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Molecular Conformation and Structural Changes in Crystalline Photochromism of 3-Furylfulgide

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The conformational changes of the photochromic 3-furylfulgide molecule have been studied in relation to its crystal structure. Intense two-photon irradiation of an initial pale yellow single crystal led to a red material that is no longer crystalline but still photochromic. Conversely, starting from a colored single crystal grown from an irradiated solution, X-ray diffraction gave the first determination of the molecular conformation and crystal structure of the colored form and showed that after visible irradiation the bleached material also lost its crystalline structure. The photoinduced molecular displacements responsible for this behavior are pointed out.

Introduction

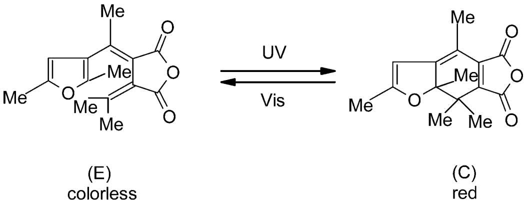
Photochromic compounds have attracted much attention because of their potential applications in molecular switches and optical data storage.[1,2] Although a large number of photochromic molecules have been synthesized and studied, only a few of them exhibit photochromism in the crystalline phase.[3−13] This is generally due to the large conformational change resulting from the photocoloration process, which occurs with difficulty in a rigid medium like a crystal. Thermal stability of the photogenerated isomer is often a necessary condition to their use in optoelectronic devices, but only some classes present this property, in particular in the single-crystalline phase.[4,13e]

Fulgides constitute a class of photochromic compounds that undergo reversible electrocyclic ring-closure and ring-opening reactions.[14−16] These reactions are induced respectively by UV and visible light irradiation, giving the closed C and open E isomer according to Scheme 1. A third isomer, Z, can be obtained by UV irradiation of E in solution but not in the crystal and consequently will not be considered here.[16,18]

Numerous studies in solution showed that upon UV irradiation an absorption band characteristic of the colored C form appears, strongly red-shifted with respect to the absorption band of the colorless E form, indicating a large delocalization of the electronic cloud.[14−17] Important changes in the molecular structure are thus expected in the absence of environmental constraints. Among the fulgides, the 2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidenesuccinic anhydride, or more briefly 3-furylfulgide, exhibits thermal stability of both isomers at room temperature and high conversion efficiencies of back and forth reactions.[18−21] Different fulgide derivatives were synthesized in order to improve their photochemical fatigue resistance property.[22]

In the crystal, photochromism of fulgides has also been observed but considered to be limited to the surface and at defect sites for two kinds of molecules: 3-thienylfulgide[23] and 3-naphthylfulgide.[24] For 3-furylfulgide, photochromism in the solid state was reported for the first time by Ulrich and Port.[18] More recently, reflection measurements on irradiated single crystals of 3-furylfulgide have shown that the photoproduced C molecules form a thin film of a few tens of nanometers, suggesting that the reaction takes place inside the crystal.[25]

SCHEME 1: Photochromism of 3-Furylfulgide



The occurrence of the photochromic reaction in the bulk would prove a compatibility between the modifications of the molecular conformation and of the crystal structure. There must be either sufficient free volume available in the crystal lattice to allow large rotations of parts of the molecules, as required in the electrocyclization of fulgides, or a change of the crystal structure itself. The aim of the present work is to verify the assumption of a reaction involving molecules inside a crystal of 3-furylfulgide, and then to test how far the conformational change resulting from the E ↔ C conversion modifies the crystalline organization.

Spectroscopic measurements on irradiated thin polycrystalline films, in which the reversibility of the coloring−bleaching processes have been checked, are reported and permit an estimate of the photoconversion efficiency. When dealing with bulky crystals (of ca. 1 mm thick), simple UV irradiation is not adapted due to the strong absorption of the medium at these wavelengths and to the limited penetration depth of the excitation. To overcome this limitation and thus transform a large amount of the crystalline sample, a two-photon irradiation technique has been performed on single crystals of the E isomer. We report here that, as long as the phototransformation efficiency is low, no significant changes in the crystal structure are observed but that it is no longer true when a long UV

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irradiation is applied either to polycrystalline thin films or to single crystals. The reverse experiment, i.e., bleaching of the C form upon visible irradiation, was conducted on previously irradiated E crystals and on pure crystals of the colored C isomer, as we succeeded in obtaining such crystals from an irradiated solution. In addition, X-ray analysis delivered the conformation of the closed form together with its crystal structure.

Experimental Section

Sample Preparation. The E and the Z isomers were synthesized according to the method previously described.[26] Their purity was checked by thin-layer chromatography (7:1 *n*-hexane:ethyl acetate as eluent on silica gel). Good yellow single crystals of E were obtained by slow evaporation from propan-2-ol. A crystal of size $0.4 \times 0.2 \times 0.2$ mm^3 and of good optical quality was chosen for data collection.

The 7,7a-dihydrobenzofuran derivative, i.e., the C isomer, was obtained by irradiation of a solution of E isomer in propan-2-ol at 330 nm. The solution was then slowly evaporated at room temperature in the dark until crystallization occurred. A deep red crystal of size $0.40 \times 0.35 \times 0.20$ mm^3 was used for X-ray analysis.

Thin polycrystalline films of the E isomer were obtained from crystals brought up to their melting point (120 °C) and then crystallized by growth between quartz plates. The film thickness was not controlled but ranged between 1 and 10 μm.

Irradiation Conditions and Spectroscopic Measurements. UV and visible irradiations were performed with a 150-W xenon lamp in association with glass filters of 100 nm bandwidth, centered respectively at 330 and 520 nm.

Two-photon excitation of single crystals of E was accomplished with a Ti:sapphire laser tuned to 720 nm and moderately focused onto the sample. The beam waist was of ca. 10 μm and the Rayleigh range was longer than the crystal thickness. The polarization and the laser power were adjusted in order to reach a good efficiency and to avoid crystal damage. The whole sample was scanned by use of a piezoelectric device.

Absorption spectra of thin crystalline samples were recorded with a Lambda-9 Perkin-Elmer spectrophotometer.

X-ray Crystallographic Analysis. X-ray crystallographic analysis was performed on single crystals at 296 K, on a MACH3 Enraf-Nonius diffractometer with Ag Kα radiation ($\lambda = 0.5608$ Å). The experimental parameters used during the intensity measurements and additional experimental details are given in the Supporting Information. The structure was solved by direct methods and refined by the full-matrix least-squares method based on F with TeXsan software.[27] H-atoms were located by difference Fourier syntheses but not refined. Their B_{iso} values were fixed by the software as similar values for their adjacent C- or O-atom equivalent isotropic parameters.

Results and Discussion

1. Photochromism of Thin Polycrystalline Films. The crystalline character of the films obtained from the melt have been checked by observation under an optical microscope with crossed polarizers. Extinction of the analyzing light is successively observed for different parts of the samples by rotation in the observation plane, proving that the films are made of differently oriented single crystalline zones. Absorption spectra of a thin polycrystalline film of 3-furylfulgide is shown in Figure 1a, before any irradiation (spectrum 1) and after UV irradiation for 360, 1500, and 4500 s (spectra 2−4, respectively). The absorption increase at $\lambda_{\max} = 520$ nm is assigned to the C isomer and the concomitant decrease at 350 nm to the decay of the E form (Figure 1b). The slight absorption increase at 350 nm observed at short irradiation durations (<400 s) is not relevant because of saturation. Indeed, the measured optical density in the UV region of the spectra shows a saturationlike maximum value of ~1.8, whereas much larger values are expected for strongly absorbing materials. This behavior is explained by the structure of the crystalline sample under study, which is very thin (see below) and presents holes through which the analyzing light is partially transmitted, artificially decreasing the optical density value for strong absorption. A small spatial drift of the irradiating beam is then able to modify this apparent saturation maximum. Thicker films do not present such holes but their UV absorption is so strong that no decay of the E isomer can be detected, and thus the use of very thin films was preferred to gain more information about the photoinduced process.

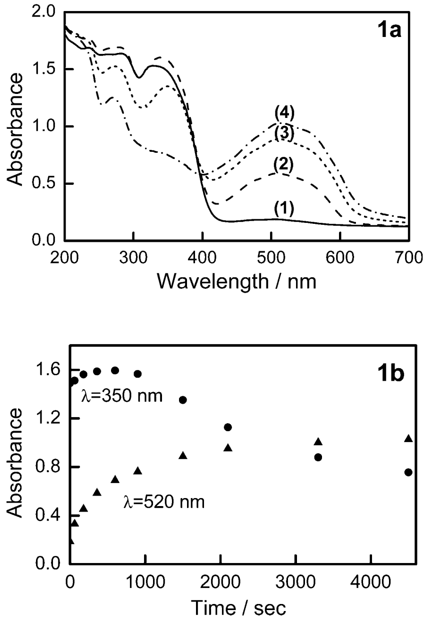

Figure 1. (a) Absorption spectra of a thin crystalline film of 3-furylfulgide before irradiation (1) and after 360(2), 1500 (3), and 4500 (4) s of irradiation with 330-nm light. (b) Corresponding time evolution of the absorbance at 350 and 520 nm as a function of irradiation duration.

The UV light penetration depth can be estimated to be less than 150 nm for a pure crystalline sample of the E form by taking a value of 6000 M^{-1} L cm^{-1} for $\epsilon_{\max}$,[17] but this depth increases during irradiation as the concentration of the E molecules decreases. Assuming that, like in solution, the reaction efficiency could reach ~95%, the contribution of the C molecules to the total absorption at 350 nm becomes comparable to that of the E ones as $\epsilon_E/\epsilon_C \sim 20$,[17] and the penetration depth is enhanced by about 1 order of magnitude. The observation that the optical density around 350 nm (Figure 1b) decreases after an irradiation of about 1500 s and becomes measurable indicates that the sample is not thicker than 1 μm. From the large OD decrease in the UV, a lower limit of roughly 50% can be given to the conversion efficiency from the E form to the C one. As the amount of molecules localized either on surfaces, at defects, or on domain walls is much smaller than this value, it is assumed that the photochromic reaction occurs in the bulk. This assumption is confirmed by the two-photon experiments described below.

The OD increase in the visible region of the spectrum and the concomitant OD decrease at 350 nm exhibit a saturation phenomenon that corresponds to the building up of a photo-

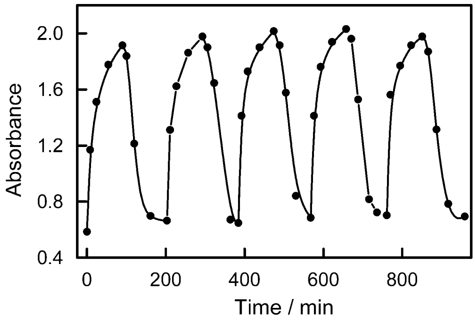

Figure 2. Absorbance changes at $\lambda = 520$ nm during alternative irradiations with 330- and 520-nm light.

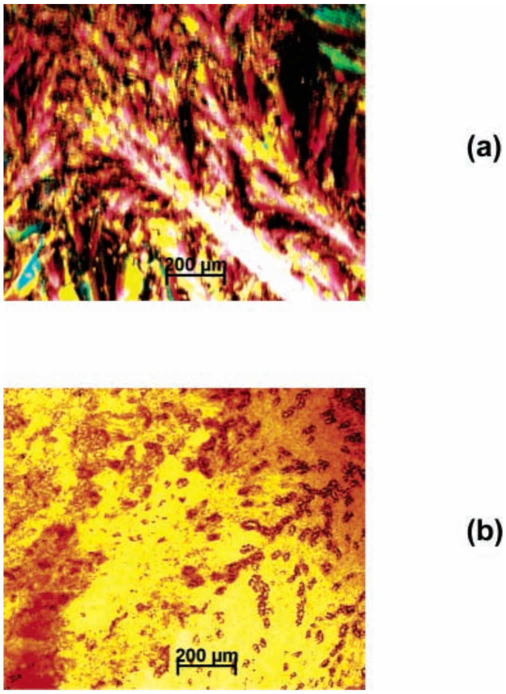

Figure 3. Photographs of a thin polycrystalline film of 3-furylfulgide between crossed polarizers before (a) and after (b) irradiation with 330-nm light.

stationnary state (Figure 1b). In thicker crystalline films, a saturation of the coloration is also observed but is in this case related to the UV light attenuation inside the sample, limiting the proportion of E isomer transformed into C.

The reversibility of the coloring−bleaching process in thin crystalline films has been checked by alternative UV and visible irradiation cycles of the same duration, using the same lamp and only changing the filtering conditions (see Experimental Section). The change in optical density during successive cycles is reproducible within a few percent (Figure 2), indicating that the photochemical fatigue of the system is low under these conditions of irradiation and cannot be responsible for the large structural modification visible on the photographs of the sample taken with an optical microscope before and after 6 coloring−bleaching cycles (Figure 3).

It appears that the structure of the film changed dramatically upon irradiation. Moreover, as no extinction of the light transmitted by irradiated films placed between crossed polarizers could be observed, we concluded that successive coloring−bleaching cycles induced a loss of crystalline order in the initially polycrystalline films.

2. Photocoloration of Single Crystals of Isomer E. Single crystals of the E isomer have been grown in order to get crystallographic information on the molecule and crystal structures before and after irradiation. Different determinations of the structure of 3-furylfulgide E isomer have been reported previously,[18,28,29] but we determined the structure again to compare it with those of irradiated samples.

Figure 4. Photograph of a single crystal of 3-furylfulgide in which photochromism results from a two-photon irradiation with a 720-nm light.

The first step was to confirm that the phototransformation is possible in the bulk of the material, as proposed from measurements on thin films, and then to obtain a good efficiency for it. For this purpose UV light was revealed to be not adapted because of its low penetration depth, limited to a few micrometers as described above. We overcome this limitation by using a two-photon absorption technique. The photograph of Figure 4, obtained with an optical microscope, shows a crystal on which a focused beam issued from a Ti:sapphire laser is sent from top to bottom. The phototransformation is clearly seen all along the light path inside the crystal, demonstrating that it occurs in the bulk.

A first attempt to transform an entire crystal was made on a sample of size $1 \times 0.4 \times 0.4$ mm^3 scanned with a beam of radius ~10 μm and a moderate laser power (20 mW) to avoid heating of the sample. Despite a very long irradiation time (more than 20 h), X-ray diffraction analysis of the resulting colored crystal indicated that most of the molecules were still open-ringed and that there were no significant changes in the cell parameters, except a small increase of the cell volume, which changed from 1350 to 1362 Å^3. Such a slight increase after a photochromic reaction in solids was previously reported for salicylideneaniline crystals, in which the occupancy factor of the phototransformed molecule was ~10%.[30] An estimation of the transformation efficiency in the irradiated E crystal was made by solving it in toluene and measuring the OD. As the crystal sizes were measured we could get a solution of known concentration and by use of an extinction coefficient value of 10 000 for the C isomer,[17] we found that the transformation efficiency was about 4%. This explains why no conformational changes (ring opening) of the molecules were detected and reflects that the transformation is difficult to achieve in the crystal, even if the coloring quantum yield has been reported to be quite high in thin films (20% ± 10%).[18]

A second attempt was performed on a much smaller crystal for which a much better conversion was reached. This could be seen by eye only, as the too-small size of this crystal forbade a correct determination of the transformation efficiency. Nevertheless, it showed that a dramatic modification of the crystal structure occurred as the sample was no longer diffracting X-rays. It leads to the conclusion that a high conversion efficiency from the E form to the C form is not possible in the crystal and leads to the loss of crystalline order.

We checked that the molecule itself was not destroyed, as it was always possible to bleach the sample with white light and to color it again with UV light, keeping the same absorption spectra.

3. Structure and Bleaching of Colored C Crystals. As mentioned above, we were able to grow a pure single crystal of the C isomer starting from a solution of the E isomer irradiated with UV light up to the photostationary state. X-ray

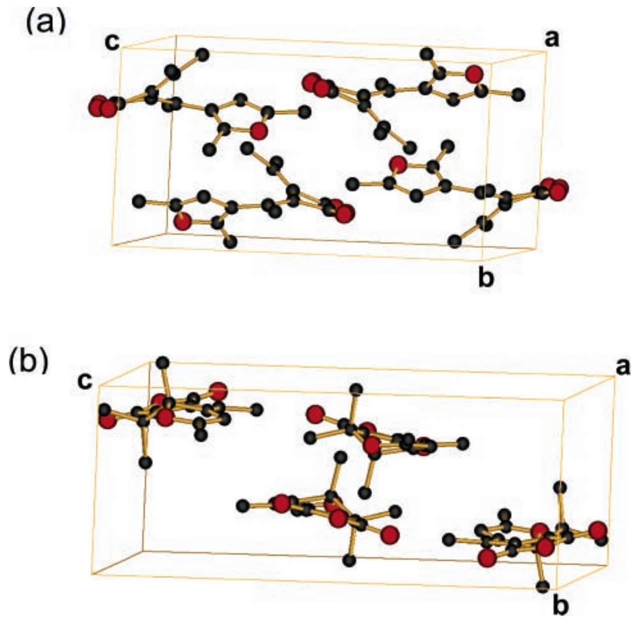

Figure 5. Unit cells of (a) open E isomer and (b) closed C isomer of 3-furylfulgide single crystals, drawn with the same scale for comparison.

TABLE 1: Crystallographic Parameters of E and C Isomers of 3-Furylfulgide at 296 K

	E crystal	C crystal
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
cell parameters		
a (Å)	12.525(4)	11.145(2)
b (Å)	7.770(3)	7.206(3)
c (Å)	14.706(9)	17.677(3)
β (deg)	109.40(4)	105.210(10)
Z	4	4
cell volume V (Å^3)	1350(1)	1370.0(6)
R	0.073	0.072

analysis of this crystal gave the following crystallographic data which are compared to those obtained for the E isomer crystal in the same experimental conditions (Table 1).

This is the first crystallographic characterization of the C isomer of 3-furylfulgide. The structure of only two C isomers of fulgides have been determined previously, one for a (*R*)-binaphthol-condensed indolylfulgide,[31] for which no photochromism has been observed in the crystalline state, and the other one for 3-thienylfulgide, in which the solid-state photochromism has been reported to be limited to the surface.[23]

E forms of fulgides are considered to exist as racemic mixtures of helical chirality due to the spiral array of the two methylene substituents on the succinic anhydride ring.[23,31] C forms exhibit also chirality, originated in the appearance of an asymmetric carbon upon cyclization. The E isomer of 3-furylfulgide crystallizes in the monoclinic achiral space group $P2_1/n$, possessing an inversion center and a 2-fold spiral axis along the *b* axis, with four molecules in the unit cell; the two mirror symmetric molecular conformations are arranged in segregated stacks along the *b* axis.[18] The C isomer of 3-furylfulgide (Table 1) crystallizes in the same space group as the E isomer with only a slight enhancement of the cell volume, but a large discrepancy appears on the *c* parameter and to a less extent on the other ones. Packing of the molecules of E and C isomers in their respective unit cells is given in Figure 5.

The structural parameters obtained by X-ray analysis for both isomers are collected in Table 2. The conformation of the C isomer was previously optimized by using ab initio molecular orbital theory,[32] and these data are in relatively good agreement with those obtained here (Table 2).

TABLE 2: Structural Parameters of the E and C Isomers of 3-Furylfulgide

	E isomer (X-ray)	C isomer[a] (theory)	C isomer (X-ray)
Bond Distances (Å)			
C1−C2	1.454(7)	1.325	1.346(5)
C1−C3	1.473(8)	1.520	1.484(6)
C2−C4	1.470(9)	1.513	1.449(5)
C1−C8	1.342(7)	1.485	1.428(5)
C2−C9	1.339(8)	1.536	1.515(5)
C8−C10	1.472(7)	1.328	1.359(5)
C10−C11	1.439(7)	1.471	1.410(5)
C10−C12	1.341(7)	1.544	1.515(5)
C11−C13	1.303(7)	1.328	1.327(5)
C9−C12	3420(8) (not a bond)	1.571	1.528(5)
Bond Angles (deg)			
C2−C1−C8	132.6(5)	123.5	125.0(3)
C1−C2−C9	131.1(5)	124.0	123.2(3)
C1−C8−C10	124.0(5)	114.8	113.8(3)
C8−C10−C12	128.3(5)	122.3	120.2(4)
C11−C10−C12	106.0(5)	103.7	105.8(3)
C10−C11−C13	107.3(5)	108.1	108.6(3)
Torsional Angles (deg)			
C3−C1−C2−C4	−16.7	1.5	4.6
C8−C1−C2−C9	−38.2	2.3	0.4
C2−C1−C8−C10	−11.3	−13.9	−10.1
C1−C8−C10−C12	−38.8	−9.8	−14.1
C12−C10−C11−C13	1.1	10.4	9.8

[a] From ref 32.

The huge conformational differences between E and C forms are clearly visible in Figure 6. Whereas the succinic anhydride and the furan ring are considerably twisted relative to each other in the E isomer, the C isomer is nearly planar, as predicted by the ab initio calculations.[32] The experimental value of the torsional angle (C1−C8−C10−C12) is lowered from 38.8° in the E isomer down to 14.1° in the C one.

A large number of studies conducted on diarylethenes in the single-crystalline phase have established a reactivity−structure relationship for this class of molecules.[13a,33] It was concluded that photocyclization of diarylethenes can occur in the crystal only when the distance between the reactive carbons is smaller than 4.2 Å. In the furylfulgide molecules reported to exhibit photochomism in the crystalline phase, the distances between the reactive carbons are 3.9(1) Å for 3-thienylfulgide,[23] 3.62 Å for 3-naphthylfulgide,[24] and 3420 Å in the 3-furylfulgide studied here. For the first two molecules, the photoreaction is considered to be limited to surfaces and defect sites. The reason invoked for the lack of photochromism inside crystals of 3-thienylfulgide is not a geometrical one at the molecular scale but is related to the packing of molecules inside the crystal. Despite a close resemblance between the unit cell dimensions of E and C crystals, the difference in the packing of the E and C 3-thienylfulgide molecules does not permit the transformation into a single crystal: a single crystal of E consists of molecules with the same chirality, whereas a single crystal of C consists of a racemic mixture.[23] In 3-furylfulgide, both E and C crystals consist of racemic mixtures. Molecules of E of a given chirality can undergo cyclization to molecules of C of the same chirality. As the packing of molecules is similar in C and E crystals, with the same symmetry elements and the same number of molecules in the unit cell, transformation between E and C single crystals of 3-furylfulgide can be expected.

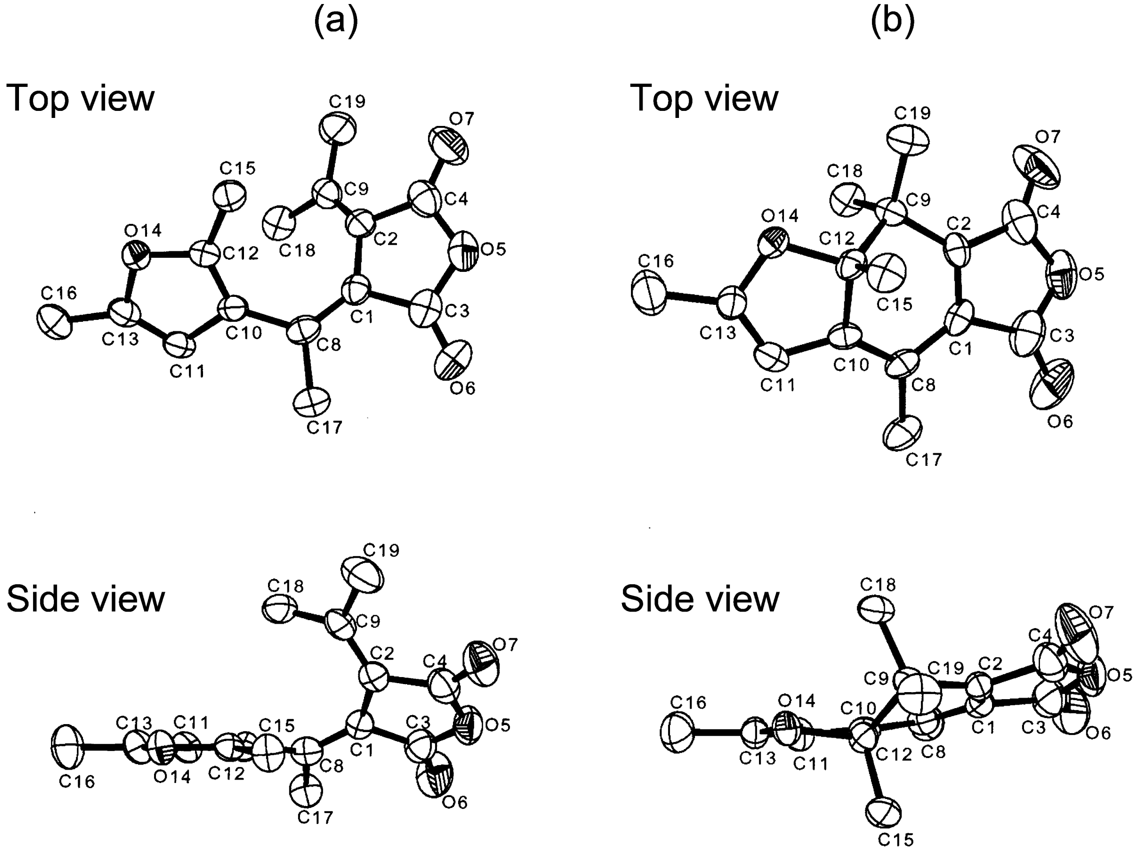

Figure 6. Molecular structures of the two isomers of 3-furylfulgide: (a) open E isomer; (b) closed C isomer.

From the photograph of Figure 4 we have concluded that the transformation occurs inside the crystal. When the conversion efficiency remains low, typically smaller than 10%, the crystalline parameters of the E crystal are unchanged, indicating that the crystalline network is able to accept such transformations. No fracture of the crystal is observed in this case. For larger conversion efficiency from E to C, some fractures are observed at a first step, followed by the loss of the crystalline character of the sample. This indicates that a phase transition between the crystallographic structures of E and C molecules does not occur, even if the crystalline structures of the two isomers are the same, with the same symmetry elements, a R (right) or L (left) molecule of E giving rise to respectively the corresponding R or L molecule of C and reciprocally.

Besides the large changes in the molecular conformation in going from the E to the C molecule, large relative molecular displacements in the unit cell are also observable as can be seen in Figure 5. The C molecules are more planar than the E ones and thus better packing along the *b* axis is possible, explaining the shortening of the *b* parameter in C crystals. Moreover, two adjacent molecular planes that are perpendicular to *b* are sliding in opposite *c* directions in E and C, explaining the increase of this parameter. This leads to the conclusion that the crystalline order cannot be maintained in the transformation.

Finally a crystal of the C isomer was irradiated with visible light until complete bleaching was achieved. X-ray analysis of this sample was done but it was no longer diffracting. We checked that, as verified for a crystal of E, the fulgide molecule is still present and that the sample can be colored again by UV irradiation. The behavior of the crystal after partial bleaching and the relation between C to E transformation efficiency and crystal structure are under investigation.

Conclusion

It has been unambiguously demonstrated that the photochromic reaction of 3-furylfulgide occurs in single crystals and is not limited to surfaces or defect sites. For a low transformation efficiency, the photoinduced disorder resulting from molecular conformational changes can be viewed as localized defect sites perturbing only slightly the crystalline structure. For high conversion efficiencies, the initially crystalline samples become amorphous, without any noticeable fatigue of the photochromic molecule. The structure of the C isomer has been elucidated from X-ray analysis. The observed large differences in the E and C molecular conformations associated with the large variations of the cell parameters in going from the E to C crystal explain why a complete transformation in the crystal is not possible without losing the crystalline order, as confirmed by the disappearance of the X-ray diffraction pattern.

Supporting Information Available: X-ray crystallographic data, including experimental details (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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