Single-Crystal-to-Single-Crystal Photodimerization of Cinnamic Acid

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[2 + 2] photodimerizations are among the most well-studied reactions in topochemistry.[1] For example, Schmidt's *topochemical principle* is based on his landmark studies of the [2 + 2] photodimerization of cinnamic acid derivatives, where the symmetry of the monomer packing was correlated with the stereochemistry of the dimer.[2] These dimerizations and other topochemical photoreactions are reported to occur heterogeneously; that is, the single crystal disintegrates into microcrystalline particles, which makes full X-ray structure analysis of the as-reacted product impossible. Indeed, topochemical single-crystal-to-single-crystal photoreactions are rare.[3–11] But typically the reactions which occur with destruction of the single-crystalline nature of the sample are effected with radiation that falls in the range of the absorption maximum of the chromophore. We wish to propose a general method for inducing single-crystal-to-single-crystal transformations, by irradiation with wavelengths corresponding to the chromophore's absorption *tail.* We present, as an example, the first homogeneous, crystal-to-crystal photodimerization of a cinnamic acid or its derivative.

When topochemical photoreactions are carried out by irradiating the chromophore with light in the maximum of its spectrum, the light intensity (and thus product formation) is high at the incident surface and drops off quickly through the inner bulk of the crystal. Thus the spatial distribution of product molecules is heterogeneous. In the course of the photoreaction, van der Waals contacts are converted to chemical bonds; and thus a dimensional mismatch between the product and reactant lattices exists. Eventually the product lattice, concentrated at the surface of the crystal, reaches its limit of solubility in the original monomer lattice due to this mismatch, and the reacting phase and product phase separate. This precipitation of the product causes the disintegration of the crystal.

However, when a photoactive crystal, such as cinnamic acid, is exposed to light for which it has a low absorption, the light intensity is comparatively even from the surface throughout the bulk of the crystal; and thus the product distribution within the crystal is homogeneous. The consequence of this is that a solid solution of reactant and product is maintained. Thus at any point in the conversion, a perfect single crystal exists with reactant and product molecules statistically occupying the same lattice sites. Therefore, it is possible that a topochemical reaction which proceeds with destruction of the single crystal under broad-band

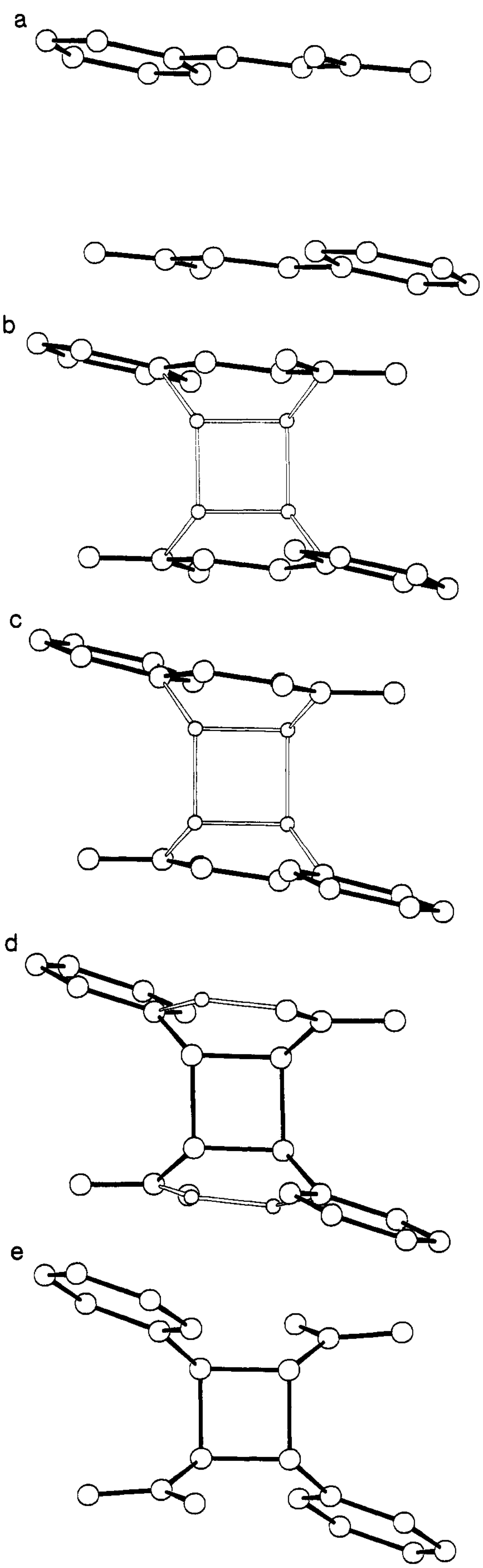

Figure 1. Projections of the crystal structures of α-*trans*-cinnamic acid single crystals at (a) 0%, (b) 28%, (c) 40%, (d) 67%, and (e) 100% conversion to dimer.

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irradiation can proceed as a single-crystal-to-single-crystal conversion with tail irradiation.

We have demonstrated this phenomenon for *trans*-cinnamic acid of the α-crystalline modification,[12] Figure 1 shows projections of the crystal structures of an unirradiated α-*trans*-cinnamic crystal, three α-*trans*-cinnamic crystals which have been partially dimerized through tail irradiation, and as-dimerized truxillic acid.[13]

To compare the structures, consider the conformational reorientation the phenyl rings are expected to undergo for dimerization. The reacting olefin bond can be viewed as a crankshaft: when it rotates into the dimer position, the stiff arm of the phenyl substituent is driven out away from the reacting partner. In other words, the phenyl substituent pivots on the connecting sp^2 ring carbon. Thus in a partially reacted crystal, the phenyl substituents should have two orientations: unreacted and reacted. The same argument follows for the carboxyl side group.

However, inspection of parts b–d of Figure shows that two distinct sets of atomic coordinates are observed only for the C atoms which are directly involved in the cyclobutane formation. They correspond to the monomer and dimer positions of those reacting carbons. Only one electron density maximum for each of the atoms in the side groups is observed for each crystal. That is, the positions of the atoms in the phenyl ring and the carboxyl side groups are the same, within the positional error of the crystal structure analysis, regardless of whether those groups are part of a reacted or unreacted molecule.

We conclude that two structures with different equilibrium conformations are constrained to the same lattice positions to form a substitutional mixed crystal, the structure of which is established by the intermolecular contacts between the side groups. The consequence of the single orientation for each side group in these structures is bond angle deformation. Note that the deformation observed for the phenyl carbon attached to the cyclobutane ring is greater than that for the phenyl carbon attached to the unreacted double bond. Thus the crystal structure may be viewed as a compromise between the conformations of the monomer and dimer, with the expected result that the species of higher concentration in the lattice is less deformed. This deformation can be measured as the angle between the plane of the phenyl ring and the axis corresponding to the bond linking the phenyl ring to the cyclobutane carbon or the unreacted olefin carbon. Table I summarizes these values.

Table I. Selected Dimensions from Crystal Structures of α-*trans*-Cinnamic Acid Single Crystals at Various Degrees of Dimerization

% dimer	phenyl ring tilt,[a] monomer/dimer (deg)	phenyl ring rotation,[b] deg
0		81.5
28	8.2/32.7	86.2
40	15.2/25.7	94.4
67	25.5/13.6	96.9
100		100.9

[a] Angle between plane of phenyl ring and the axis along the bond linking the phenyl ring to the double bond or cyclobutane ring. [b] Dihedral angle the plane of the phenyl ring makes with the plane of the cyclobutane ring. Note that, for the undimerized crystal, the cyclobutane plane for the dihedral angle was defined using the atomic coordinates of the cyclobutane rings in the 28% and 40% dimer crystals.

As the dimer lattice evolves, the side groups also rotate along the axes of the bonds which connect them to the reacting centers. The rotational conformation of the phenyl rings, as well as the carboxyl side groups, shows significant differences in the 28% dimerized mixed crystal compared to the 40%. For example, in Figure 1b, the view of the phenyl substituent behind the plane of the cyclobutane ring is to the side of the phenyl ring which faces the reacting partner, whereas in Figure 1c, the view is on the opposite side. The rotation of the phenyl rings, measured as the dihedral angle between the plane of the cyclobutane ring and the plane of the phenyl ring, is listed for each structure in Table I.

Many topochemical photoreactions, which up until now have been driven heterogeneously, may proceed homogeneously with absorption-tail irradiation to yield intact single crystals of the photoproduct. This has been demonstrated not only for the dimerization of cinnamic acid but also for a variety of styrylpyrylium salts,[14] as well as for the photopolymerization of DSP.[9] Along these lines, it is important to note that Kaupp's recently reported atomic force microscope studies of the surface of cinnamic acid crystals irradiated with broad-band irradiation offer no evidence in violation of the topochemical principle.[15] Rather it is simply the texture that evolves in a heterogeneous transformation due to phase separation.

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Supplementary Material Available: A listing of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for cinnamic acid, 28%, 40%, and 67% dimerized cinnamic acid, and truxillic acid (14 pages); structure factors for cinnamic acid, 28%, 40%, and 67% dimerized cinnamic acid, and truxillic acid (39 pages). Ordering information is given on any current masthead page.

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(12) α-*trans*-Cinnamic acid monomer crystals, varying from 0.3 to 0.7 mm along one edge, were obtained by evaporation of an ether solution of the acid. The irradiation was done at room temperature with a 450-W xenon lamp from Photon Technology International Inc., Model A 5000. A quartz diffusor was placed in the beam focus, 17 cm from the lamp housing, with an air-cooled Schott long-pass filter at 21 cm. The transmission vs wavelength cutoff curves for these filters shift toward longer wavelengths as the filter number increases. For example, Schott filter WG345 has a degree of transmission of 0.60 at $\lambda = 350$ nm, whereas WG360 has a degree of transmission of 0.05 at that wavelength. A thin-walled NMR tube containing the crystals was placed immediately adjacent to the edge filter in the beam. The 28% dimer crystals were obtained after irradiation in an NMR tube of 10-mm diameter, with long-pass filter WG345 for 100 h. The degree of conversion was determined by integration of the cyclobutane and vinyl signals in the ^{1}H NMR and was consistent with the percent conversion derived from the population parameters in the crystallographic analysis. The 40%, 67%, and 100% dimer crystals were obtained from a batch of crystals irradiated in an NMR tube of 5-mm diameter, with long-pass filter WG360 for 100 h. ^{1}H NMR sampling of the batch indicated an average conversion of over 90%. The percent conversions of the individual crystals were derived from the population parameters of the crystallographic analysis.

(13) X-ray structure analyses: Enraf-Nonius diffractometer CAD-4, graphite-monochromated Cu Kα radiation ($\lambda = 1.5405$ Å), $\theta = 55°$. The structures were solved by direct methods (SIR) and refined by full-matrix least-squares analysis with anisotropic temperature factors for C and O. The H atoms were refined in the riding mode with fixed isotropic temperature factors. The occupancy factors were included in the refinement and constrained so that the total occupancy was 1.0. The esd of the occupancy factor was less than 1%. For the monomer crystal at $T = 165$ K, $a = 7.7163(18)$ Å, $b = 17.6101(68)$ Å, $c = 5.5655(19)$ Å, $\beta = 96.396(24)°$, $V = 751.6$ Å^3, $Z = 4$, $D_{calcd} = 1.307$ g cm^{-3}, group = $P2_1/n$, $\mu = 7.17$, 985 reflections measured, 775 observed ($I > 3\sigma(I)$), $R = 0.066$, $R_w = 0.077$. For the 28% converted mixed crystal at $T = 165$ K, $a = 7.658(6)$ Å, $b = 18.217(6)$ Å, $c = 5.533(2)$ Å, $\beta = 100.68(5)°$, $V = 758.5$ Å^3, $Z = 4$, $D_{calcd} = 1.302$ g cm^{-3}, group = $P2_1/n$, $\mu = 7.13$, 993 reflections measured, 547 observed ($I > 3\sigma(I)$), $R = 0.100$, $R_w = 0.077$. For the 40% converted mixed crystal at $T = 165$ K, $a = 7.625(7)$ Å, $b = 18.283(9)$ Å, $c = 5.550(5)$ Å, $\beta = 102.41(7)°$, $V = 755.5$ Å^3, $Z = 4$, $D_{calcd} = 1.300$ g cm^{-3}, group = $P2_1/n$, $\mu = 7.13$, 917 reflections measured, 575 observed ($I > 3\sigma(I)$), $R = 0.080$, $R_w = 0.073$. For the 67% converted mixed crystal at $T = 165$ K, $a = 7.593$ Å, $b = 18.322$ Å, $c = 5.594$ Å, $\beta = 104.415°$, $V = 753.8$ Å^3, $Z = 4$, $D_{calcd} = 1.306$ g cm^{-3}, group = $P2_1/n$, $\mu = 7.16$, 984 reflections measured, 616 observed ($I > 3\sigma(I)$), $R = 0.073$, $R_w = 0.074$. For the 100% converted crystal at $T = 165$ K, $a = 7.668(5)$ Å, $b = 18.231(8)$ Å, $c = 5.595(2)$ Å, $\beta = 106.24(4)°$, $V = 750.9$ Å^3, $Z = 4$, $D_{calcd} = 1.311$ g cm^{-3}, group = $P2_1/n$, $\mu = 7.19$, 983 reflections measured, 746 observed ($I > 3\sigma(I)$), $R = 0.040$, $R_w = 0.040$.

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