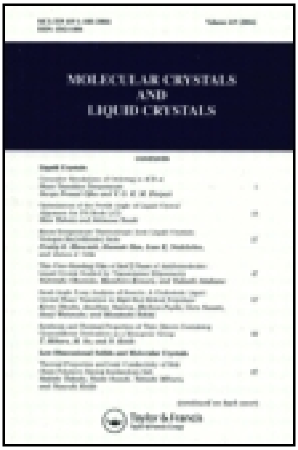


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochemical Single-Crystal-to-Single-Crystal Transformations

Vera Buchholz [a] & Volker Enkelmann [a]

[a] Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128, Mainz, Germany

Version of record first published: 04 Oct 2006

To cite this article: Vera Buchholz & Volker Enkelmann (1998): Photochemical Single-Crystal-to-Single-Crystal Transformations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 309-314

To link to this article: http://dx.doi.org/10.1080/10587259808044292

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 309–314
Reprints available directly from the publisher
Photocopying permitted by license only

Photochemical Single-Crystal-to-Single-Crystal Transformations

VERA BUCHHOLZ and VOLKER ENKELMANN
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128 Mainz, Germany

Single-crystal-to-single-crystal reactions of a series of (E)-2,6-di-*tert*-butyl-4-[2-(4-methylphenyl)-ethenyl]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.

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

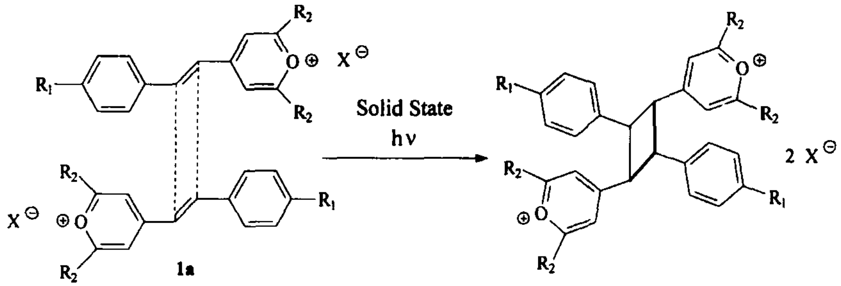
INTRODUCTION

Under topochemical control, photochemical reactions such as [2+2]-cycloadditions in crystals often proceed heterogeneously. At a certain conversion rate, phase separation occurs which leads to destruction of the reacting crystal and therefore hinders a kinetic investigation of the solid state reaction.[1-5]

It can be shown 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 mixed crystals result, in which monomer and dimer units statistically occupy the same places in the crystal lattice. In such cases intermediate stages of the transformation can be analyzed crystallographically.[1-4] Most noteworthy, the as-dimerized structures do not represent equilibrium structures. Therefore, in some cases a thermal backreaction to the monomer structure is possible. Recrystallized dimers show a different, thermally stable structure.[1]

REACTIVE 4-METHYLSTYRYLPYRYLIUM SALTS

Along with other systems, such as distyrylpyrazine and α-trans-cinnamic acid, a number of styrylpyrylium salts of type **1a** exhibit reactivity in the solid state (Scheme 1).[1,4,6] In continuation of this work, an extended series of these salts was synthesized with variation of the substituents attached to the phenyl ring (R_1) and the counterions (X) in order to study their influence on crystal packing and photoreactivity.



R_1 = Me R_2 = *t*-Bu X = BF_4 **2a**
ClO_4 **3a**
ReO_4 **4a**

R_1 = Me R_2 = *t*-Bu X = BF_4 **2b**
ClO_4 **3b**
ReO_4 **4b**

SCHEME 1 Dimerization of styrylpyrylium salts in the solid state.

(E)-2,6-di-*tert*-butyl-4-[2-(4-methylphenyl)-ethenyl]-pyrylium salts with R_1 = 4-Me, R_2 = *t*-Bu and tetrahedral counterions such as tetrafluoroborate **2a**, perchlorate **3a** and perrhenate **4a** form an isomorphous, photochemically reactive series which crystallizes in the monoclinic space group Cc.

Figure 1 shows the asymmetric unit for the 4-methylstyrylpyrylium perchlorate **3a** including four crystallographically independent molecules. Five of eight *tert*-butyl groups are disordered at room temperature. Two orientations are observed with almost equal occupancies. The reactive double bonds have a spacing between 3.66 and 3.70 Å, well within the 4.2 Å limit for topochemical reactions.[7]

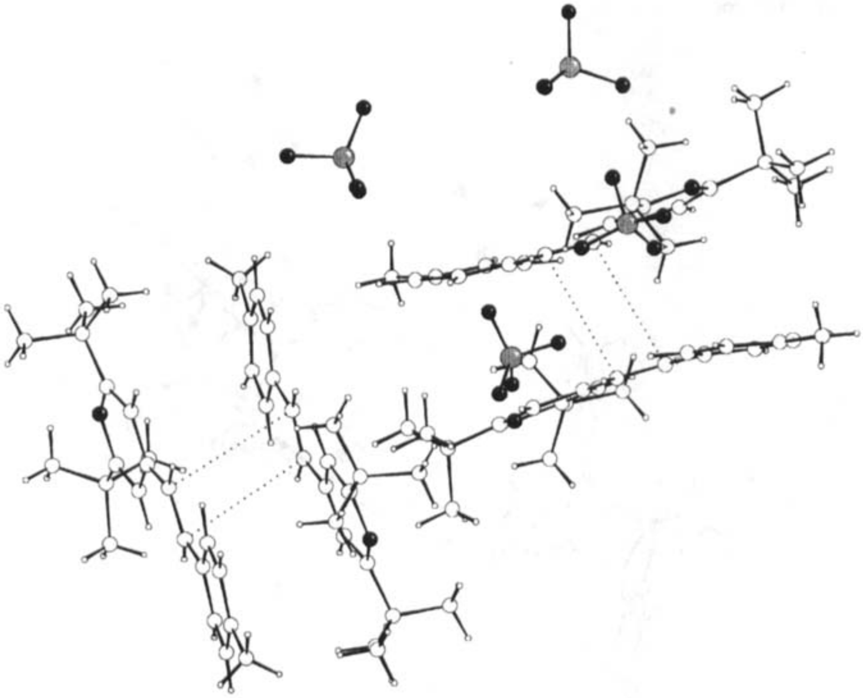


FIGURE 1 Asymmetric unit of the 4-methylstyrylpyrylium perchlorate monomer structure **3a**. Only one orientation of the *tert*-butyl groups is shown. View along the c-axis showing the reactive double bonds connected by dotted lines. C and H white, O black, Cl grey.

When crystals are exposed to long wavelength irradiation at 528.7 nm (116 nm from the maximum of the absorption band), a homogeneous single-crystal-to-single-crystal transformation is induced which leads to the corresponding dimer **3b** as shown in Figure 2. Note that in the as-dimerized structure the orientation of the toluyl and pyrylium side groups as well as the orientation of the perchlorate counterions has changed compared to the monomer structure. In the dimer structure, six *tert*-butyl groups show disorder at room temperature.

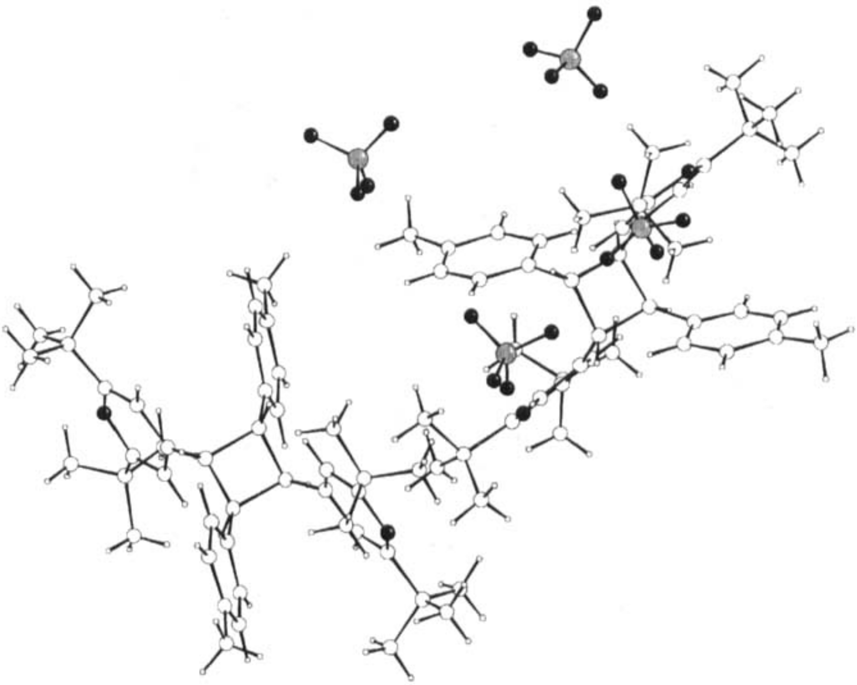


FIGURE 2 Asymmetric unit of the corresponding as-dimerized structure **3b** after homogeneous photoreaction in the solid state. Only one orientation of the *tert*-butyl groups is shown. View along the c-axis. C and H white, O black, Cl grey.

The changes in lattice parameters after dimerization of the three isomorphous 4-methylstyrylpyrylium salts are summarized in Figure 3, indicating a maximum change of 2.75 % typical for topochemical control.

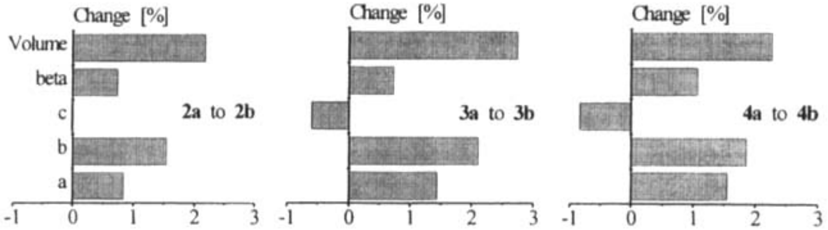


FIGURE 3 Change in lattice parameters for the isomorphous series of 4-methylstyrylpyrylium salts **2a**, **3a** and **4a** after topochemical dimerization to **2b**, **3b** and **4b**, respectively.

EXPERIMENTAL

Sample preparation and irradiation

4-Methylstyrylpyrylium salts **1a** were synthesized in an analogous fashion to the literature procedure[6,8] using different acids to introduce the desired counterions. **2a**, **3a** and **4a** were recrystallized by slow evaporation of a methanol or ethanol / ether (1:1) solution, respectively. Irradiations were performed with a Coherent Innova Ar laser at 528.7 nm for 15 min. 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 (Delft Instruments) KappaCCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by direct methods (SHELXS-86)[9] and refined by block matrix least-squares with anisotropic temperature factors for C, O and Cl using CRYSTALS.[10] H atoms were refined in riding mode (fixed isotropic temperature factors). For **3a** at T= 296 K, a = 18.594(2) Å, b = 18.421(4) Å, c = 26.962(6) Å, β = 99.17(1)°, Volume = 9117.1 $Å^3$, space group = Cc, Z = 16, D_c = 1.197 g cm^{-3}, 9743 reflections measured, 6831 observed (I > 3σ(I)), R = 0.087, R_w = 0.092. For dimer **3b** at T= 296 K, a = 18.863(6) Å, b = 18.811(6) Å, c = 26.800(5) Å, β = 99.91(1)°, Volume = 9367.7 $Å^3$, space group = Cc, Z = 8, D_c = 1.160 g cm^{-3}, 11074 reflections measured, 5208 observed (I > 3σ(I)), R = 0.096, R_w = 0.125.

Acknowledgments

Prof. Dr. G. Wegner, Max-Planck-Institut für Polymerforschung, Mainz, and Prof. B. M. Foxman, Brandeis University, Waltham, MA, are gratefully acknowledged for valuable discussions and helpful advice. The authors also thank Dr. M. Adam (NONIUS), B. Zimmer and T. K. Däubler for technical support.

References

[1] K. Novak, V. Enkelmann, G. Wegner and K. B. Wagener, *Angew. Chem.*, **105**, 1678 (1993).
[2] V. Enkelmann, G. Wegner, K. Novak and K. B. Wagener, *J. Am. Chem. Soc.*, **115**, 10390 (1993).
[3] V. Enkelmann, G. Wegner, K. Novak and K. B. Wagener, *Mol. Cryst. Liq. Cryst.*, **240**, 121 (1994).
[4] K. Novak, V. Enkelmann, W. Köhler, G. Wegner and K. B. Wagener, *Mol. Cryst. Liq. Cryst.*, **242**, 1 (1994).
[5] W. Köhler, K. Novak and V. Enkelmann, *J. Chem. Phys.*, **101**, 10474 (1994).
[6] K. Hesse and S. Hünig, *Liebigs Ann. Chem.*, 715 (1985).
[7] G. M. J. Schmidt, *Solid State Photochemistry*, in *Monographs in Modern Chemistry*, Vol. 8, edited by D. Ginsburg (VCH, New York, 1976).
[8] A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann. Chem.*, 74 (1959).
[9] G. M. Sheldrick, *Acta Crystallogr.*, **A46**, 467 (1990).
[10] D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996.