A.* Single crystals of compound **1a** (see Ref. 21) were irradiated with the non-filtered light of an incandescent lamp with a power of 150 W from a distance of 25—30 cm at 25 °C or in hexane with stirring and cooling to −25 °C for 48 h, or with the non-filtered light from a mercury lamp (500 W) from a distance of 35—40 cm at 25—30 °C for 12 h. The reaction course was monitored by IR and UV spectroscopy (DRA), as well as by ^{1}H NMR spectroscopy. The ratio of *E,E*/*E,Z*-isomers was estimated by ^{1}H NMR spectroscopy and chromatography using the reverse-phase variant of HPLC (RP HPLC) on an Agilent 1100 analytical liquid chromatograph. The column was Lichrosorb RP-18, LKB, 4.0×250 mm, and

Table 1. Parameters of crystals and characteristics of X-ray diffraction experiments for structures **1a**, **1b**, and **2a**

Parameter	**1a**	**1b**	**2a**
Molecular formula	$C_{32}H_{26}O_4$	$C_{34}H_{30}O_5$	$C_{64}H_{52}O_8$
Molecular weight/g mol^{-1}	474.53	518.58	949.06
Crystal system	Monoclinic	Monoclinic	Triclinic
Z	4	4	1
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a/Å	7.8756(6)	15.6193(10)	11.2128(14)
b/Å	14.7565(12)	11.6107(7)	11.5318(16)
c/Å	20.9574(17)	15.0945(10)	11.834(2)
α/deg	90	90	115.245(16)
β/deg	91.5210(10)	105.9180(10)	98.443(13)
γ/deg	90	90	105.961(12)
V/Å^3	2434.7(3)	2632.4(3)	1248.0(3)
d_{calc}/g cm^{-3}	1.295	1.308	1.263
F(000)	1000	1096	500
μ(Mo-Kα)/mm^{-1}	0.084	0.087	0.082
Crystal size/mm	0.22×0.22×0.18	0.38×0.22×0.18	0.45×0.28×0.11
Temperature/K	120.0(2)	120.0(2)	295
Radiation (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Scan mode	ω	ω	ω
θ range/deg	1.69—29.50	2.22—29.98	2.74—26.42
hkl ranges	$-10 \le h \le 10$, $-20 \le k \le 20$, $-29 \le l \le 29$	$-21 \le h \le 21$, $-16 \le k \le 16$, $-21 \le l \le 20$	$-14 \le h \le 12$, $-14 \le k \le 14$, $-14 \le l \le 14$
Number of measured reflections	25558	13407	14790
Number of independent reflections	6776 ($R_{int} = 0.0399$)	3825 ($R_{int} = 0.0349$)	4910 ($R_{int} = 0.0377$)
Number of reflections with $I > 2\sigma(I)$	5042	2848	1973
Number refinement variables	430	237	325
R Factors on $I > 2\sigma(I)$	$R_1 = 0.0449$, $wR_2 = 0.1049$	$R_1 = 0.0462$, $wR_2 = 0.1113$	$R_1 = 0.0370$, $wR_2 = 0.0389$
R Factors on all reflections	$R_1 = 0.0662$, $wR_2 = 0.1126$	$R_1 = 0.0673$, $wR_2 = 0.1198$	$R_1 = 0.1322$, $wR_2 = 0.0427$
Goodness-of-fit on F^2	1.049	1.043	1.002
Absorption coefficient	0.0004(4)	—	—
Residual electron density/e · Å^{-3}, ρ_{min}/ρ_{max}	−0.244/0.292	−0.200/0.377	−0.116/0.119

the particle size was 5 μm. The temperature of the column was 35±1 °C. Water was used as the mobile phase, and 60% acetonitrile served as the mobile phase *B*. The elution was performed as follows. At first the gradient regime was carried out from 0 to 100% *B* within 20 min, and then the isocratic regime with the mobile phase *B* occurred within 40 min, the solvent flow rate being 0.8 mL min^{-1}. A sample dissolved in DMF was introduced into the injector (10 μL). Detection was carried out using the diode matrix detector in the UV range at the wavelength 254 nm. The retention time of the *E,Z*-isomer was 17.1 min, and that of the *E,E*-isomer was 34.9 min.

B. Single crystals of compound **1a** were triturated uniformly distributing on the subsupport (ashless filter) and irradiated with the non-filtered light from the incandescent lamp with a power of 150 W from the distance 30 cm for 48 h or with the non-filtered light of the mercury lamp (500 W) from the distance 35—40 cm at 25—30 °C for 12 h. The completeness of the reaction was monitored by IR and UV spectroscopy (DRA) and by ^{1}H NMR spectroscopy. The ratio of the PCA products, including **2a**, in the reaction mixture was estimated by the composition of integral intensities of signals from the α,β-protons of the *E,Z*-isomers and the protons of the cyclobutane groups in the ^{1}H NMR spectra. The photolysis product of **2a** was purified by column chromatography (SiO$_2$, eluent benzene—ethyl acetate (50 : 1)).

The yield was 12%, m.p. 194—196 °C. ^{1}H NMR, δ: 3.96, 4.15, 4.33, 4.50 (m, 8 H, O—CH$_2$—CH$_2$—O); 4.68, 4.96 (both dd, 4 H, —CH—CH—C(O)—, ^3J = 10.8 Hz, ^3J = 7.6 Hz); 6.69 (m, 4 H, Ar); 7.00 (ddd, 2 H, Ar, ^3J = 8.0 Hz, ^3J = 7.2 Hz, ^4J = 1.6 Hz); 7.04 (d, 2 H, Ar, ^3J = 7.2 Hz); 7.13 (m, 10 H, C(O)Ar´, Ar); 7.28 (d, 2 H, Ar, ^3J = 8.0 Hz); 7.34 (m, 2 H, C(O)Ar´); 7.41 (m, 6 H, C(O)Ar´); 7.54 (ddd, 2 H, Ar, ^3J = 7.6 Hz, ^3J = 7.2 Hz, ^4J = 1.6 Hz); 7.77 (d, 4 H, C(O)Ar´, ^3J = 7.6 Hz); 7.94 (dd, 2 H, Ar, ^3J = 8.0 Hz, ^4J = 1.6 Hz); 7.94 (d, 2 H, CH=CH—C(O), ^3J = 16.0 Hz); 8.01 (d, 2 H, CH=CH—C(O), ^3J = 16.0 Hz). IR (DRA), ν/cm^{-1}: 595, 617; 693, 729, 753 (arom.); 809, 866, 899, 939, 991; 1015, 1057, 1122, 1164, 1178, 1214, 1236 (ν$_s$, ν$_{as}$, C$_{arom}$—O—C$_{alk}$, C$_{alk}$—O—C$_{alk}$); 1274, 1305, 1332, 1448, 1490; 1568, 1597 (C=C); 1651, 1672 (C=O); 2837, 2884, 2920, 2927 (C$_{alk}$—H); 3037, 3060 (C$_{arom}$—H). Found (%): C, 81.03; H, 5.44. $C_{64}H_{52}O_8$. Calculated (%): C, 80.92; H, 5.47.

Solid-phase synthesis of oligomer containing the 1*r*,3*t*-dibenzoyl-2*c*,4*t*-di(2-phenoxy)cyclobutane fragment (2b). Crystal **1b** (see Ref. 22) was irradiated with the non-filtered light from the incandescent lamp with a power of 150 W from a distance of 25—30 cm for 60 h or with the solar light (June) for 1 week. The completeness of the reaction was monitored by IR and UV spectroscopy (DRA) and ^{1}H NMR spectroscopy.

X-ray diffraction study. Crystals of chalcone podands **1a,b** were obtained by the slow evaporation of the solution in acetonitrile. X-ray diffraction analysis was carried out on a Bruker SMART-APEX-II automated diffractometer with a CCD detector (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, *T* = 120(2) K). Experimental reflections were processed using the SAINT program.[23] Structures were solved by direct methods and refined by full-matrix least squares in the anisotropic approximation on F^2 for all non-hydrogen atoms using the SHELXTL-Plus program package.[24] All hydrogen atoms were revealed in the difference synthesis; however, their geometrically calculated positions were used for further calculations. The crystallographic parameters and the main characteristics of experiment and structure determination and refinement are given in Table 1.

The crystals of **2a** were obtained by the slow evaporation of the acetonitrile solution. X-ray diffraction analysis was carried out on an Xcalibur 3 automated diffractometer with a CCD detector (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator, *T* = 295 K). The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation on F^2 for all non-hydrogen atoms using the SHELXS97 and SHELXL97 programs.[25,26] All hydrogen atoms were revealed in the difference synthesis and refined in the isotropic approximation, The crystallographic parameters and the main characteristics of experiment and structure determination and refinement are given in Table 1.

Results and Discussion

Molecular and crystal structures of 1a and 1b. The structure of molecule **1a** is shown in Fig. 1. The molecule has the non-crystallographic symmetry C_2. This symmetry is not rigid, because the molecule occupies the general position in crystal, which appears as the difference in conformation parameters of two chemically equivalent halves of the molecules.

In molecule **1a** the chemically equivalent fragments C(2)—C(1)—C(8)=C(9)—C(10) and C(2´)—C(1´)—C(8´)=C(9´)—C(10´) are almost planar, the benzene rings C(2)...C(7)/C(10)...C(15) and C(2´)...C(7´)/C(10´)...C(15´) are turned from the plane of the corresponding frag-

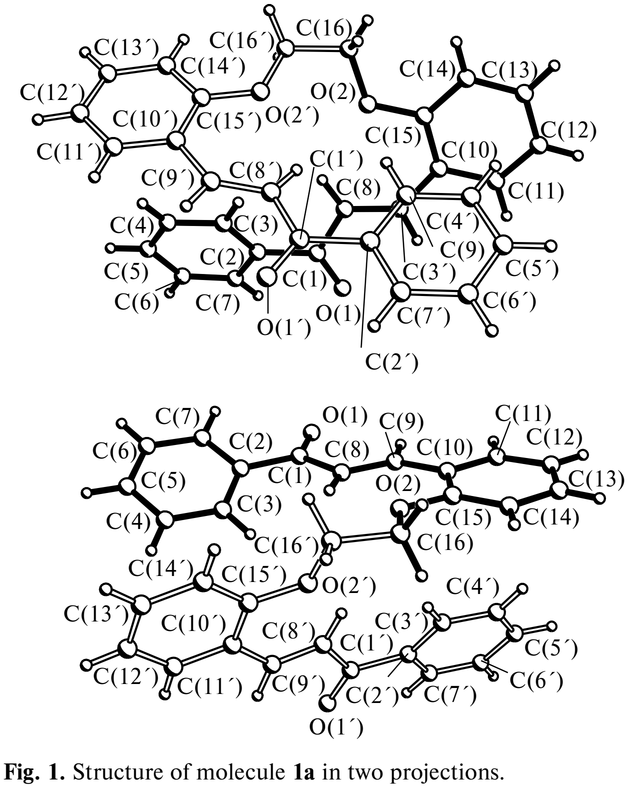


Fig. 1. Structure of molecule **1a** in two projections.

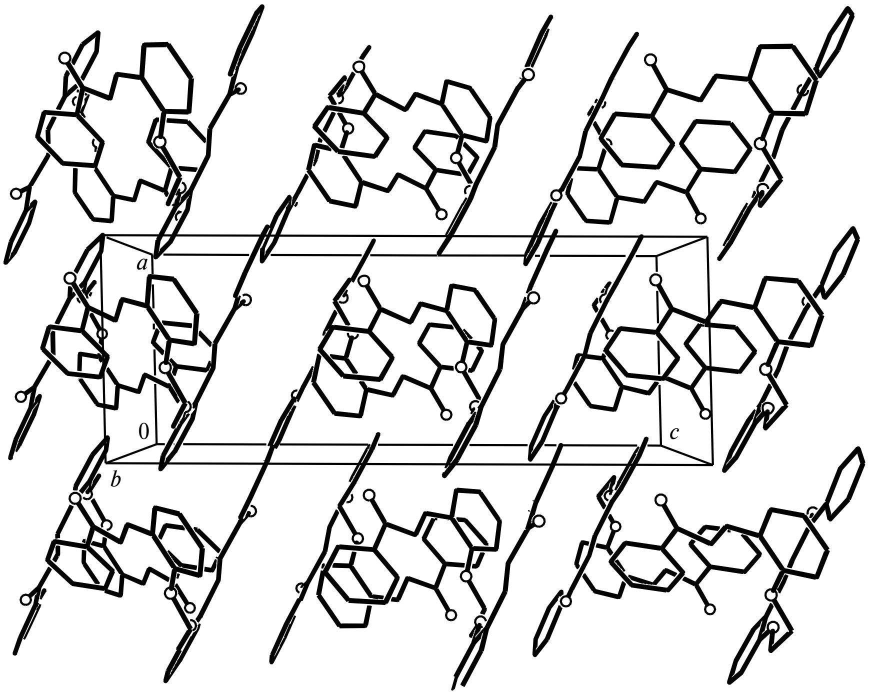


Fig. 2. Fragment of the crystal packing of **1a**.

ment by the angles 23.7(5)/3.0(5)° and 3.0(5)/4.9(5)°. The torsion angles C(16)—O(2)—C(15)—C(10) and C(16´)—O(2´)—C(15´)—C(10´) are 176.9(6) and 175.2(6)°, respectively, and the torsion angle O(2)—C(16)—C(16´)—O(2´) about the central bond equal to 62.2(5)° corresponds to the *gauche*-conformation. The dihedral angle between the planes of ethylene groups —C=C— is 77.0(5)°. The bond length distribution in the fragments C(2)—C(1)—C(8)=C(9)—C(10) and C(2´)—C(1´)—C(8´)=C(9´)—C(10´) 1.494(2), 1.479(2), 1.339(2), 1.455(2) Å and 1.498(2), 1.478(2), 1.336(2), 1.462(2) Å indicate an almost full localization of the π-electron density on the ethylene bond, which is important for the PCA reaction to occur.

The general position of the molecule in crystal implies that two ethylene groups in it are crystallographically nonequivalent and must not have an identical crystalline environment. Therefore, only one of the ethylene fragments of the molecule in crystal, namely, C(8)=C(9), has rather short contact with the like fragment of the adjacent molecule. The second ethylene group C(8´)=C(9´) forms no short contacts with the analogous group of the adjacent molecule.

The crystal packing of the molecules is built of centrosymmetric sandwich dimers (Fig. 2).

The structure of one of the dimers is shown in Fig. 3. The distance between the carbon atoms of the ethylene moieties C(8)...C(9A) and C(9)...C(8A) is 4.155(2) Å,

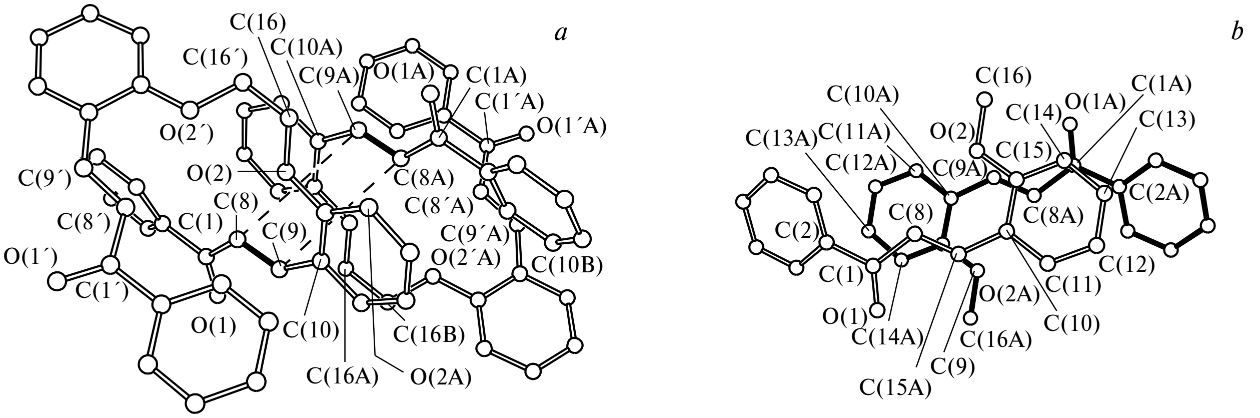


Fig. 3. Structure of the centrosymmetric sandwich dimer **1a** (*a*) and the view of π...π-overlapping of the conjugated fragments of the dimer (*b*, non-overlapped halves of the dimer molecules are omitted).

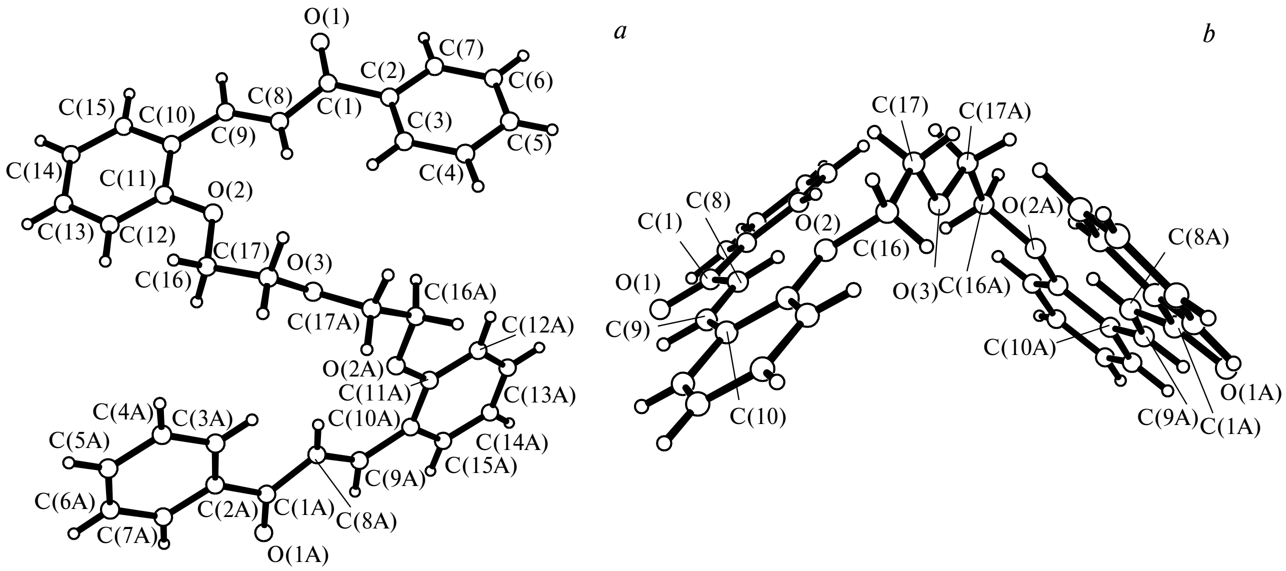


Fig. 4. Structure of molecule **1b** in two projections.

which corresponds to the upper limit of the values (4.2 Å) at which the PCA reaction can occur. The noticeable shift of the ethylene bonds in parallel planes observed in the sandwich dimer does not prevent the PCA reaction to occur.[15—18] In the case when the PCA reaction occurs in this crystal, the centrosymmetric isomer of substituted cyclobutane should be formed.

The structure of molecule **1b** is shown in Fig. 4. Unlike the previous case, in this crystal the molecule occupies the partial position on the 2-fold axis passing through the central oxygen atom O(3) perpendicularly to the plane of Fig. 4, *a*. Therefore, the both ethylene moieties of the molecule are crystallographically equivalent.

The torsion angle O(3)—C(17)—C(16)—O(2) is 66.0(5)°. The C(2)—C(1)—C(8)=C(9)—C(10) fragment is planar, and the benzene rings C(2)...C(7) and C(10)...C(15) are turned toward this plane by angles of 10.7(5) and 5.5(5)°, respectively. The dihedral angle between the ethylene groups is 72.2(5)°. The bond length distribution in the C(2)—C(1)—C(8)=C(9)—C(10) fragment of molecule **1b** (1.500(2), 1.471(2), 1.339(2), 1.460(2) Å) coincides in fact with that found for molecule **1a**.

The crystal packing of **1b** is rather complicated. One can distinguish the infinite ribbon motive with short contacts of the C(8)...C(9) type between all ethylene moieties (Fig. 5). These short contacts occur between the molecules joined by the symmetry centers, being 3.629(2) Å. The PCA reaction in such a crystal should be accompanied by the formation of a zigzag ribbon polymer.

The question whether loose regions, which can compensate (due to conformational tuning) internal strains in crystal that appear as a consequence of considerable atomic shifts of the ethylene fragments during the PCA reaction, exist in these packings or not should be answered after the fact of occurrence of this reaction in the single crystal would experimentally be established. This problem can be solved by a comparison of the structure of the initial single crystal and the structure of the same single crystal after the PCA reaction has completed in it.

Photochemical behavior of compounds 1a,b. The X-ray diffraction data for structures **1a** and **1b** indicate that both photodimerization (**1a**) and photopolymerization (**1b**) processes are possible as a result of topotactic control.

According to the ^{1}H NMR and IR spectroscopy (DRA) data, no PCA processes were observed upon the irradiation of single crystals **1a** with the visible (or solar) light for 48 h at 25—30 °C. Obviously, the oxyethylene moiety in photoexcited molecules have no enough conformational mobility for the compensation of internal strains in the

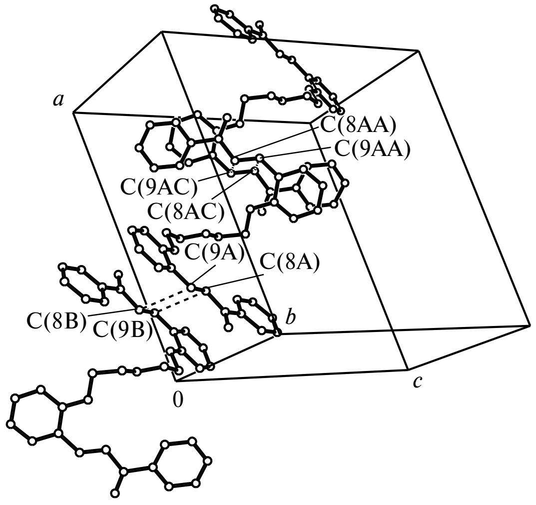


Fig. 5. Ribbon fragment of the crystal packing of compound **1b** with short intermolecular contacts of the ethylene groups.

crystal, which should appear due to large atomic shifts between two ethylene moieties in the intermolecular sandwich upon excimer formation.[27] The principle of "dense packing" shows that this restriction of motion of reacting molecules is related to the influence of the nearest environment (adjacent molecules) through intermolecular interactions.[5]

However, the comparison of the ^{1}H NMR spectra of the initial and irradiated samples of compound **1a** revealed the fact of photoinduced *E—Z*-isomerization. The interpretation of the ^{1}H NMR spectra data, including the comparison of the spectra of the synthesized chalcone podands,[20,21] crown-containing styryl dyes,[28] and compound **2a** (Fig. 6, *b*), made it possible to establish that only one of the terminal chalcone groups of podand **1a** is isomerized during photochemical transformations (Scheme 1). For example, along with the signals of protons of the CH=CH moiety of enone in the *Z*-configuration at δ 6.66 and 7.35 as two doublets with the spin—spin coupling constant (SSCC) 12.7 Hz, the spectra contain signals at δ 8.01 and 8.05 of analogous protons of the second moiety in the *E*-configuration with the SSCC 15.6 Hz (Fig. 7).

Analogous processes of *E—Z*-izomerization were also observed upon the irradiation of the single crystals with the visible light at –25 °C and with the non-filtered light from the mercury lamp at 25—30 °C for 48 and 12 h, respectively. According to the HPLC data, the yield of the isomerization product increased from 5 to 12% in the latter case. No isomerization usually occurs in crystals, because it should be accompanied by such a global rear-

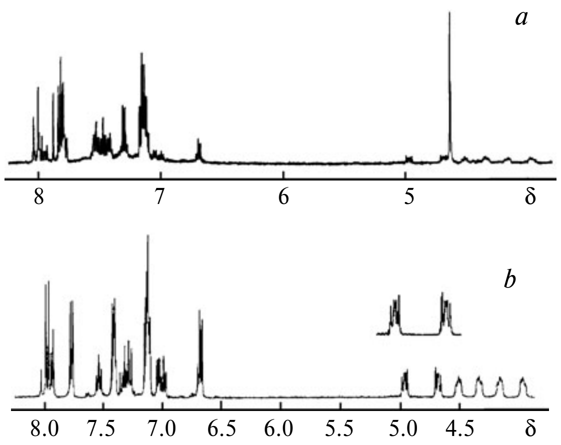


Fig. 6. ^{1}H NMR spectra of the reaction mixture after the irradiation of powdered compound **1a** (*a*) and PCA product **2a** (*b*) with the non-filtered light from a mercury lamp.

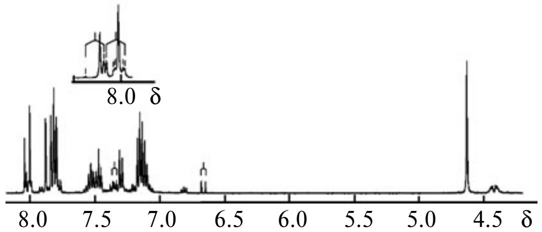
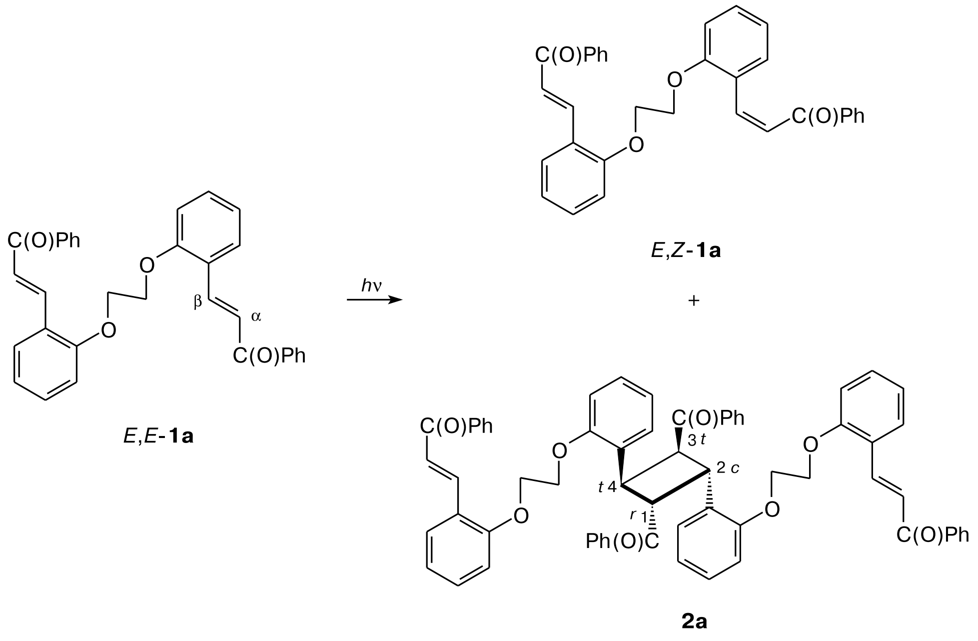


Fig. 7. ^{1}H NMR spectrum of compound *E*,*E*-**1a** after the irradiation of the single crystals with the non-filtered light from a mercury light (fraction enriched with isomer *E*,*Z*-**1a**, see Scheme 1).

Scheme 1



rangement of the molecular skeleton, which is impossible in the rigid crystalline environment of the molecules. However, there are examples of this type of solid-phase transformations (*Z—E*-isomerization) proceeding presumably through the metastable excimer complex for some *ortho*- and α-substituted cinnamic acids.[10—12] Another example is the so-called "pedal" isomerization that occurs in crystals of stilbenes and azobenzenes. Its essence is that the C=C or N=N double bond is twisted relative to the aromatic six-membered rings that experience only small migrations in their own planes.[29] This isomerization in the heterostyryl dyes[15—18] results in the appearance and accumulation in crystal of the second conformer, which is related to the initial one by the noncrystallographic 2-fold axis running along the main axis of the molecule, *i.e.*, the appearance of the disordering corresponding to the turn of the molecule by 180° about this axis. This isomerization is temperature-dependent, whereas the PCA reaction is temperature-independent. In the case of "pedal" isomerization, the process occurs within the "van der Walls contours" of the molecules, *i.e.*, the region of the crystal that is assigned to each molecule in the crystalline packing and, hence, the process in the crystal becomes possible.

The results of our studies suggest that the photochemical processes of *E—Z*-isomerization occur, most likely, on defects and/or faces of crystals involving the terminal chalcone group, which is not related by stacking interactions and partially liberated from the influence of the neighboring environment (see Fig. 3), and accompanied by the destruction of the crystal. The presence of the benzoyl substituent at the CH=CH bond of chalcone podand **1a** capable of increasing the single—triplet intersystem crossing constant (sensibilizing ability) increases the probability of photoinduced *E—Z*-isomerization.[30]

To shift the reaction toward isomerization, the single crystals of chalcone podand **1a** were triturated with the uniform distribution of the powder over the whole support surface (ashless filter), which was further irradiated for 12 h with the non-filtered light from the mercury lamp. The reaction course was monitored by UV spectra (DRA), which demonstrated the exponential decrease in the light absorption of the initial compound in the range from 200 to 400 nm up to the establishment of the photostationary state after 6 h after (Fig. 8).

The exhaustive explanation of the changes observed was obtained by the analysis of the ^{1}H NMR spectra of the reaction mixture, which contained, along with the signals of protons of the initial podand, the signals of protons of the *E—Z*-isomerization and PCA products in a ratio of ~83 : 5 : 12, respectively (see Fig. 6, Scheme 1). The signals of protons of the cyclobutane fragment of dipodand **2a** in the ^{1}H NMR spectra represent the symmetric spin system of the AA´BB´ type as two doublets of doublets with the SSCC $^3J_{1,2}$ = 10.8 and $^3J_{2,3}$ = 7.6 Hz at δ 4.68 and 4.96, which is characteristic of the *rctt*-isomer (see Fig. 6) formed due to the stereospecific photodimerization of chalcone podand **1a** according to the *syn*-"head-to-tail" type.[28,31] In the IR spectra (DRA), the appearance of cyclobutane-containing photoadduct **2a** is accompanied by the appearance of the new, higher-frequency absorption band in the region of stretching vibrations of the carbonyl group at 1672 cm^{-1} along with 1651 cm^{-1} (stretching vibrations of the C=O group of the conjugated system of the chalcone), the absorption band at 2927 cm^{-1} (region of stretching vibrations of the C—H bonds,) and the redistribution of absorption band intensities in the region of bending vibrations of the C—O—C bonds in the oxyethylene fragment at 1238—1214 and 1057—1015 cm^{-1} (see Fig. 8).

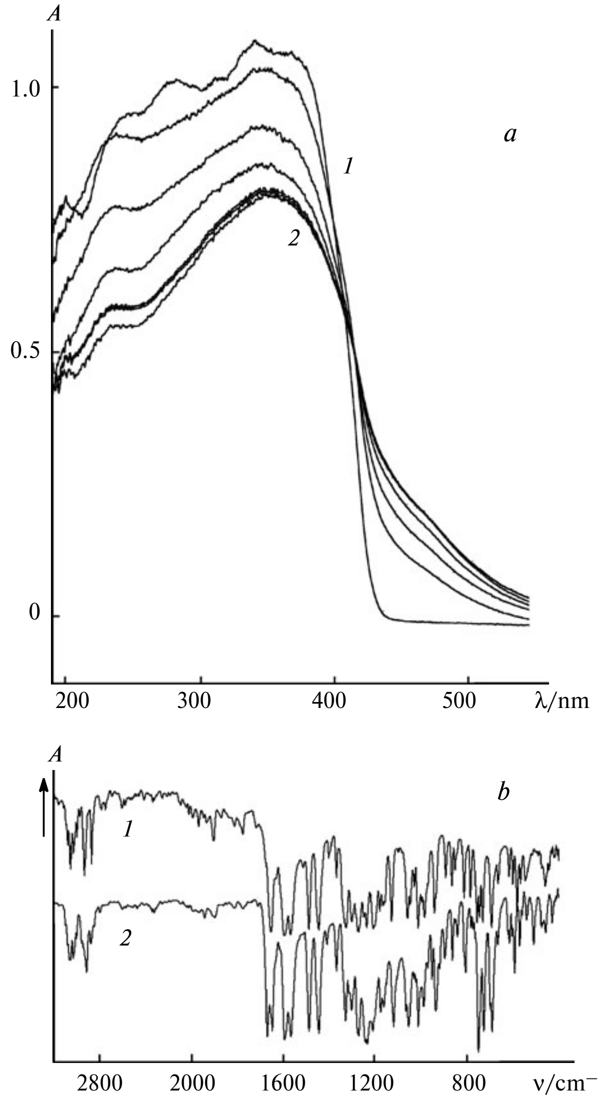


Fig. 8. (*a*) Change in the UV absorption spectra (DRA) of compound **1a** upon the irradiation with the non-filtered light from a mercury lamp: the spectrum of the starting compound (*1*) and the spectrum after irradiation for 12 h (*2*); (*b*) IR absorption spectra (DRA) of chalcone podand **1a** (*1*) and cyclobutane-containing dipodand **2a** (*2*).

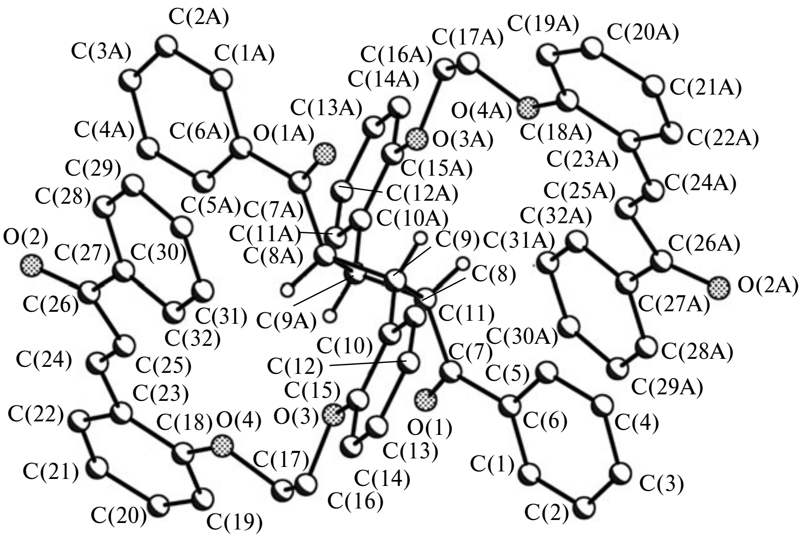


Fig. 9. Geometry of a molecule of cyclobutane-containing dipodand **2a** according to the X-ray diffraction data.

The molecular structure and type of stereoisomerism of the cyclobutane moiety of dipodand **2a** assigned to the point symmetry group C_i were unambiguously confirmed by the X-ray diffraction analysis for the crystal grown from an acetonitrile solution (Fig. 9). The molecule is situated in the symmetry center of the crystal and, therefore, its four-membered cycle is rigidly planar. In cyclobutane the C(8)—C(9) (1.546(1) Å) and C(8)—C(9A) (1.574(1) Å) bond lengths differ insignificantly, as well as the conjugated angles C(9A)—C(8A)—C(9) and C(8)—C(9)—C(8A) (91.33(1)° and 88.67(1)°, respectively). The torsion angles C(10A)—C(9A)—C(8)—C(7) and C(10)—C(9)—C(8)—C(7) are 102.7(2)° and 1.2(2)°, respectively.

Thus, the mechanical destruction of crystal **1a** allows the PCA reaction to occur in the solid phase. It is most likely that this treatment increases the surface of the polycrystalline sample, which contains stacking dimers preorganized to PCA and partially withdrawn from the rigid environment of the crystalline lattice.

On the contrary, as mentioned above, on going to **1b** an elongation of the oxyethylene fragment in molecules favor the formation of a system of parallel ethylene dimers with better (than in **1a**) initial geometric characteristics of preorganization to the PCA reaction (see Fig. 5). In turn, an increase in the reactivity of molecules **1b** results in the occurrence of the PCA process in the whole volume of the sample irradiated with the visible (or solar) light for 50—60 h at 25—30 °C. The crystal decomposes during the reaction retaining its shape and remaining almost transparent. This is indicated by both the disappearance of the diffraction pattern from the irradiated single crystals and the fact that the former single crystals stop quenching during their rotation under a microscope in the polarized light. In addition to the loss of crystallinity of the initial sample, the polymerization process in the single crystals of podand **1b** due to photolysis is accompanied by the appearance of many small cracks on the surface (Fig. 10). Similar morphological changes occur in single crystals of 2,5-distyrylpyrazine.[5] Analogous processes

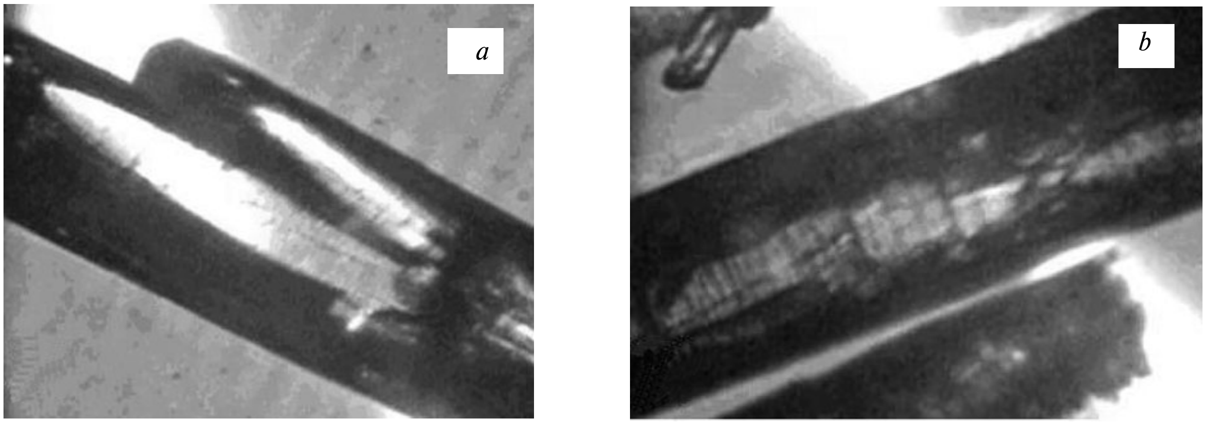


Fig. 10. Crystals of compound **1b** before the irradiation with the visible light (*a*) and after irradiation for 24 h (*b*).

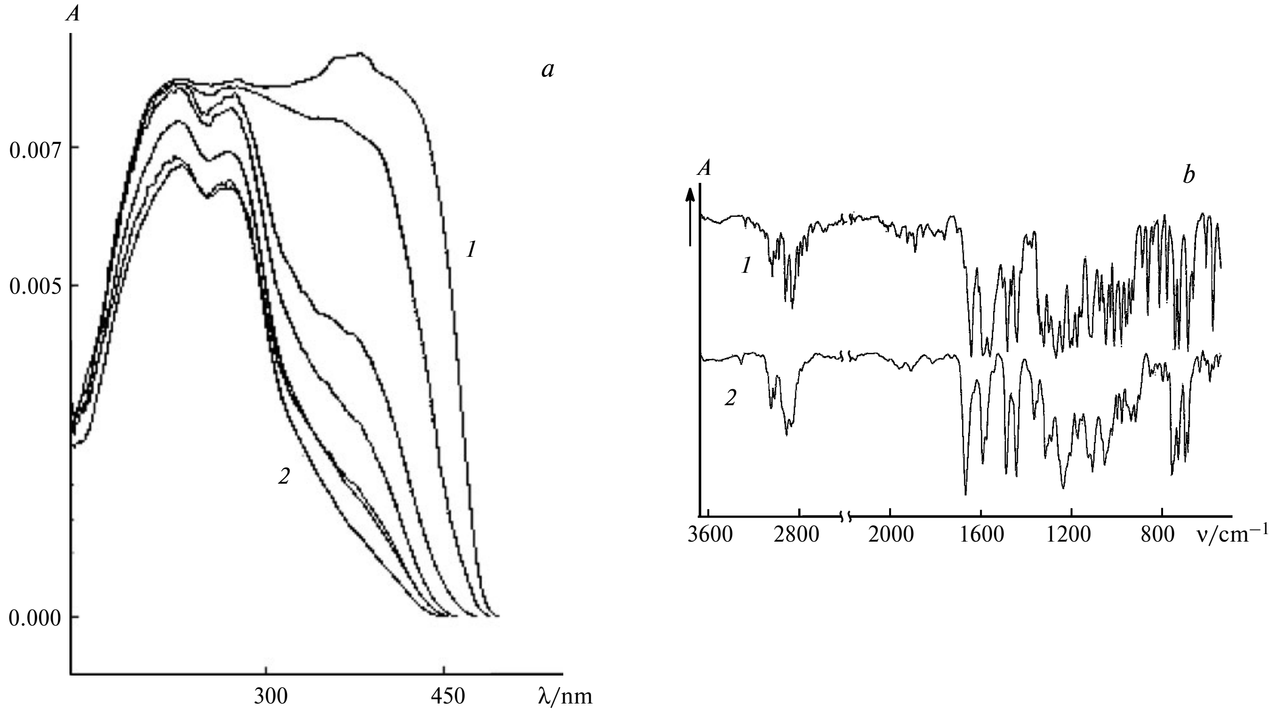


Fig. 11. (*a*) UV absorption spectra (DRA) of compound **1b** upon the visible light irradiation: the starting compound (*1*) and the product of the PCA reaction (*2*); (*b*) IR absorption spectra (DRA) of chalcone podand **1b** (*1*) and cyclobutane-containing oligomer **2b** (*2*).

caused by the accumulation of disordering regions in the crystal along with cracking of the initial samples have been observed earlier for the styryl dyes.[15,18]

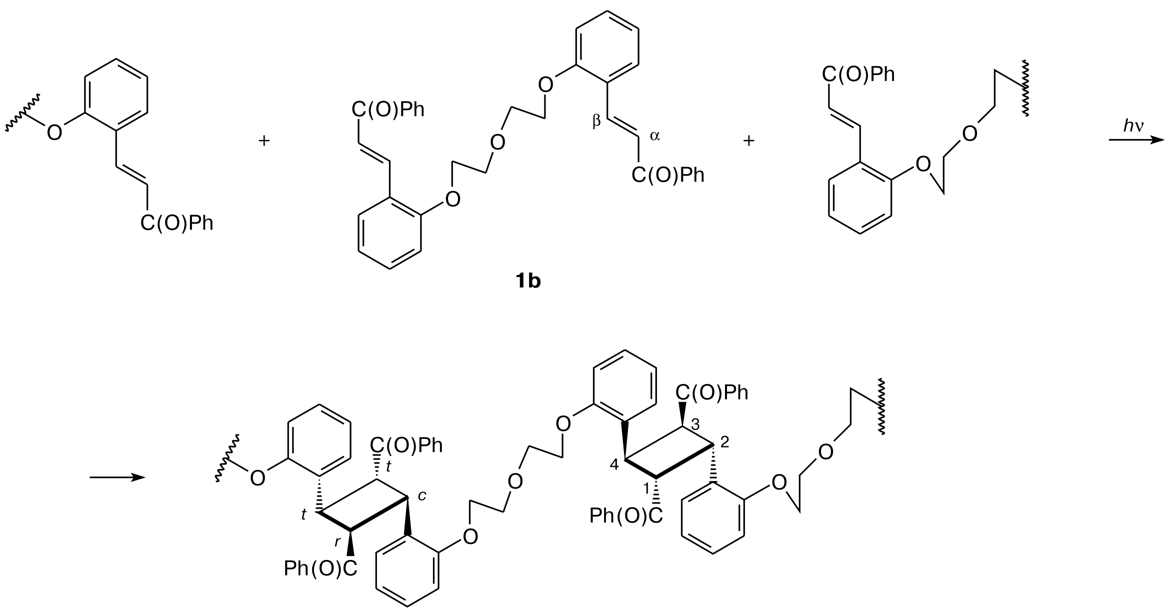
In the UV spectra (DRA) of the chalcone podand, the disappearance of conjugation of the chromophoric moieties is accompanied by a decrease in the light absorption maximum ($\lambda = 370$ nm) with the simultaneous hypsochromic shift of the absorption band in the wavelength region 288—460 nm (Fig. 11). Similarly, the IR spectra (DRA) (see Fig. 11) exhibit the disappearance of the IR absorption band at 1567 cm^{-1} responsible for stretching vibrations of the C=C bond of the propenone moiety. On the contrary, the formation of the cyclobutane ring is observed as the appearance of a new absorption band at 2926 cm^{-1} (the region of stretching vibrations of the C—H bonds) and the high-frequency shift by 22 cm^{-1} of the absorption maximum of stretching vibrations of the carbonyl group (1672 cm^{-1} (C=O)).

The transition of the ordered structure of single crystals to the "pseudomorphous" state[5] during the PCA did not allow the X-ray diffraction study to be carried out and, therefore, the compound was characterized using IR, Raman, and ^{1}H NMR spectroscopy. As known, the structure of topochemical reaction products in crystals is directly determined by the supramolecular preorganization of the initial compounds. Based on the X-ray diffraction analysis of the molecular packing of podand **1b**, we proposed the following scheme for the synthesis of compound **2b** (Scheme 2).

The formation of the [2+2] cycloaddition product was detected in the ^{1}H NMR spectra by the disappearance of signals of protons of the ethylene moiety of chalcone at δ 7.95 and 8.01 in the region of signals of aromatic groups and by the appearance of the symmetric spin system (AA´BB´) of protons at δ 5 characteristic of *rctt*-cyclobutane (Fig. 12). Only one set of signals of protons in the spectrum indicated that the process is stereospecific. The multiplicity of signals of protons of the four-membered cycle has a shape of doublets of doublets with the SSCC $^3J_{1,2} = 10.8$ and $^3J_{2,3} = 7.6$ Hz analogous for the signals of protons of the cyclobutane moiety of dipodand **2a** (see Fig. 6). Thus, the formation of the four-membered cycle of α-truxillic structure is confirmed by both the type of the spin system of protons of the cyclobutane moiety[28,31] and the structural preorganization "head-to-tail" of the chalcone groups of the adjacent molecules in the crystal packing of compound **1b** (see Fig. 5).

This assertion is indicated by substantial differences in the IR and Raman spectra[32] of compound **2b** in the wavelength region from 500 to 2000 cm^{-1}. The product of **2b** dimerization is characterized by the IR absorption bands at 1370, 1320, 1177, 1110, 982, 941, 920, 699, and 687 cm^{-1} and the signals in the Raman spectrum at 1208, 1160, 1028, 959, 843, and 616 cm^{-1}. According to the rule of "alternative inhibition" for molecules with the point symmetry group C_i (the cyclobutane ring of the α-truxillic type is characterized by the C_i symmetry), the normal vibration (A_g, A_u) can be active either only in IR spectra,

Scheme 2



or only in Raman spectra.[33] Indeed, the comparison of the spectral data shows the absence in the Raman spectra of a series of bands responsible for stretching and bending vibrations of the hydrocarbon skeleton and identical to absorption bands in the IR spectrum and *vice versa*.

An important evidence for polymer chain formation is some broadening of all signals of protons in the ^{1}H NMR spectrum and of the IR absorption bands in the region of stretching vibrations of the C—H bond (2950—2750 cm^{-1}) and bending vibrations of the C—O—C bonds of the oxyethylene moiety (1238—1057 cm^{-1}) (see Figs 11, 12). The linear structure of compound **2b** is confirmed by the ^{1}H NMR broadened singlet signal of the geminal protons bonded to the second carbon atom of the oxyethylene moiety (Ar—O—CH$_2$—C$\underline{H}_2$—O). For comparison, in the macrocycles (for example, of cyclobutane-containing dibenzocrown ether[22]) considerable changes in the polyether chain geometry affect the complication of the spin system of all protons of this fragment. The X-ray diffraction analysis results for compound **1b** suggest that a stereoregular polymer in the form of a macromolecular helix is formed during the photoinitiated self-assembling of chalcone podand molecules in crystal due to the oxyethylene moiety (see Fig. 5, Scheme 2). Since the ^{1}H NMR spectrum of compound **2b** contains no chemical shifts of protons of the terminal chalcone groups, the number of units (*n*) in the oligomer chains can approximately be estimated (more than 100).

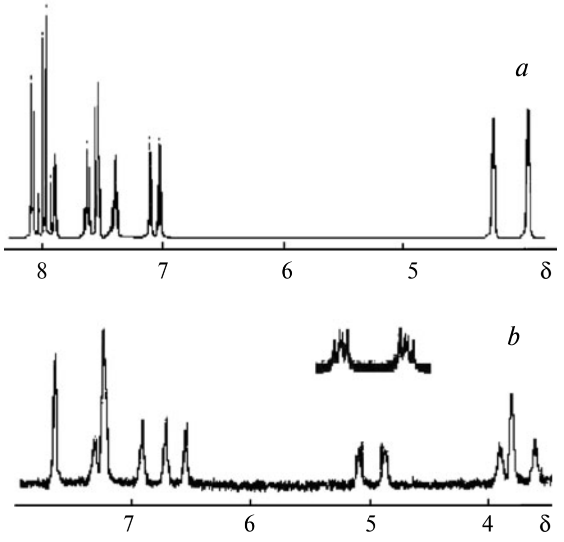


Fig. 12. ^{1}H NMR spectra of chalcone podand **1b** (*1*) and cyclobutane-containing oligomer **2b** (*2*).

Thus, the influence of the structural preorganization of chalcone podands **1a** and **1b** with the propenone group in the *ortho*-position to the polyether fragment of the bridging aryl substituent on the ability to photoinduced [2+2] cycloaddition reactions under the solid-phase synthesis conditions. An example of rare stereospecific photopolymerization for compound **1b** in crystals belonging to the space group *C*2/*c* was found. A substantial role of both topochemical control from adjacent molecules and the oligooxyethylene fragment length in the molecules in controlling of the distance between approached double C=C bonds of the intermolecular sandwich system was revealed. An increase in the polyether chain length on going from compound **1a** to **1b** was found to favor the appearance of rather loose regions in the crystal surrounding the dimeric π-stacking fragments and, as a consequence, the depth of occurrence of the PCA reaction (over the whole crystal volume). However, this conformational tuning was insufficient to compensate internal strains in the crystal and to retain its structure.

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References

1. J.-M. Lehn, *Supramolecular Chemistry. Concepts and Perspectives*, VCH, Weinheim, 1995, Ch. **8**.
2. T. Subbiah, G. S. Bhat, R. W. Tock, S. Parameswaran, S. S. Ramkumar, *J. Appl. Polym. Sci.*, 2005, **96**, 557.
3. L. R. MacGillivray, G. S. Papaefstathiou, T. Friščić, D. B. Varshney, T. D. Hamilton, *Top. Curr. Chem.*, 2005, **248**, 201.
4. D. A. M. Egbe, B. Carbonnier, E. L. Paul, D. Mühlbacher, T. Kietzke, E. Birckner, D. Neher, U.-W. Grummt, T. Pakula, *Macromolecules*, 2005, **38**, 6269.
5. M. Hasegawa, *Chem. Rev.*, 1983, **83**, 507.
6. L. Addadi, J. Mil, M. Lahav, *J. Am. Chem. Soc.*, 1982, **104**, 3422.
7. K. Tashiro, T. Kamae, M. Kobayashi, A. Matsumoto, K. Yokoi, S. Aoki, *Macromolecules*, 1999, **32**, 2449.
8. A. Matsumoto, S. Oshita, D. Fujioka, *J. Am. Chem. Soc.*, 2002, **124**, 13749.
9. R. O. Al-Kaysi, R. J. Dillon, J. M. Kaiser, L. J. Mueller, G. Guirado, C. J. Bardeen, *Macromolecules*, 2007, **40**, 9040.
10. M. D. Cohen, G. M. Schmidt, *J. Chem. Soc.*, 1964, 1996.
11. M. D. Cohen, G. M. Schmidt, F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.
12. G. M. Schmidt, *J. Chem. Soc.*, 1964, 2014.
13. M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara, H. Nakanishi, *J. Am. Chem. Soc.*, 1985, **107**, 2788.
14. M. Berrada, F. Carriere, P. Nonjol, H. Sekiguchi, *Chem. Mater.*, 1996, **8**, 1022.
15. L. G. Kuz´mina, A. I. Vedernikov, S. K. Sazonov, N. A. Lobova, P. S. Loginov, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Kristallografiya*, 2008, **53**, 460 [*Crystallogr. Repts* (*Engl. Transl.*), 2008, **53**].
16. A. I. Vedernikov, L. G. Kuz´mina, S. K. Sazonov, N. A. Lobova, P. S. Loginov, A. V. Churakov, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1797 [*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1860].
17. L. G. Kuz'mina, A. I. Vedernikov, N. A. Lobova, A. V. Churakov, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *New J. Chem.*, 2007, **31**, 980.
18. L. G. Kuz´mina, A. I. Vedernikov, J. A. K. Howard, M. V. Alfimov, S. P. Gromov, *Ros. Nanotekhnologii* [*Russian Nanotechnologies*], 2008, **3**, Nos 7—8, 32 (in Russian).
19. S. Akabori, Y. Habata, M. Nakasawa, Y. Yamada, Y. Shindo, T. Sugimura, S. Sato, *Bull. Chem. Soc. Jpn*, 1987, **60**, 3453.
20. S. Akabori, T. Kumagai, Y. Habata, S. Sato, *Bull. Chem. Soc. Jpn*, 1988, **61**, 2459.
21. I. G. Ovchinnikova, O. V. Fedorova, P. A. Slepukhin, I. A. Litvinov, G. L. Rusinov, *Kristallografiya*, 2009, **54**, 32 [*Crystallogr. Repts* (*Engl. Transl.*), 2009, **54**].
22. I. G. Ovchinnikova, O. V. Fedorova, P. A. Slepukhin, G. L. Rusinov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 204 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 209].
23. *SAINT, Version 6.02A*, Bruker AXS Inc., Madison, Wisconsin (USA), 1997.
24. *SHELXTL-Plus, Version 5.10*, Bruker AXS Inc., Madison, Wisconsin (USA), 1997.
25. G. M. Sheldrick, *Acta Crystallogr.*, *Sec. A*, 1990, **46**, 467.
26. G. M. Sheldrick, *Acta Crystallogr.*, *Sec. A*, 2008, **64**, 112.
27. M. D. Cohen, A. Ludmer, V. Yakhot, *Chem. Phys. Lett.*, 1976, **38**, 398.
28. A. I. Vedernikov, S. P. Gromov, N. A. Lobova, L. G. Kuz´mina, Yu. A. Strelenko, J. A. K. Howard, M. V. Alfimov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 1896 [*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 1954].
29. J. Harada, K. Ogawa, *J. Am. Chem. Soc.*, 2004, **126**, 3539.
30. F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry. Part A; Structure and Mechanisms, 5. Photochemistry*, Springer US, New York, 2007, **12**, 1073.
31. G. Montaudo, S. Caccamese, *J. Org. Chem.*, 1973, **38**, 710.
32. S. D. M. Atkinson, M. J. Almond, G. A. Bowmaker, M. G. B. Drew, E. J. Feltham, P. Hollins, S. L. Jenkins, K. S. Wiltshire, *J. Chem. Soc.*, *Perkin Trans. 2*, 2002, 1533.
33. Yu. A. Pentin, L. V. Vilkov, *Fizicheskie metody issledovaniya v khimii* [*Physical Methods of Investigation in Chemistry*], Mir, Moscow, 2006, 683 pp. (in Russian).

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