In the crystal structure of (II), there is an intermolecular hydrogen bond between O(1) (x, y, z) and O(7) $(1-x, \frac{1}{2}+y, \frac{3}{2}-z)$ atoms, but in (III) the hydrogen bond is made between O(1) (x, y, z) and N(1) $(\frac{1}{2}+x, \frac{3}{2}-y, -z)$ atoms. Their distances and angles are as follows: O(1)$\cdots$O(7) = 2·768 (5) Å, O(1)—H$\cdots$O(7) = 173°, O(1)$\cdots$N(1) = 2·815 (5) Å, O(1)—H$\cdots$N(1) = 148°. The significant lengthening of N(1)—C(17) and N(1)—C(18) bonds in (III) may be due to the effect of the intermolecular hydrogen bond. The N atom in (III) is more pyramidal than that in (II). The deviations of the N atoms from the plane defined by C10, C17, and C18 atoms are 0·370 (3) and 0·402 (3) Å in (II) and (III), respectively.

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Topochemical Studies. X.* Structures of 4-Methyl-*trans*-cinnamic Acid and 4,4′-Dimethyl-α-truxillic Acid

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Abstract. 4-Methyl-*trans*-cinnamic acid (1), $C_{10}H_{10}O_2$, $M_r = 162{\cdot}19$, triclinic, $P\bar{1}$, $a = 7{\cdot}968$ (2), $b = 9{\cdot}144$ (2), $c = 7{\cdot}733$ (2) Å, $\alpha = 106{\cdot}87$ (2), $\beta = 125{\cdot}46$ (2), $\gamma = 86{\cdot}87$ (2)°, $V = 434{\cdot}5$ (2) Å^3, $Z = 2$, $D_m = 1{\cdot}20$, $D_x = 1{\cdot}240$ Mg m^{-3}, $\mu = 0{\cdot}71$ mm^{-1}, $F(000) = 172$, $R = 0{\cdot}061$ for 1395 unique reflections. 4,4′-Dimethyl-α-truxillic acid (2) [2,4-bis(*p*-tolyl)-1,3-cyclobutanedicarboxylic acid], $C_{20}H_{20}O_4$, $M_r = 324{\cdot}38$, monoclinic, $P2_1/a$, $a = 17{\cdot}767$ (3), $b = 8{\cdot}431$ (2), $c = 5{\cdot}578$ (2) Å, $\beta = 92{\cdot}94$ (2)°, $V = 834{\cdot}4$ (4) Å^3, $Z = 2$, $D_m = 1{\cdot}27$, $D_x = 1{\cdot}291$ Mg m^{-3}, $\mu = 0{\cdot}74$ mm^{-1}, $F(000) = 344$, $R = 0{\cdot}086$ for 1338 unique reflections. $T = 295$ K, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å. Structures have been determined on a photoreactive compound (1) and its photodimer (2) formed in the solid state. In the crystals of (1) the C=C double bonds of the nearest neighbours are related by $\bar{1}$ with C$\cdots$C distance of 4·133 (4) Å. The molecule of (2) has $\bar{1}$ symmetry in the crystal, indicating the topochemical formation of (2).

Introduction. The space groups and lattice parameters for the crystals of (1) and (2) have been reported by Schmidt and his co-workers in their early works on topochemistry (Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). However, the three-dimensional structures have been left to be solved. In order to elucidate the mechanism of the solid-state photoreaction in detail, it is desirable to know the crystal and molecular structures of both the reactants and the products. We have undertaken X-ray structure analysis of photoreactive monomers and their products as an extension of studies of molecular overlapping and packing of unsaturated organic compounds in crystals (Haisa, Kashino, Yuasa & Akigawa, 1976). We report results for a classical pair of compounds, (1) and (2).

Experimental. Experimental details for (1) and (2) are listed in Table 1. Crystals of (1) grown from an ethanol solution by slow evaporation. Photodimer (2) prepared following the method described by Cohen, Schmidt & Sonntag (1964); crystals of (1) exposed to sunlight for two months. Single crystals of (2) grown from an ethanol solution of the irradiated sample by slow evaporation. D_m by flotation in aqueous KI. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode; ω–2θ scan method (scan speed 4° min^{-1} in ω, scan range in ω: $1{\cdot}2° + 0{\cdot}15° \tan\theta$); Ni-filtered Cu $K\alpha$, 40 kV, 200 mA; background measured for 4 s on either side of the peak; three standard reflections recorded every 57 reflections; Lorentz and polarization corrections; no absorption correction. All unique

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* Part IX: Haisa, Kashino, Yuasa & Akigawa (1976).

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reflections including zero reflections within $(\sin\theta)/\lambda = 0{\cdot}5753$ Å^{-1} used in the structure analyses and refinements; structure of (1) solved by Patterson method, and that of (2) by *MULTAN*78. The positions of the H atoms determined from difference Fourier maps. The structures refined by block-diagonal least squares with anisotropic thermal parameters for non-H atoms and isotropic for H atoms; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1{\cdot}0/[\sigma(F_o)^2 + p|F_o| + q|F_o|^2]$ for $|F_o| > 0$, $w = r$ for $|F_o| = 0$. Correction for secondary extinction with $I_{\rm corr} = I_o\,(1 + 1{\cdot}2 \times 10^{-5} I_c)$ applied for three strongest reflections of (1), but no correction for (2). Somewhat high R value for (2) ascribed to the mosaic spread of the crystal: high background observed for some reflections (001, 002, 602). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs *RSSFR*-5 (Sakurai, 1967), *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLS*-V and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971). Computations carried out at the Crystallographic Research Center, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Table 1. *Experimental details.*

	(1)	(2)
M.p. (K)	471–477	566
Crystal habits	Prismatic *c*	Prismatic *c*
Size of specimen (mm)	0·10 × 0·20 × 0·30	0·10 × 0·10 × 0·30
Reflections for lattice parameters		
Number	20	20
2θ range (°)	20–46	19–43
Systematic absences	No condition	*h*0*l*, *h* odd 0*k*0, *k* odd
$2\theta_{\rm max}$ (°)	125	125
Range of *h, k, l*	$-9 \le h \le 9$ $-10 \le k \le 10$ $0 \le l \le 8$	$-20 \le h \le 20$ $0 \le k \le 9$ $0 \le l \le 6$
Fluctuation of standard reflections		
$\sum(\lvert F_o\rvert/\lvert F_{o\,\rm initial}\rvert)/3$	1·007–0·983	1·000–0·986
Number of unique reflections	1395	1338
Number of reflections with $\lvert F_o\rvert > \sigma(F_o)$	1264	1254
$R_{\rm int}$	0·014 for 117 *hk*0 reflections	0·011 for 151 *hk*0 reflections
Number of parameters	150	150
R	0·061	0·086
wR	0·085	0·129
Constants for w		
p	0·0140	0·1643
q	0·0012	−0·0009
r	16·8835	2·6461
S	0·98	0·96
$(\Delta/\sigma)_{\rm max}$	0·2	0·7
$\Delta\rho$ max. (min.) (e Å^{-3})	0·15(−0·11)	0·28(−0·38)

Table 2. *Final atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{\rm eq} = (4/3)\sum\beta_{ii}/a_{ii}^{*2}.$$

	x	y	z	$B_{\rm eq}$(Å^2)
4-Methyl-*trans*-cinnamic acid (1)				
O(1)	9905 (3)	−355 (2)	7666 (3)	8·22 (9)
O(2)	8190 (2)	1178 (2)	8717 (3)	7·94 (8)
C(1)	5062 (3)	2437 (2)	2791 (3)	5·61 (9)
C(2)	5462 (3)	2044 (3)	1208 (4)	6·6 (1)
C(3)	4377 (4)	2543 (3)	−633 (4)	6·7 (1)
C(4)	2871 (3)	3481 (3)	−964 (3)	6·1 (1)
C(5)	2492 (4)	3884 (4)	610 (5)	8·6 (1)
C(6)	3565 (4)	3386 (3)	2466 (4)	8·4 (1)
C(7)	6171 (3)	1935 (3)	4768 (3)	6·2 (1)
C(8)	7628 (3)	1037 (3)	5326 (4)	6·3 (1)
C(9)	8631 (3)	590 (2)	7342 (3)	6·2 (1)
C(10)	1699 (4)	4022 (3)	−2981 (4)	7·9 (1)
4,4′-Dimethyl-α-truxillic acid (2)				
O(1)	5364 (2)	8561 (3)	2862 (5)	4·5 (1)
O(2)	4643 (2)	8383 (3)	6011 (5)	4·3 (1)
C(1)	3705 (2)	4372 (3)	3984 (6)	2·8 (1)
C(2)	2989 (2)	4762 (4)	4687 (6)	3·3 (1)
C(3)	2356 (2)	4312 (5)	3334 (7)	3·9 (2)
C(4)	2404 (2)	3460 (4)	1236 (7)	3·5 (1)
C(5)	3121 (2)	3027 (4)	582 (7)	3·6 (2)
C(6)	3757 (2)	3488 (4)	1911 (7)	3·4 (1)
C(7)	4385 (2)	5039 (3)	5340 (6)	2·7 (1)
C(8)	4922 (2)	6034 (4)	3804 (6)	2·7 (1)
C(9)	4958 (2)	7768 (4)	4362 (6)	3·0 (1)
C(10)	1715 (2)	3047 (7)	−298 (8)	5·2 (2)

Discussion. The final atomic parameters are listed in Table 2.[*] The thermal ellipsoids of the molecules are shown in Fig. 1, with atomic numbering. Bond lengths and interbond angles are listed in Table 3. Stereoviews of the crystal structures are shown in Fig. 2.

The molecule of (1) is approximately planar; the benzene ring is planar within 0·008 (5) Å. C(7) and C(10) lie in this plane. The torsion angles C(2)—C(1)—C(7)—C(8), C(1)—C(7)—C(8)—C(9) and C(7)—C(8)—C(9)—O(2) are −1·8 (5), −179·4 (3) and −5·1 (5)°, respectively. C(1)—C(7)—C(8) is widened as found in other cinnamic acids (Glusker, Zacharias & Carrell, 1975). The inner angle at C(4) is smaller than the sp^2 angle as commonly observed in methyl-substituted benzene derivatives (Domenicano, Vaciago & Coulson, 1975). The length of the C=C double bond is in agreement with those found in 4-chlorocinnamic acid (Glusker, Zacharias & Carrell, 1975) and in 4-formylcinnamic acid (Nakanishi, Hasegawa & Mori, 1985).

In the crystal the molecules of (1) form a centrosymmetric dimer through hydrogen bonds between the carboxyl groups [O···O 2·620 (3), H···O 1·49 (4) Å, O—H···O 174 (4)°]. The dimers are packed side by side to form a sheet nearly parallel to $(1\bar{2}1)$. The sheets are stacked along [111]. The C=C double bonds of the molecules in the nearest sheets are related by $\bar{1}$ at ($\frac{1}{2}$, 0, $\frac{1}{2}$) with a C(7)···C(8) distance of 4·133 (4) Å, the interplanar spacing being 3·514 (4) Å for the plane through C(1), C(7), C(8) and C(9).

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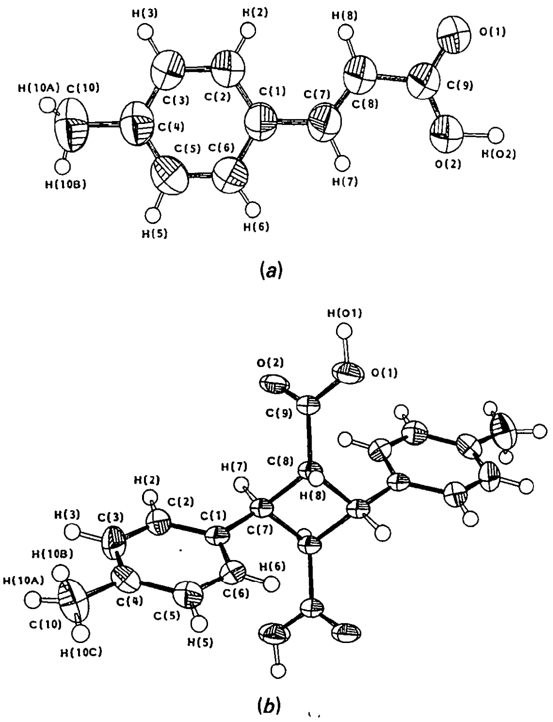
[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Centre as Supplementary Publication No. SUP 51375 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(*a*)

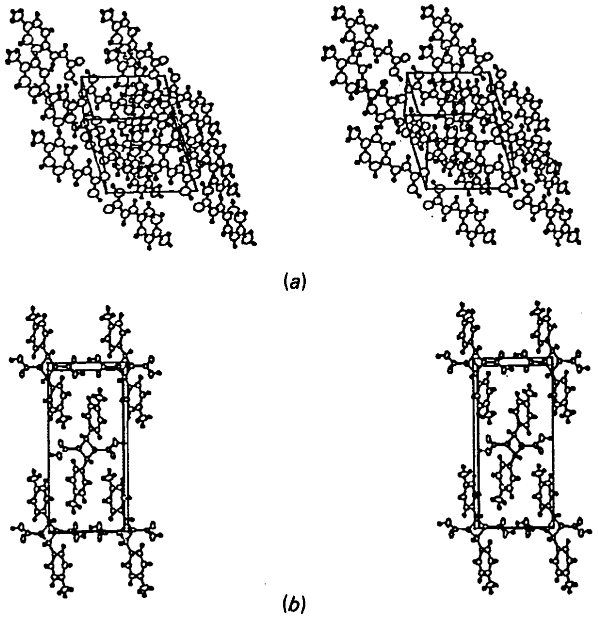
(*b*)

Fig. 1. The thermal ellipsoids of the molecules with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2; (*a*) 4-methyl-*trans*-cinnamic acid (1), (*b*) 4,4′-dimethyl-α-truxillic acid (2).

Table 3. *Bond lengths* (Å) *and interbond angles* (°) *with e.s.d.'s in parentheses*

Atoms translated by a center of symmetry in the molecule of (2) are shown with a prime.

	4-Methyl-*trans*-cinnamic acid (1)	4,4′-Dimethyl-α-truxillic acid (2)
O(1)—C(9)	1·255 (4)	1·315 (4)
O(2)—C(9)	1·274 (4)	1·217 (4)
C(1)—C(2)	1·384 (4)	1·390 (4)
C(1)—C(6)	1·380 (4)	1·383 (5)
C(1)—C(7)	1·458 (4)	1·501 (4)
C(2)—C(3)	1·374 (4)	1·375 (5)
C(3)—C(4)	1·378 (4)	1·379 (6)
C(4)—C(5)	1·365 (5)	1·392 (6)
C(4)—C(10)	1·502 (4)	1·498 (7)
C(5)—C(6)	1·383 (5)	1·375 (6)
C(7)—C(8)	1·315 (4)	1·559 (4)
C(8)—C(9)	1·458 (4)	1·495 (4)
C(7)—C(8′)		1·582 (4)
C(2)—C(1)—C(6)	116·9 (3)	117·7 (3)
C(2)—C(1)—C(7)	123·4 (3)	119·6 (3)
C(6)—C(1)—C(7)	119·7 (3)	122·5 (3)
C(1)—C(2)—C(3)	121·4 (3)	121·0 (3)
C(2)—C(3)—C(4)	121·6 (3)	121·7 (4)
C(3)—C(4)—C(5)	117·1 (3)	117·1 (4)
C(3)—C(4)—C(10)	121·1 (3)	121·4 (4)
C(5)—C(4)—C(10)	121·9 (3)	121·4 (4)
C(4)—C(5)—C(6)	122·0 (3)	121·5 (4)
C(1)—C(6)—C(5)	121·0 (3)	121·0 (4)
C(1)—C(7)—C(8)	127·4 (3)	115·1 (3)
C(7)—C(8)—C(9)	123·1 (3)	115·6 (3)
O(1)—C(9)—O(2)	122·4 (3)	123·6 (3)
O(1)—C(9)—C(8)	118·8 (3)	112·6 (3)
O(2)—C(9)—C(8)	118·8 (3)	123·9 (3)
C(8)—C(7)—C(8′)		89·1 (2)
C(7)—C(8)—C(7′)		90·9 (2)
C(1)—C(7)—C(8′)		122·1 (3)
C(7′)—C(8)—C(9)		118·2 (3)



(*a*)

(*b*)

Fig. 2. Stereoviews of molecular packing. (*a*) 4-Methyl-*trans*-cinnamic acid (1); the *a* axis points onto the plane of the paper, the *b* axis from left to right, and the *c* axis upwards. (*b*) 4,4′-Dimethyl-α-truxillic acid (2); the *a* axis points upwards, the *b* axis from left to right, and the *c* axis into the plane of the paper.

The molecule of (2) has $\bar{1}$ at the center of the cyclobutane ring, indicating that the molecule is topochemically formed from (1) (the atoms related by the $\bar{1}$ are denoted with a prime hereafter). The conformations of the exocyclic bonds are *gauche* for C(1)—C(7)—C(8)—C(9) [$\tau = 112{\cdot}5\,(3)°$], and *cis* for C(1)—C(7)—C(8′)—C(9′) [$\tau = -0{\cdot}5\,(4)°$]. Thus, it is concluded that the dimerization occurred between C(7) and C(8′) based on the topochemical principle of minimum amount of atomic movement in the solid-state reaction (Cohen & Schmidt, 1964). Consistent with the conformations, C(1)—C(7)—C(8′) and C(7)—C(8′)—C(9′) are wider than C(1)—C(7)—C(8) and C(7)—C(8)—C(9), and C(7)—C(8′) is lengthened with respect to C(7)—C(8) by a steric repulsion C(1)···C(9′), 3·086 (4) Å. Widening of C(1)—C(7)—C(8′) is also caused by an intramolecular repulsion C(6)···C(8′), 3·288 (5) Å.

In the crystal the molecules of (2) are held together by O—H···O hydrogen bonds [O···O 2·652 (4), H···O 1·85 (7) Å, O—H···O 143 (6)°] around the $\bar{1}$ at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and ($\frac{1}{2}$, 1, $\frac{1}{2}$) to form a chain of molecules along **b**.

However, the crystals are elongated along **c** by large numbers of van der Waals interactions between the molecules related by a **c** translation.

The present results make it possible to estimate the minimum displacements ΔR of the C=C double bonds in the reaction from the geometry of the cyclobutane ring of (2) and the arrangements of the C=C double bonds related by the $\bar{1}$ in the crystals of monomers. ΔR is composed of three components, $\Delta X, \Delta Y, \Delta Z$:

$$\Delta R^2 = \Delta X^2 + \Delta Y^2 + \Delta Z^2$$

where ΔX is the displacement perpendicular to the C=C double bond in the molecular plane, ΔY the displacement parallel to the C=C double bond in the molecular plane, and ΔZ the displacement perpendicular to the molecular plane. For the reaction from (1) and (2) one estimates $\Delta X = 1{\cdot}12$, $\Delta Y = 0{\cdot}00$, $\Delta Z = 0{\cdot}97$ and $\Delta R = 1{\cdot}48$ Å. The corresponding values are in the range $\Delta X = 0{\cdot}22$ to 0·66 Å, $\Delta Y = 0{\cdot}10$ to 0·66 Å, $\Delta Z = 0{\cdot}92$ to 0·96 Å and $\Delta R = 1{\cdot}11$ to 1·21 Å for a series of photoreactive cinnamic acids whose crystal structures have been determined [cinnamic acid (Bryan & Freyberg, 1975); 4-hydroxycinnamic acid (Bryan & Forcier, 1980); 3-hydroxycinnamic acid (Raghunathan & Pattabhi, 1981); 2-hydroxycinnamic acid (Raghunathan & Pattabhi, 1979)] and the centrosymmetric photodimers have been identified (Schmidt, 1964). How such geometrical factors govern the photoreactivity in the solid state would be clarified by extending the type of compounds.

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