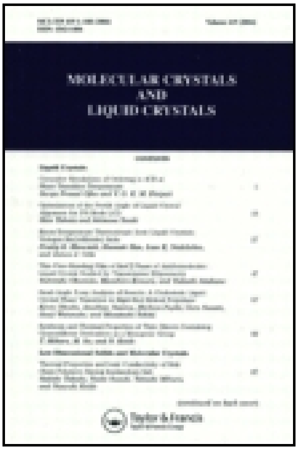

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Single-Crystal-to-Single-Crystal Transformations: The Long Wavelength Tail Irradiation Technique

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Single-Crystal-to-Single-Crystal Transformations : The long wavelength tail irradiation technique

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Most [2+2] photodimerization reactions proceed heterogeneously. At a small conversion phase separation leads to the destruction of the parent crystal. The crystal fragmentation can be avoided by irradiation in the long wavelength tail of the absorption. The intermediate mixed crystalline states as well as thermally reversible systems have been studied.

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

INTRODUCTION

[2+2] photodimerizations are among the most well-studied reactions in organic solid-state chemistry. The archetype for these reactions is the photodimerization of α-*trans* cinnamic acid derivatives. In a landmark study G.M.J. Schmidt derived with these systems the topochemical principles [1] which still hold until today. Most [2+2] photodimerizations proceed heterogeneously, i.e. at a certain (small) conversion phase separation between the monomer and product occurs and the parent crystal disintegrates into microcrystalline particles. While this phenomenon is of little significance for preparative purposes a heterogeneous reaction poses severe obstacles in the detailed study of the reaction mechanism.

In the crystal disintegration process additional surface is formed which causes scattering of the incident light. Thus the sample becomes increasingly opaque in the course of the reaction and constant light intensity throughout the sample which is a prerequisite for kinetic studies can not longer be achieved. Equally important is the question about the topochemical control in heterogeneous solid-state reactions. The packing geometry which has been found to be the most important factor for the reactivity may be different in the bulk and at the newly formed surface so that in unfavourable cases even different isomers could be formed in the different environments.

One experimental parameter which has been found to have a decisive influence on the reaction mechanism of topochemical [2+2] photodimerizations is the irradiation wavelength. Normally the irradiation is carried out in the vicinity of λ_{max} of the chromophore. Owing to the high absorption coefficient in this wavelength region the light intensity will fall off steeply in the crystal under these irradiation conditions. Consequently an equally steep concentration profile of the reaction product will develop. Most solid-state reactions are connected with anisotropic changes of all lattice parameters. In a simple approach which led to the long wavelength tail irradiation technique is was assumed that this (albeit small) lattice mismatch is the key factor for a heterogeneous mechanism. The concept is illustrated in Fig. 1 for the well investigated dimerization of a styrylpyrylium salt, (*E*)-2,6-Di-*tert*-butyl-4-[2-(4-methoxyphenyl)-ethenyl] pyrylium- trifluormethansulfonate [2,3,10]. If crystals of this compound are irradiated at 420 nm the depth at which the intensity drops to 1/2, $x_{1/2}$, is according to Beer's law 0.002 mm. If the irradiation is carried out, however, in the very tail of the absorption the light intensity will much more even throughout the crystal. At 570nm and 620 nm $x_{1/2}$ is 0.1mm and 1mm, respectively. While irradiation at λ_{max} caused the crystals to shatter it was shown that in the wavelength range between 570 and 635 nm under tail irradiation conditions the dimerization proceeds as a single-crystal-to-single-crystal process. It should be noted, however, that regardless of the irradiation wavelength in all cases the same product phase is formed, indicating that there is no change of photochemistry connected to the tail irradiation.

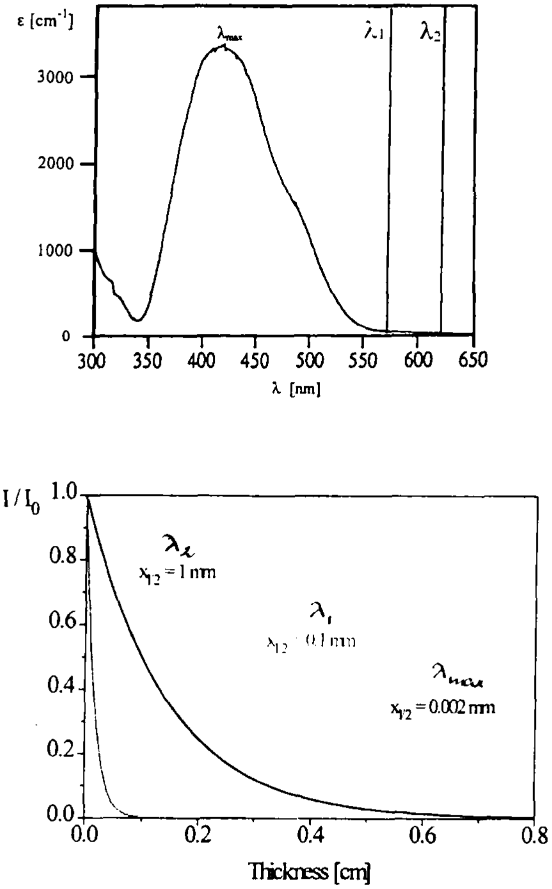


FIGURE 1 Absorption spectrum (top) and intensity profiles at 570 and 620 nm (bottom) for a styrylpyrylium salt.

The long wavelength tail irradiation technique has been successfully used with topochemical photoreactions which previously had been characterized to proceed heterogeneously under normal irradiation conditions, e.g. the dimerization of cinnamic acid derivatives [4,5] and the four-center photopolymerization of reactive diolefins [6,7] . As an example the crystal structures of α-*trans* cinnamic acid and *as-dimerized* truxillic acid are shown in Fig. 2 in comparison.

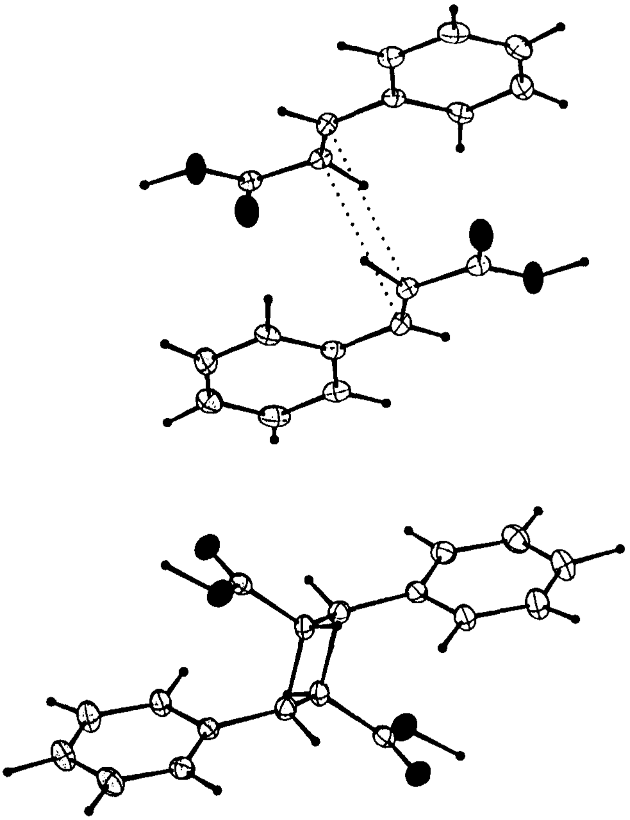


FIGURE 2 Crystal structures of α-*trans* cinnamic acid and *as-dimerized* truxillic acid [4] .

THE REACTION INTERMEDIATES

In a continuous transformation of the monomer crystal into the dimer crystal the intermediate state must be described as a substitutional mixed crystal in which monomer pairs and dimer molecules statistically occupy the same lattice site with an occupancy according to the conversion. For a true homogeneous transition the spatial distribution of dimers in the crystal is random, i.e. no clustering occurs. Homogeneous solid-state reactions thus offer the unique opportunity to study the transformation process in the entire conversion range. The intermediate mixed crystals are available by limiting the irradiation time to give crystals of the desired conversion. In Fig. 3 the crystal structure of a crystal with 40 percent conversion which had been prepared by the photodimerization of α-*trans* cinnamic acid under tail irradiation conditions is shown. Certain characteristic details which are found for all intermediates in the crystal-to-crystal dimerizations should be noted: (i): as explained above we deal here with a substitutional mixed crystal, to plot shown in Fig. 3 is the superposition of the dimer and monomer pair which occupy the same lattice site. The partially occupied atoms of the cyclobutane ring and double bonds are well resolved and within the expected limits of bonding geometry. (ii): All other atoms except those directly involved in the cycloaddition reaction have identical coordinates. (iii): The mixed crystal must be regarded as a compromise between the periodic lattice of the crystal and the conformational requirements of the two partner involved. This is why at intermediate states both partner are deformed, i.e. the bonds from the double bond and the cyclobutane ring, respectively to the side groups are deformed out of planarity. This is shown in Fig. 3 by the deviation both bonds make with the direction of a bond in perfect sp^2 geometry (tilt angle). In the monomer and the pure dimer this deformation is absent. The deformation of the minority component is found to be larger than the one found for the majority component, the conversion dependencies of the tilt angles of monomer and dimer are approximately mirror images of each other. It should be noted that the deformation from planarity is quite large since tilt angles up to 40 degrees are observed.

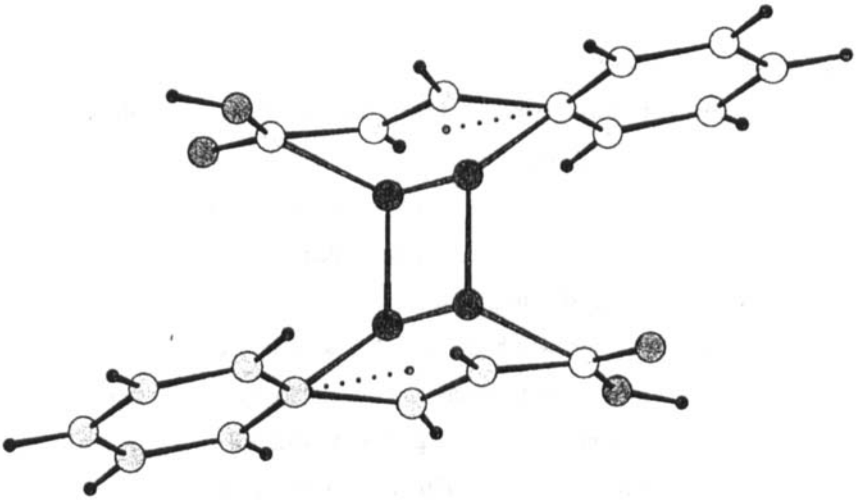
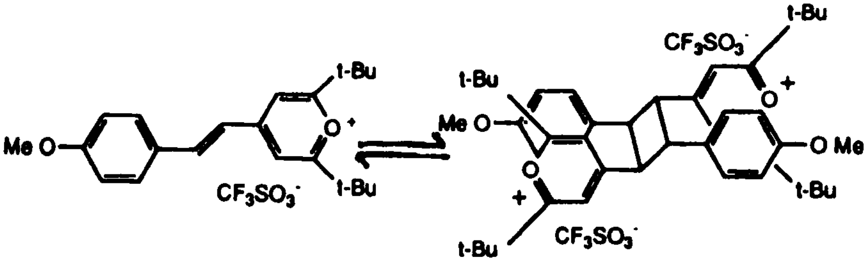


FIGURE 3 Crystal structure of a mixed crystal intermediate in the tail irradiation of α-*trans* cinnamic acid at 40 percent conversion.

REVERSIBLE REACTIONS

The dimer crystals obtained as described above are in most cases a non-equilibrium state, e.g. *as-dimerized* truxillic acid will transform at higher temperatures into another, stable crystal structure which is also obtained by recrystallization. In the vicinity of the melting point (approximately 280 °C) also some cleavage of the dimer into the monomer is observed. This thermal cleavage occurs in crystals of the styrylpyrilium salts at much lower temperatures. The triflate salt shown in Scheme 1 cleaves at mild temperatures around 100 °C in a clean reaction with retention of the single crystal. The facility of cyclobutane cleavage in this system is a property of the metastable crystalline state. The recrystallized dimer crystallizes in another crystal structure and is stable at elevated temperatures. Thus this system can be regarded as a reversible photochromic system which can be switched several times between the (red) monomer and (yellow) dimer state without loss of crystal quality. This makes it possible to study the intermediate mixed crystal both in the photochemical forward reactions and the thermal back reaction.



SCHEME 1 Reversible [2+2] photodimerization in the crystal

The investigation of the intermediate mixed crystals revealed in the thermal back reaction a large hysteresis of the tilt angles, i.e. the monomer pair formed by cleavage of a dimer is less deformed as on the forward reaction [8]. The reason for this behaviour is a crankshaft motion of the double bond which releaves some of the strain. The conversion dependence of tilt angles is shown in Fig. 4.

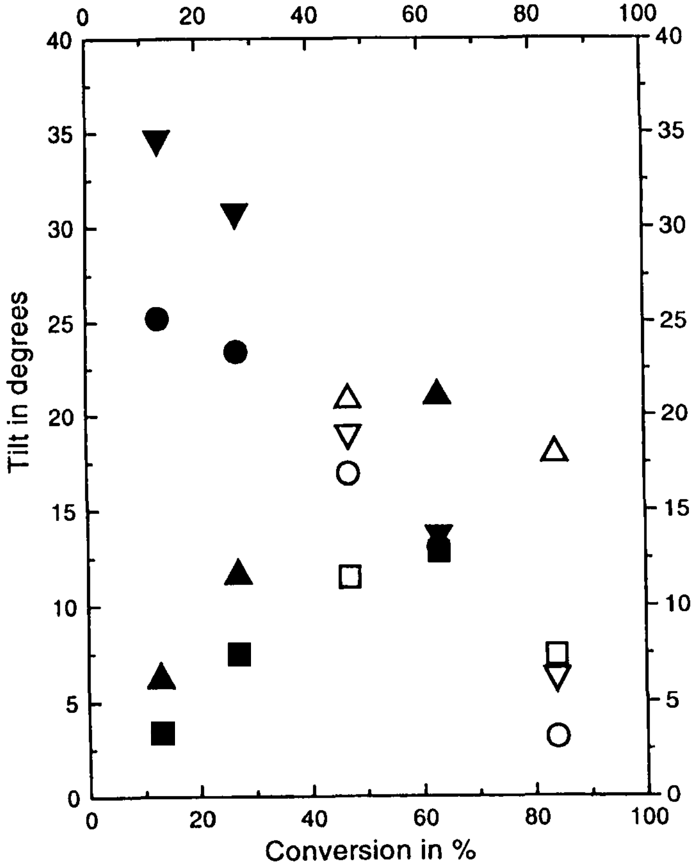


FIGURE 4 Conversion dependence of tilt angles for the triflate styrylpyrilium salt. Closed symbols: photochemical forward reaction, open symbols: thermal back reaction.

The homogeneous character of this photoreaction makes is possible to use a holographic grating technique as a highly sensitive tool to determine the reaction kinetics [8,9] . By irradiation of the crystal with an optical interference grating at a wavelength with the tail absorption a periodic spatial distribution of the monomer and dimer which extended over the entire crystal could be obtained. By monitoring the photoinduced growth and thermal decay of the diffraction efficiency of the resulting refractive index grating the reaction kinetics could be followed in great detail. From the temperature dependence of the holographic growth and decay curves an upper limit for the activation energy for the photodimerization is obtained to 15.2 kJ/mol. For the thermal cyclobutane cleavage an activation energy of 99 kJ/mol and an attempt frequency of 1.2 x 10^{12} s^{-1} are found. The kinetic data for the thermal cleavage are compared in Table 1 with literature data.

TABLE 1 Comparison of kinetic data on cyclobutane cleavage: attempt frequencies R_0 and activation engies E_a .

Compound	R_0 (s^{-1})	E_a (kJ/mol)
Cyclobutane [11]	4 x 10^{15}	262
1,2,3,4-Tetracyano-*anti*-tricyclo [4.2.0.0]octane [12]	4 x 10^{15}	146
Styrylpyrilium photodimer [9]	1.2 x 10^{12}	99