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HOMOGENEOUS PHOTODIMERIZATION AND THERMAL BACK REACTION OF A STYRYLPYRYLIUM TRIFLATE

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Abstract The work reported here demonstrates for the first time a forward and reverse topochemical, single-crystal-to-single-crystal reaction. By full crystal structure analysis of the product and substitutional crystals of intermediate conversion, it is proven that the forward topochemical photodimerization proceeds homogeneously through a solid solution of monomer and dimer over the entire range of conversion. The photoreaction is shown to be driven homogeneously or heterogeneously through choice of irradiation conditions.

INTRODUCTION

Many topochemical reactions are reported to be heterogeneous, that is, at a certain point in the conversion, phase separation of the product occurs which usually leads to the disintegration of the crystal. The classic example is the photodimerization of cinnamic acid and its derivatives, studied by Schmidt in his landmark work which produced the "topochemical principle."[1] Certainly, examples of single-crystal-to-single-crystal topochemical reactions in the literature are rare.[2-8] These transformations may take place homogenously;[2] that is, instead of phase separation, solid solutions of the product and reactant exist throughout the conversion. In this case, the states at intermediate conversions are substitutional mixed crystals where monomer and dimer molecules statistically occupy the same lattice sites.

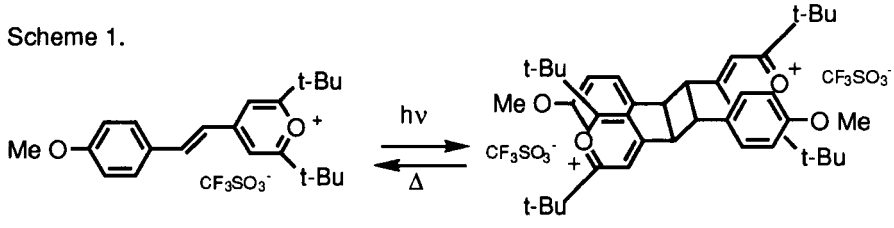
We wish to report an example of a [2+2] photodimerization that is heterogeneous under typical irradiation conditions, but proceeds homogeneously when exposed to light in long wavelength tail of its absorption. However, not only is the cyclobutane formation in this system homogeneous, the thermally induced back reaction to monomer is also observed to be homogeneous. Thus single crystal-to-single crystal transformations between monomer and dimer states are possible. Up until now, homogeneous back reactions have been unreported in the literature.

ABSORPTION-TAIL IRRADIATION OF MONOMER CRYSTALS

The photodimerization and thermal cycloreversion investigated is shown in Scheme 1.[9] When the irradiation is done in the maximum absorption of the

styrylpyrylium chromophore (420nm), the typical heterogeneous reaction is observed. The surface of the originally red crystals first become covered with a fine yellow powder, eventually breaking down into microcrystalline particles. However, when the irradiation is in the tail of the absorption (570nm and above), single crystals can be obtained in the entire range of conversion from monomer to dimer.

Scheme 1.



The key to the homogeneous conversion in this photodimerization is the irradiation in the absorption tail of the chromophore. This same effect has been observed in the photopolymerization of DSP[6] and very recently in the photodimerization of cinnamic acid (see "Crystal to Crystal Photodimerizations", Enkelmann, Novak, Proceedings of the 11th International Conference on the Chemistry of the Organic Solid State, Mol. Cryst. and Liq. Cryst.) and can be explained by considering the light intensity gradient through a cross-section of an irradiated crystal. When the crystal is exposed to light for which it has a high absorptivity, the light intensity will be high at the incident surface and will drop off quickly through the inner bulk of the crystal. Thus product accumulates quickly at the surface, precipitating out as a separate phase due to dimensional mismatch between the product and reactant lattices. When the crystal is exposed to light for which it has a low absorptivity, the light intensity will be comparatively even from the surface throughout the bulk of the crystal. Thus product is formed randomly within the crystal. It should be noted that the heterogeneously-formed dimer has the same crystal modification as the dimer formed homogeneously: the experimental powder diffractogram of the dimer formed from absorption maximum irradiation matches that calculated from the dimer formed from absorption tail irradiation.

ANALYSIS OF SUBSTITUTIONAL MIXED CRYSTALS

A series of crystals at various conversions, determined by IR, were prepared and their cell parameters determined. In homogeneous topochemical reactions the overall volume change may be low, whereas the change in a given lattice parameter may be larger, since in certain directions Van der Waals contacts are transformed into chemical

bonds. This is the case here, where, though the volume change from monomer to dimer is less than 2%, the percent change in cell parameters totals over 10%. We deal here with a truly homogeneous reaction since these large changes of the cell parameters are nevertheless continuous. Thus at any point in the conversion, a perfect single crystal exists which can be used for a crystal structure analysis.

Full crystal structures on the monomer, dimer and two crystals of intermediate conversion have been determined. In the mixed crystals separate atomic coordinates are observed only for the two C atoms which are directly involved in the cyclobutane formation. *All other atoms occupy identical positions within the error of the analysis.* For example, Figure 1 shows a projection of the crystal structure of a substitutional mixed monomer / dimer crystal, with 67% dimer.

It has been observed that bulky side groups are often a common factor in topochemical processes demonstrated to be homogeneous. There are two phenomena at work here: one involves an "anchoring" effect, the other involves conformational mobility. The side groups can be seen as anchors in that they determine the intermolecular contacts existing in the crystal lattice. During the course of the conversion, the atomic displacements in these side groups are not large since they are removed from the reacting centers. Thus the side groups preserve the overall packing, stabilizing the evolving lattice changes, and making the continuous shift in lattice parameters possible. On the other hand, the side groups provide the conformational flexibility required such that the reacting centers may approach each other. Table 1 lists some selected dimensions from the crystal structures at various degrees of conversion.

For example, the methoxy-substituted phenyl ring is seen to rotate through 18° in the conversion from monomer to dimer. This rotation seems to be continuous throughout the reaction as can be seen in Table 1. Similar but much smaller continuous conformational changes are observed in the pyrylium ring and the counterion. Note that the phenyl ring occupies the same lattice position whether it is attached to a double bond or a cyclobutane ring. Thus in crystals at intermediate conversion, nonplanarity is observed for the bonds from the sp^2 carbon linking the phenyl ring to the cyclobutane ring or double bond. This deformation is listed as phenyl ring "tilt" in Table 1. As would be expected, the deformation is less severe for the unreacted species at lower conversions; and at higher conversions, it is less severe for the cyclobutane. It is interesting to note that the overall deformation decreases with increasing conversion. This can be explained by considering that in converting van der Waals contacts to chemical bonds, the overall modulus of this system increases. Thus a more rigid system permits less deformation. Furthermore, at higher conversions, the monomer can be considered as a guest in the dimer lattice, thus the carbon atoms in the reacting

double bonds are 0.35Å closer in the single crystal with 67% dimer than in the monomer single crystal.

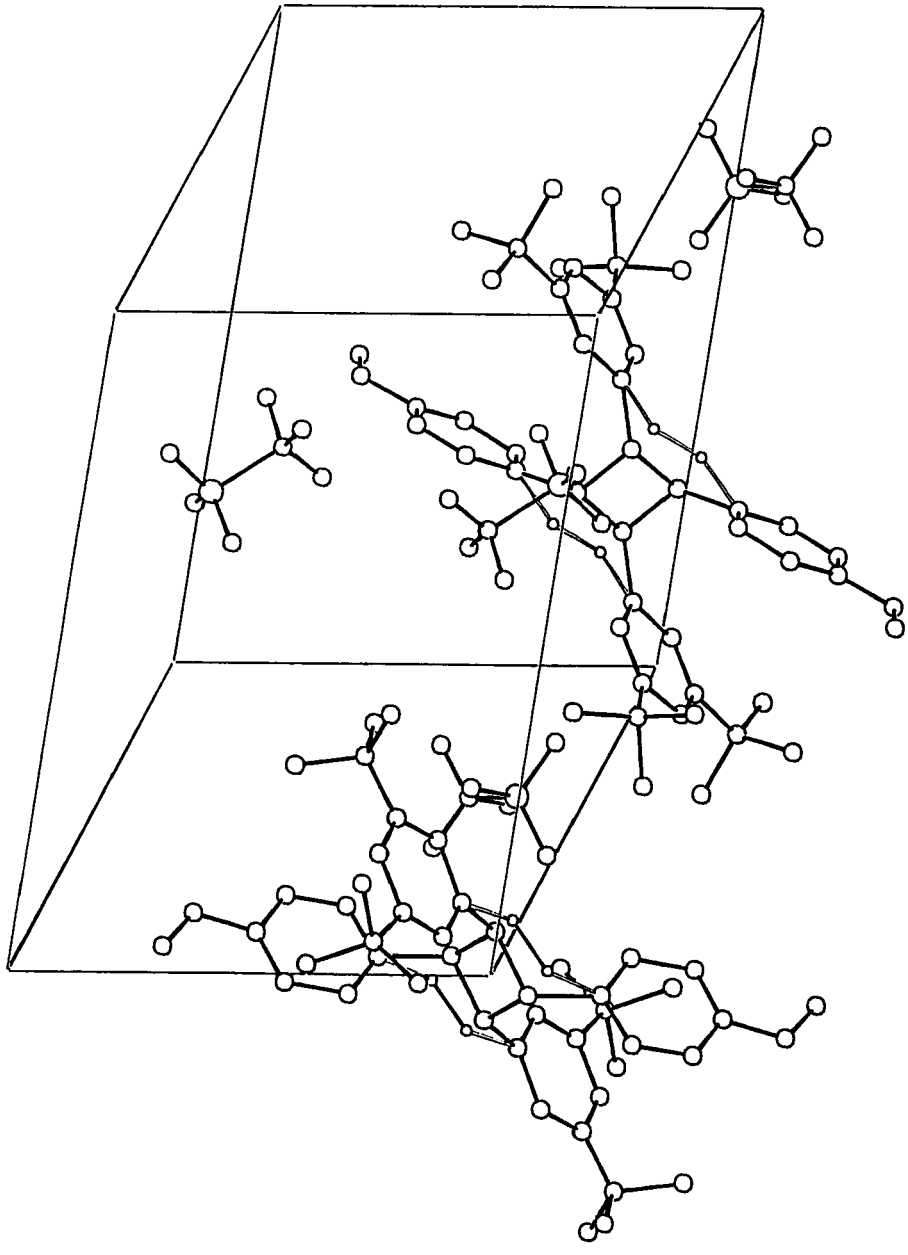


FIGURE 1. Projection of the crystal structure of a styrylpyrylium monomer / dimer substitutional mixed crystal, 67% dimer.

Table I. Selected dimensions from crystal structures of a styrylpyrylium triflate single crystals at various degrees of dimerization.

% dimer	phenyl ring tilt[a] monomer / dimer	phenyl ring rotation[b]	C-C[c] distance, Å
0	3.8° / (37.3°)	94.49 (±0.26)°	3.42
13	6.2° / 34.7°	93.62 (±0.28)°	3.42
67	21.0° / 13.7°	79.78 (±1.06)°	3.07
100	(31.2°) / 5.1°	77.36 (±0.20)°	

[a] Angle between plane of phenyl ring and the axis along the bond linking the phenyl ring to the double bond or cyclobutane ring. Note that in the undimerized crystal, this axis is defined using the coordinates for the cyclobutane ring in the 13% dimerized crystal. In the fully dimerized crystal, this axis was defined using the coordinates for the double bond in the 67% converted crystal. [b] Dihedral angle the plane of the phenyl ring makes with plane of cyclobutane ring. For the undimerized crystal, the cyclobutane plane for the dihedral angle was defined using the atomic coordinates of the cyclobutane rings in the 13% dimer crystals. [c] Distance between the olefin carbon adjacent to the phenyl ring in an unreacted monomer and the carbon adjacent to the pyrylium group in its reaction partner.

The monomer exhibits disorder in the counterion and t-butyl groups. Two orientations for each of those moieties are observed at room temperature. The fact that the solid state C-13 MAS spectrum of the monomer showed only one t-butyl signal suggests that this is a dynamic process. This is further confirmed by the observation that when the crystal structure is determined at 165K, this disorder vanishes. Surprisingly, this disorder is absent at room temperature in the as-dimerized dimer, indicating that the shapes of the original cavities that permitted these rotations in the monomer, evolve in such a way so as to prevent these rotations in the dimer. The recrystallized dimer, however, exhibits the full disorder present in the monomer. Thus the as-dimerized dimer is in a metastable state, that is, its as-reacted conformation is not its equillibrium conformation. The consequence of this is a lattice strain which facilitates the back reaction. In the recrystallized dimer, assumed to be much closer to the equillibrium conformation, this lattice strain is absent and consequently the cyclobutane dimer does not cleave.

This thermal cycloreversion of the as-dimerized dimer to monomer occurs at 105°C with an unusually low enthalpy of reaction of 18 kcal·mol^{-1}. Even more unusual

is that this process is also a homogeneous conversion to the original monomer state with retention of the single crystalline character. A full crystal structure analysis of the thermally regenerated monomer was performed and within experimental error gave identical atomic parameters. This suggests the possibility to homogeneously cycle these monomer and dimer states.

THERMALLY ERASABLE HOLOGRAPHIC GRATING

Studies involving homogeneously cycling the monomer and dimer states have begun. It is possible to create a periodic spatial distribution of monomer and dimer within a single crystal by irradiating it with an optical interference grating, created by

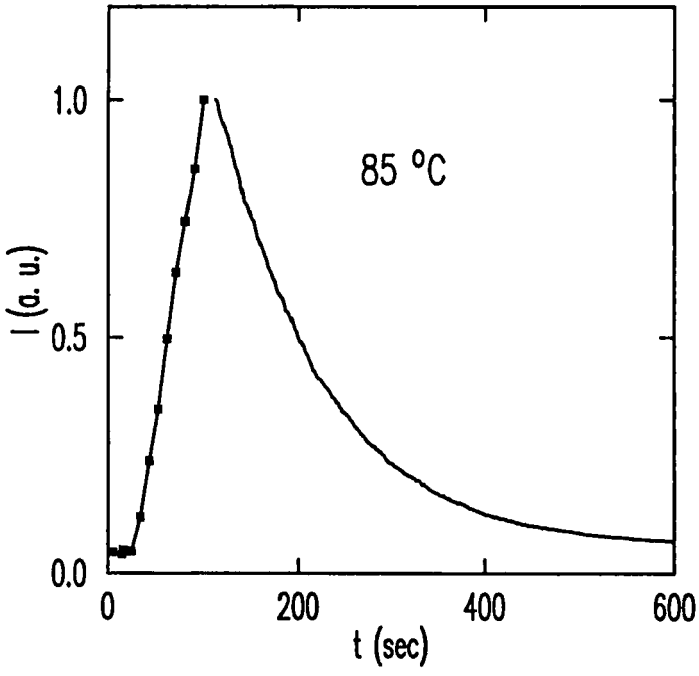


FIGURE 2. Growth and decay curves for a holographic grating written into a styrylpyrylium crystal. The grating was written and "read" in a stepwise manner at 85°C until the desired diffraction intensity had been reached. Filters were then used to reduce the intensity of the reading beam by a factor of 2000 to avoid bleaching out the grating. The thermal decay of the grating was then monitored continuously at 85°C. Both the growth and the decay curve are normalized to 1 at the time where the filter was inserted

two intersecting beams from a He-Ne laser (633nm). The grating can then be erased by heating the crystal. Figure 2 shows the growth of diffraction efficiency of a grating, with increasing writing exposure, followed by the decay on heating. The growth and decay curves at various temperatures have been measured and energies of activation for the thermal back reaction and photodimerization have been calculated at 99 and 15 kJ mol^{-1}, respectively.

CONCLUSION

As mentioned above, this homogeneous photodimerization is not a unique case. Cinnamic acid and distyrylpyrazine also react homogeneously by tail irriadiation to form single crystals of photoproduct. Furthermore, styrylpyrylium monomers with a variety of counterions (eg. BF_4^-, ClO_4^-, ReO_4^-, SbF_6^-, $AuCl_2^-$, $SnCl_5^-$ etc.) have been prepared. Some have also been found to be reactive in the crystalline state, homogeneously forming dimers through tail absorption irradiation. Thus, many solid state photoreactions, up until now considered heterogeneous, may proceed homogeneously when driven by irradiation at wavelengths limited to the absorption tail of the chromophore.

EXPERIMENTAL

Sample Preparation and Irradiation

The styrylpyrylium monomer was prepared and recrystallized as described elsewhere.[9] For each conversion, 8-9 crystals, 0.3-0.5mm in length, were aligned along the same optical axis using the crystal habit as a guide. Irradiations were performed with a Coherent Innova 90 Kr laser. The crystals were rotated in a beam in an area of uniform intensity created with a beam expander. After each dosage, 2-3 of the crystals were submitted for crystallographic study while the balance of the crystals were taken for IR percent conversion analysis. An IR calibration curve was created using monomer irradiated with a Xenon lamp and analyzed by proton NMR.

X-ray Analysis

X-ray structure analyses: Enraf-Nonius diffractometer CAD-4, graphite monochromated CuKα radiation (λ=1.5405Å). The structures were solved by direct methods (SIR) and refined by full matrix least-squares analysis with anisotropic temperature factors for C, O, S, F. The H atoms were refined in the riding mode with fixed isotropic temperature factors. For the 67% dimerized substitutional mixed crystal at T=165°K, a=10.7497(12), b=14.2531(13), c=16.4773(15), β=105.267(7)°, V=2435.5 $Å^3$, Z=4, D_x=1.294 gcm^{-3}, group=$P2_1/c$, μ=16.187, 3215 relfections measured, 1863 observed, ($I>3\sigma(I)$), R=0.090, R_w=0.082.

Solid State NMR

The solid state C-13 NMR was performed on a Bruker MSL 300 at 75.47 MHz. The MAS (Magic Angle Spinning) speed was 3 kHz, the Cross Polarization time was 2 msec. A Total Suppresion of Spinning Side Bands (TOSS) pulse sequence was used.

The signal acquisition was done over 35 msec., the 90° pulse length was 4.5μsec., and the spectral width was 29,411 Hz. 2048 data points were collected.

Thermal Analysis

The enthalpy of reaction for the cyclobutane cleavage was measured on a Mettler DSC 30 at a sweep rate of 5°C/min.

Holography

Holographic interference gratings with a fringe spacing 17.3 μm were written by means of a 30 mW He-Ne laser (633nm). Between the writing periods of typically 10 seconds, one of the two beams was blocked by a shutter and the diffraction efficiency was measured with the remaining beam during an integration time of 0.5 seconds. Drift was eliminated by active phase stabilization of the interference grating. For temperature control, the crystal was mounted on a glass fiber and inserted together with a Pt 100 resistor in a cylindrical oven of 20 mm in length and 10 mm in diameter. For measuring the decay curves, the probe beam was attenuated a factor of at least 2000.

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