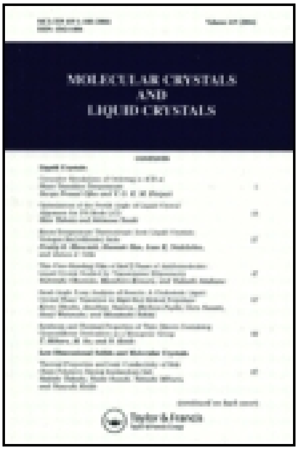

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Crystal-to-Crystal Photodimerizattons

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CRYSTAL-TO-CRYSTAL PHOTODIMERIZATIONS

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Abstract Most [2+2] photodimerizations proceed heterogeneously, i.e. at a certain conversion phase separation occurs which leads to the destruction of the parent crystal. The crystal fragmentation can be avoided by irradiation in the long wavelength tail of the absorption.

INTRODUCTION

[2+2] photodimerizations are among the most well-studied reactions in topochemistry. The archetype of these reactions is the photodimerization of cinnamic acid derivatives for which most of the principles of topochemistry have been derived. These dimerizations and other solid-state photoreactions are reported to proceed heterogeneously, i.e. at a certain (small) conversion phase separation occurs and the parent crystal disintegrates into microcrystalline particles. This hampers structural and kinetic investigations.

One experimental parameter which has been found to have a decisive influence of the mechanism of topochemical [2+2] photodimerizations has been found to be the wavelength of irradiation. The heterogeneous mechanism described above is observed if the irradiation is in the vicinity of λ_{max} of the chromophore. Since the absorptivity of the sample is high under these conditions a steep profile of product concentration from the incident surface will develop. In the course of the reaction, van-der-Waals contacts are converted to chemical bonds and thus a dimensional mismatch between monomer and product lattice exists. The combination of steep concentration profile and lattice mismatch is one of the reasons for the heterogeneous character of these reactions. However, if the irradiation is in the very tail of the absorption so that the absorption is low, the light intensity is comparatively even throughout the crystal. Many topochemical photoreactions, which up until now have been driven heterogeneously, may proceed homogeneously with absorption-tail irradiation to yield intact crystals of the photoproduct. This has been demonstrated for three different systems, the photopolymerization of distyrylpyrazine, DSP[1-5], the dimerization of a variety of styrylpyrilium salts [6,7] and the dimerization of α-trans cinnamic acid [6,8].

RESULTS AND DISCUSSION

Oligo-DSP

Fig. 1 shows the absorption spectra of DSP monomer, oligomer and polymer. The monomer shows an absorption at 370 nm. If the crystals are exposed to irradiation of 400 nm high polymer is formed. Under these conditions the reaction proceeds heterogeneously. At very low conversions polymer phases separate in the monomer lattice. These have been characterized by electron microscopy and electron diffraction LIT. If the irradiation is carried out, however, at λ = 478 nm in the very tail of the absorption, single crystals of DSP oligomer are obtained. In the oligomer only pendent double bonds at the ends of the molecules are retained. Consequently the maximum of the absorption is shifted to shorter wavelengths. These double bonds cannot be excited at 478 nm so that the polymerization does not proceed further. GPC analysis of this product has shown that the number average degree of polymerization is $P_n = 3.2$.

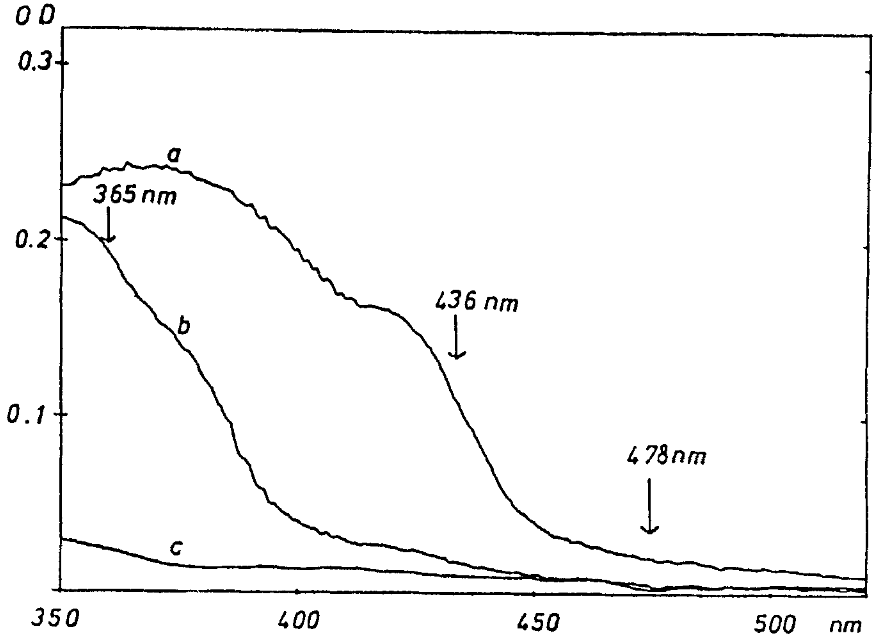

Figure 1 UV absorption spectra of DSP. a) monomer, b) oligomer, c) polymer

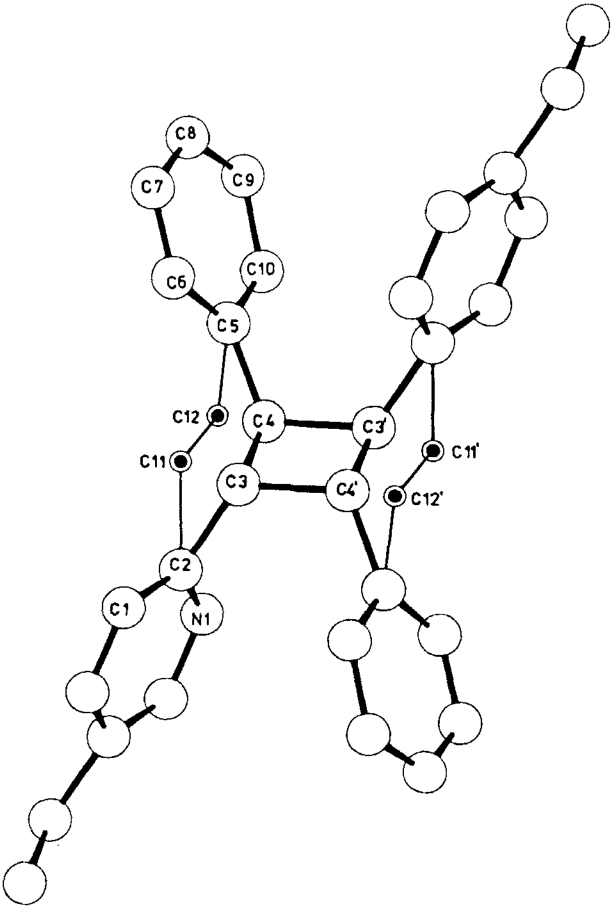

Fig. 2 Crystal structure of DSP oligomer

The crystal structure of oligomer DSP is shown in Fig. 2. It can be characterized as a substitutional mixed crystal of oligomers with different chain length in which cyclobutane rings and double bonds statistically occupy the same lattice sites. Some characteristic details which are found with all single-crystal-to-single-crystal [2+2] photodimerizations are visible in these figures: (i): At intermediate conversions mixed crystals are formed in which dimer or polymer repeat units and monomer molecules statistically occupy the same lattice sites. (ii): All atoms in the side groups have identical coordinates, separate electron density maxima are only found for the two C atoms directly involved in the cycloaddition reaction. (iii): Since the conformation of the molecule changes the side group orientation can be regarded as a compromise between the packing in the mixed crystal and the conformational requirements of the two partners involved. Thus the bond from the double bond and the cyclobutane ring to the side group is deformed out of planarity. The deformation of the minority component is larger the one found for the majority component. (iv): The distances of the residual double bonds in partially converted crystals will change owing to the lattice changes. This will influence reaction kinetics since the reactivity in topochemical reactions is controlled by this distance.

α-Trans cinnamic acid

The concept of long wavelength tail irradiation has been used in the dimerization of α-trans cinnamic acid [9]. When crystals of α-trans cinnamic acid were irradiated at $\lambda >$ 365 nm single crystals of the dimer α-truxillic acid were obtained. By changing the irradiation times intermediate mixed single crystals with dimer contents of 28%, 40% and 67%,respectively, were isolated. Projections of the crystal structures are shown in Fig. 3.

In topochemical reactions side group packing plays an important role. In a first approximation the side groups keep their packing in the mixed crystals which are a necessary intermediate of single-crystal-to-single-crystal transformations and accomodate the large atomic displacements of the reacting atoms. Thus bulky and flexible side groups have a favourable effect on the reactivity and on the stability of the mixed crystals [10]. In α-trans cinnamic acid the two side groups, tightly hydrogen bound -COOH group and directly attached phenyl ring are not flexible. As a consequence a large distortion of the lattice in the course of the reaction is observed. It can be seen in Fig. 3 that the side group orientation changes continuously in the reaction. Pertinent values of the dependencies of phenyl ring rotation and bond angle deformation are given in Table 1.

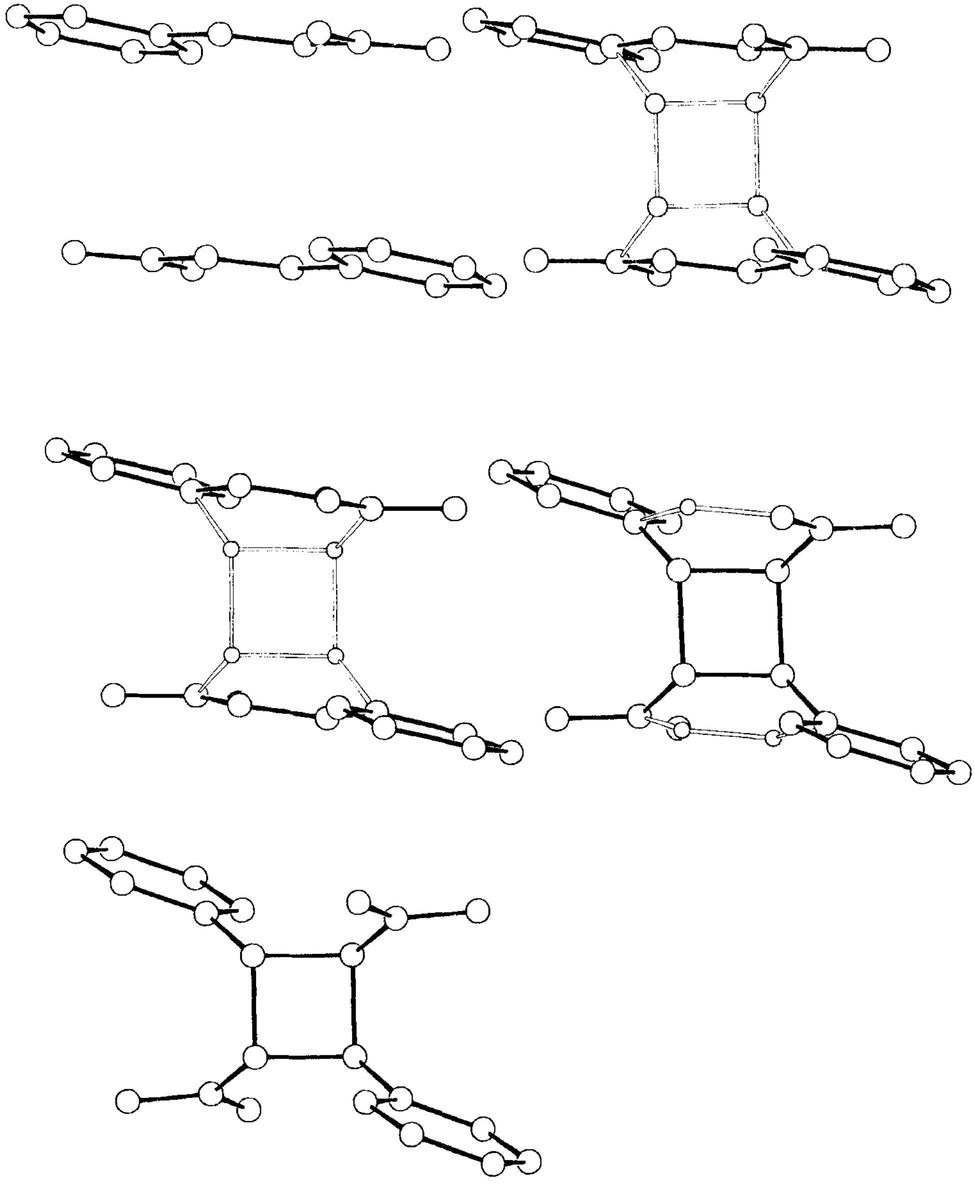

Fig. 3 Projections of the crystals structures of α-trans cinnamic acid, as-dimerized α-truxillic acid and their mixed crystal intermediates on the plane of the cyclobutane ring. Top left: α-trans cinnamic acid, top right: 28% conversion, middle left: 40% conversion, middle right: 67% conversion, bottom: as-dimerized α-truxillic acid. Crystal structures have been determined at 165 K.

TABLE 1 Conformational changes in the photodimerization of α-trans cinnamic acid

Conversion (%)	tilt(monomer)	tilt(dimer)[a]	ϕ (deg.)[b]	d(C2-3')(Å)
0	---	---	81.5	3.59
28	8.2	32.7	86.2	3.48
40	15.2	25.7	94.4	3.49
67	25.5	13.6	96.9	3.52
100	---	---	100.9	---

[a] defined as the angle between the bond phenyl ring - double bond/ cyclobutane and a fictitious bond in perfect sp^2 geometry

[b] dihedral angle between phenyl ring and cyclobutane ring

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