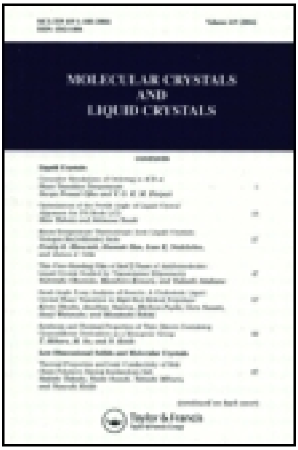

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Photochemical Single-Crystal-To-Single-Crystal Dimerizations and Polymerizations

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Version of record first published: 24 Sep 2006

To cite this article: Vera Buchholz & Volker Enkelmann (2001): Photochemical Single-Crystal-To-Single-Crystal Dimerizations and Polymerizations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 315-325

To link to this article: http://dx.doi.org/10.1080/10587250108023711

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 315-325
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Printed in Malaysia

Photochemical Single-Crystal-To-Single-Crystal Dimerizations and Polymerizations

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Single-crystal-to-single-crystal reactions of a series of bifunctional styrylyl]pyrylium salts have been investigated using long wavelength irradiation conditions. The dimerization of the reactive olefins in the solid state was followed by X-ray crystallography. The results demonstrate that a homogeneous photoreaction occurred under topochemical control. Two systems which can be polymerized in the solid-state are described.

Keywords: solid state reactivity; topochemical reactions; photodimerization; photopolymerization; stryrylpyrylium salts

INTRODUCTION

[2+2] photodimerizations are among the most well-studied reactions in organic solid-state chemistry. Most of these reactions proceed heterogeneously, i.e. at a certain (small) conversion between the monomer and product occurs and the parent crystal disintegrates into microcrystalline particles. This phenomenon hinders detailed investigations of the mechanism and kinetics of solid state reaction.[1-5]

It has been demonstrated previously that the irradiation wavelength is the decisive factor affecting the course of the reaction. When irradiating in the long wavelength tail of the absorption band, the [2+2]-cycloaddition of many photoreactive crystals proceeds homogeneously as a single-crystal-to-single-crystal conversion. At short irradiation times and incomplete conversions the intermediate states are substitutional mixed crystals, in which monomer and dimer units statistically occupy the same lattice sites. In such cases intermediate stages of the transformation can be analyzed crystallographically.[1-4] Some characteristic details should be noted:

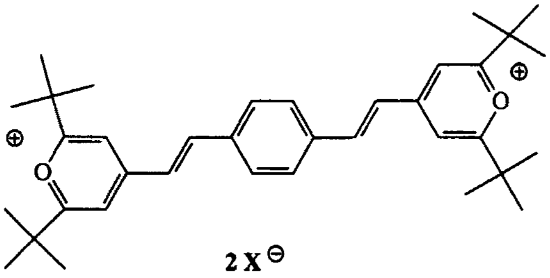
(i) As explained above the intermediate state in the transformation is a mixed crystal. Thus the crystal structure is the superposition of the monomer and the dimer. (ii) In the majority of all cases studied so far only the atoms which are directly involved in the cycloaddition (double bond and cyclobutane, respectively) show separate and well-resolved electron density maxima. All others have identical positions. (iii) The mixed crystal can be regarded as a compromise between the partners sharing a common lattice. This is why in the intermediate state both monomer and dimer are deformed, i.e. the bonds from the double bond system and the cyclobutane ring, respectively are deformed out of planarity (tilt). The tilt angles are quite large (30 to 40 °). (iv) The *as-dimerized* structures do not represent equilibrium structures.

Therefore, in some cases a thermal backreaction to the monomer is observed which also can proceed homogeneously. Recrystallized dimers form stable polymorphs which are thermally stable.

REACTIONS IN BIFUNCTIONAL STYRYLPYRILIUM SALTS

Styrylpyrilium salts have been found to be attractive systems for the study of topochemical [2+2] photodimerizations. By changing the substitution pattern of the cation and introducing counterions of different shape and size the packing of the monomers can be changed in a controlled fashion. This is necessary because solid-state reactivity is only observed if the double bonds are separated by a distance of less than 4 Å. Thus a large fraction of monomers turn out to be photostable. Bifunctional monomers are of special interest because they offer the opportunity to prepare polymers. Similar systems have been extensively studied in the past, e.g. the 4-center type photopolymerization of reactive diolefins (DSP, Hasegawa et al. [11]). The bifunctional styrylpyrilium monomer which was used for a systematic investigation of the packing and solid-state reactivity is shown in Scheme 1.

SCHEME 1 Bifunctional styrylpyrilium salts.



X^- :	BF_4^-	**1**
	ClO_4^-	**2**
	$SnCl_6^{2-}$	**3**
	$[SnCl_4(HCOO)]_n^-$	**4**
	$[SnCl_4(HCOO)(H_2O)]_n^-$	**5**

Crystals of **1**, **2** and **3** are photostable. Details of the crystal structures showing the packing of neighboring monomer units are shown in Fig. 1 in comparison. It can be seen that in these cases there are no close contacts between the double bond systems so that the distances are much too large in order to allow a photodimerization in the crystalline state.

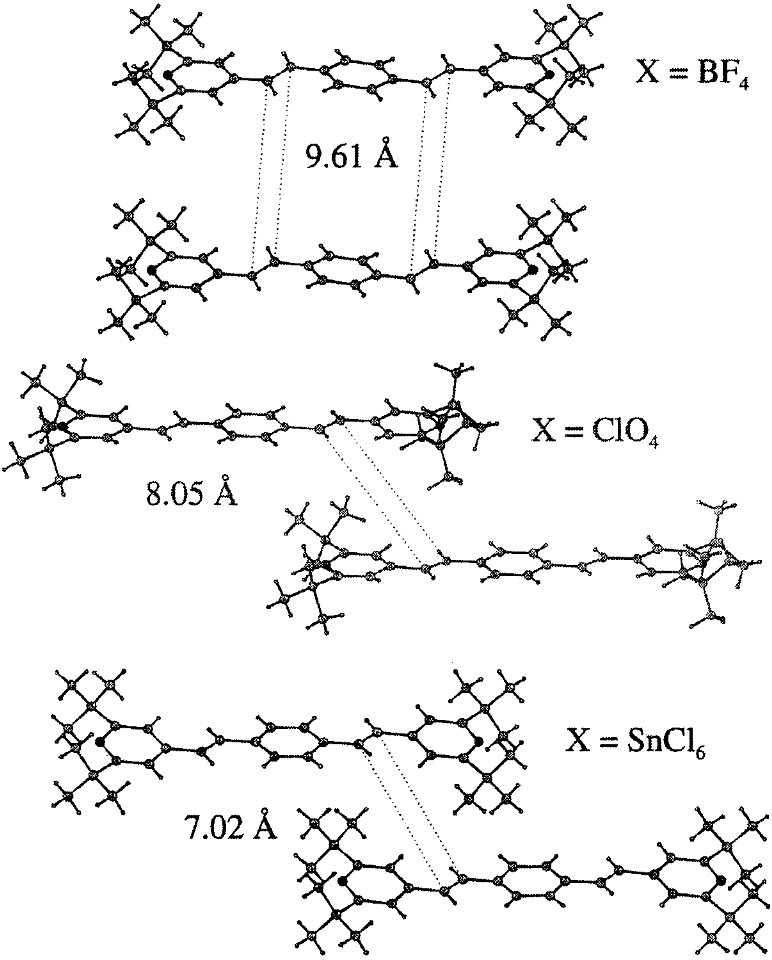


FIGURE 1 Monomer packing in the crystal structures of **1** (top) **2** (middle) and **3** (bottom).

Under the conditions of monomer synthesis the $SnCl_6^{2-}$ anion partially hydrolyses to hydroxoanions $[SnCl_{6-x}(OH)_x]^{2-}$. When the monomer was crystallized from formic acid two modifications (**4** and **5**) were obtained. In both modifications the counteranions are polymeric forming hydrogen bonded ribbons. They are shown in Fig. 2 in comparison.

Both crystal modifications are photoreactive and were exposed to long wavelength tail irradiation at 528.7 nm (more than 70 nm from the maximum of the absorption band). Under these conditions homogeneous single-crystal-to-single crystal transformations were observed.

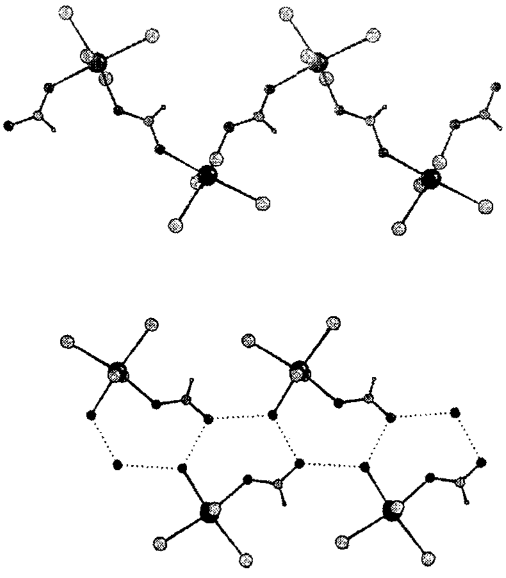


FIGURE 2 Polymeric counterions in **4** (top) and **5** (bottom).

The double bonds in **4** are separated by 4.05 Å. Upon irradiation the colour of the crystals changed from orange to yellow. The crystal structure analysis of the product shows that a homogeneous cyclodimerization has taken place.

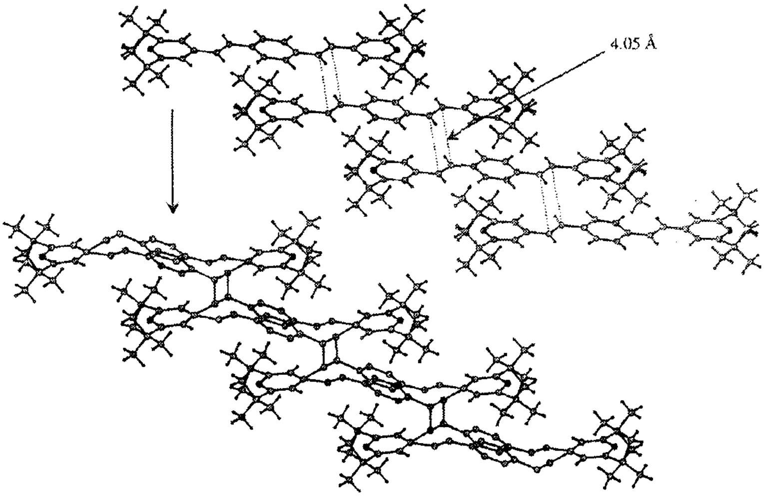


FIGURE 3 Crystal structure of **4** and the reaction product of the photoreaction at 528.7 nm.

However, although the staggered orientation of the bifunctional monomers suggests that a polymerization is possible **4** forms only disordered dimers. The crystal structures of monomer and reaction product are shown in Fig. 3 in comparison. It can be seen that in the dimer the phenyl ring is present in two positions which are each populated by 50 percent. Apparently the distance of the double bonds is sufficient for a cycloaddition but too large to allow the phenyl rings to rotate about their center as expected by the topochemical principle. Thus the phenyl rings follow the movement of the reacting atoms in a translation. The distance of the residual double bonds decreases to 3.69 Å. The absorption maximum of the dimer state is shifted by approximately 70 nm to lower wavelengths so that at the chosen irradiation wavelength of 528.7 nm the residual double bonds probably cannot be excited to induce the completion of the reaction. It should be noted that the projection shown in Fig. 3 is a superposition of the two components in the disordered structure, i.e. the two dimers plotted in different colours are both present with a 50 percent probability.

In the second modification the distance between the double bonds is much smaller. The observed spacing of 3.55 Å is among the shortest contacts we have observed in styrylpyrilium monomers. Upon irradiation at 528.7 nm the photoreaction of **5** is complete within 10 minutes irradiation at 1.4 W/cm^2 . Projections of the monomer and oligomer **5a** are shown in Fig. 5. The packing found here is apart from the shorter double bond distance quite similar to the structure of **4** with the same staggered arrangement of the monomer molecules. However, here the phenyl rings rotate during the reaction about theier centers. The conversion of double bonds is 80 percent. Using Carother's equation a degree of polymerization $P_n = 5$ can be calculated. Similar values have been previously obtained in the solid-state photopolymerization of DSP under the conditions of the long wavelength tail irradiation [12,13]. The reason for this limited conversion is as explained above the shift of the absorption of the residual double bonds to smaller wavelengths.

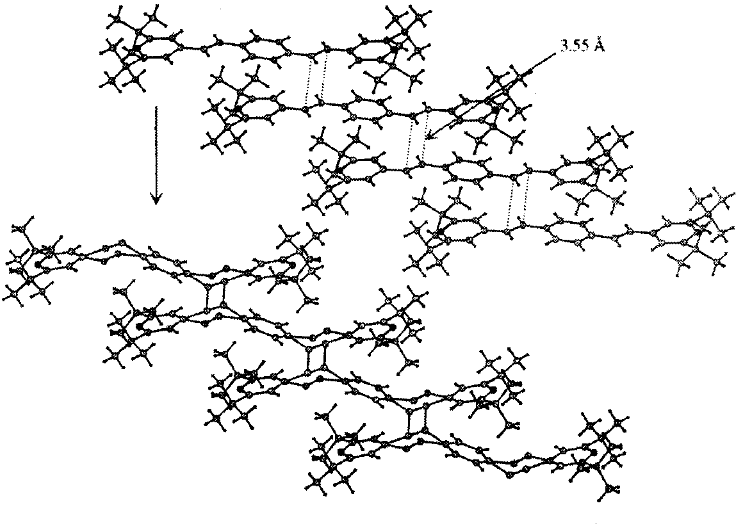


FIGURE 4 Crystal structures of **5** and its photoreaction product **5a**..

EXPERIMENTAL

Sample preparation and irradiation

Styrylpyrylium salts were synthesized in an analogous fashion to the literature procedure[6,8] using different acids to introduce the desired counterions. Irradiations were performed with a Coherent Innova Ar laser at 528.7 nm. The crystals were rotated in a beam of uniform intensity created with a beam expander having 1.4 W / cm^2.

X-ray structure analysis

X-ray structure analysis was performed using a NONIUS GmbH KappaCCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS-86)[9] and refined by full-matrix least-squares with anisotropic temperature factors for all non-hydrogen atoms using CRYSTALS.[10] H atoms were refined in riding mode (fixed isotropic temperature factors).

1 : monoclinic, $P2_1/n$, a = 9.6146(5), b = 14.980(1), c = 19.714(2) Å, β = 92.527(5) °, Z = 4, D_x = 1.40 gcm^{-2}, 4545 reflections, 1528 observed; R = 0.0957, R_w = 0.0984; unit weights; T = -97 °C.
2 : monoclinic, C2, a = 24.157(2), b = 8.4839(7), c = 10.1881(5) Å, β = 112.293(4) °, Z = 4, D_x = 1.22 gcm^{-2}, 1959 reflections, 1179 observed; R = 0.0936, R_w = 0.111; unit weights; T = -97 °C.
3 : triclinic, P-1, a = 10.7392(3), b = 11.6340(4), c = 12.1405(3) Å, α = 111.272(2), β = 98.922(2), γ = 109.560(1) °, Z = 2, D_x = 1.32 gcm^{-2}, 5198 reflections, 4880 observed; R = 0.0323, R_w = 0.0338; unit weights; T = -97 °C.

4 : monoclinic, $P2_1/n$, a = 12.0240(3), b = 8.5101(1), c = 23.8144(5) Å, β = 102.107(1) °, Z = 4, D_x = 1.57 gcm^{-2}, 5372 reflections, 4795 observed; R = 0.0441, R_w = 0.0556; unit weights; T = -97 °C.
4a : monoclinic, $P2_1/n$, a = 12.400(1), b = 8.1029(7), c = 24.180(2) Å, β = 101.021(4) °, Z = 4, D_x = 1.56 gcm^{-2}, 4535 reflections, 3259 observed; R = 0.0603, R_w = 0.0618; unit weights; T = -97 °C.
5 : monoclinic, $P2_1/n$, a = 13.4875(3), b = 7.3862(1), c = 25.4960(6) Å, β = 91.796(1) °, Z = 4, D_x = 1.52 gcm^{-2}, 5664 reflections, 4609 observed; R = 0.0407, R_w = 0.0531; unit weights; T = -97 °C.
5a : monoclinic, $P2_1/n$, a = 13.1093(6), b = 7.4201(2), c = 25.873(1) Å, β = 92.458(1) °, Z = 4, D_x = 1.53 gcm^{-2}, 4963 reflections, 3318 observed; R = 0.0477, R_w = 0.0598; unit weights; T = -97 °C.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained on application from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email deposit@ccdc.cam.ac.uk).

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