

Crystal-to-crystal photodimerization of  
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In the crystals of *trans*-4-methylcinnamamide, C<sub>10</sub>H<sub>11</sub>NO (I), *trans*-4-chlorocinnamamide, C<sub>9</sub>H<sub>8</sub>ClNO (II), *trans*-3-(2-thienyl)acrylamide, C<sub>7</sub>H<sub>7</sub>NOS (III), and *trans*-cinnamamide, C<sub>9</sub>H<sub>9</sub>NO (IV), the shortest intermolecular C···C distances between the C=C double bonds are 3.670 (2), 3.632 (2), 3.762 (3) and 4.120 (2) Å, respectively, for the pair of molecules related by a center of symmetry. The structure analysis was also carried out for *trans*-2-(*p*-chlorophenyl)-*cis*-4-(*p*-chlorophenyl)-1-*trans*-3-diamidocyclobutane, C<sub>18</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (V), which is the α-type photodimer of (II). The N—H···O hydrogen-bond networks in (I)–(III) are composed of two-dimensional pleated sheets, and those in (IV) and (V) of one-dimensional flat ribbons. The single crystals of (I), (II) and (IV) were photoirradiated with a 250 W ultra-high-pressure mercury lamp through a band-pass filter or a long-pass filter for 2–5 h. The photodimer was produced in each crystal with retention of the single-crystal form. The populations of the dimers were converged to 86.2 (4), 48.4 (6) and 4.5 (2)% in the refinement of the crystals after photoirradiation, (I'), (II') and (IV'), respectively. Although the intermolecular N—H···O hydrogen-bond network remained in (I') and (II'), the network was partly broken in (IV') in the process of photoreaction.

## 1. Introduction

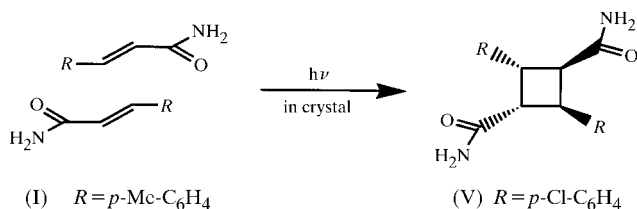
Solid-state [2 + 2] photodimerization of *trans*-cinnamic acids was extensively investigated by Schmidt and coworkers to establish the topochemical principles (Cohen & Schmidt, 1964; Cohen *et al.*, 1964; Schmidt, 1964). The crystal structures and hydrogen-bond networks of the *trans*-cinnamamide (IV) and the 4-chloro derivative (II) were also investigated (Rabinovich, 1969; Leiserowitz & Schmidt, 1969) as well as the [2 + 2] photoreaction of (I)–(III) (Hung *et al.*, 1972). An exposure of a single-crystal of (IV) to sunlight deformed the X-ray diffraction peaks, suggesting lattice distortion owing to photoreaction (Osaki & Schmidt, 1972). The photoreactivities of (I)–(IV) redetermined in the present study are shown in Table 1. The yields of α-type dimers of (I)–(III) were 97–100% after photoirradiation for 20 h. On the other hand, the yield of the dimer was only 18% for (IV). The C···C distance between the C=C double bonds in (IV) was reported to be 4.109 (4) Å (Iwamoto *et al.*, 1989), which is almost the maximum limit for the solid-state reaction. Moreover, the intermolecular N—H···O hydrogen-bond network in (IV) is different from that in (II). The hydrogen-bond networks in (I) and (III) are expected to be similar to that of (II) (Leiserowitz & Schmidt, 1969).

**Table 1**  
Photoreactivities of *trans*-cinnamamides in the solid state.

Compound	(I)	(II)	(III)	(IV)
Aromatic moiety	4-Me-Ph	4-Cl-Ph	2-Thienyl	Ph
Radiation time (h) <sup>†</sup>	20	20	20	20
Product yield (%) <sup>‡</sup>	100	100	97	18

<sup>†</sup> Powdered crystals were spread between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp under an argon stream at room temperature. <sup>‡</sup> Only the  $\alpha$ -truxillamides were obtained. The yields were estimated by NMR spectra.

A single-crystal-to-single-crystal transformation is an excellent method to observe *in situ* the reactions in the solid state (Suzuki, 1996; Tokitoh *et al.*, 1998; Hosomi *et al.*, 1998; Leibovitch *et al.*, 1998; Harada *et al.*, 1999; Hosomi *et al.*, 2000,



- (I)  $R = p\text{-Me-C}_6\text{H}_4$   
 (II)  $R = p\text{-Cl-C}_6\text{H}_4$   
 (III)  $R = \text{C}_4\text{H}_3\text{S}$   
 (IV)  $R = \text{C}_6\text{H}_5$

(V)  $R = p\text{-Cl-C}_6\text{H}_4$

and references therein). Photoirradiation far into the long wavelength absorption tail is effective for protecting the single crystals from degradation by the photoreaction (Enkelmann *et al.*, 1993; Novak *et al.*, 1993). This technique has been applied to the [2 + 2] photodimerization of *trans*-cinnamamides to see whether the photoreaction proceeds keeping the intermolecular hydrogen bonds.

## 2. Experimental

*trans*-4-Chlorocinnamamide (II) and *trans*-cinnamamide (IV) were commercially available. *trans*-4-Methylcinnamamide (I) and *trans*-3-(2-thienyl)acrylamide (III) were prepared according to the method reported (Hung *et al.*, 1972; Mason & Nord, 1951). The  $\alpha$ -type photodimer (V) was prepared by the solid-state reaction of (II). The crystals were grown by slow evaporation from ethanol (I), 2-propanol/ethanol (II), methylene chloride (III) and chloroform (IV)–(V) solutions.

Crystal data, experimental conditions and refinement details are listed in Table 2.<sup>1</sup> Absorption corrections were made by integration from crystal shape (Coppens *et al.*, 1965) for (II)–(III), and by  $\psi$ -scan for (V) (North *et al.*, 1968). Selected bond distances and angles are listed in Table 3, and the hydrogen-bonding geometry in Table 4.

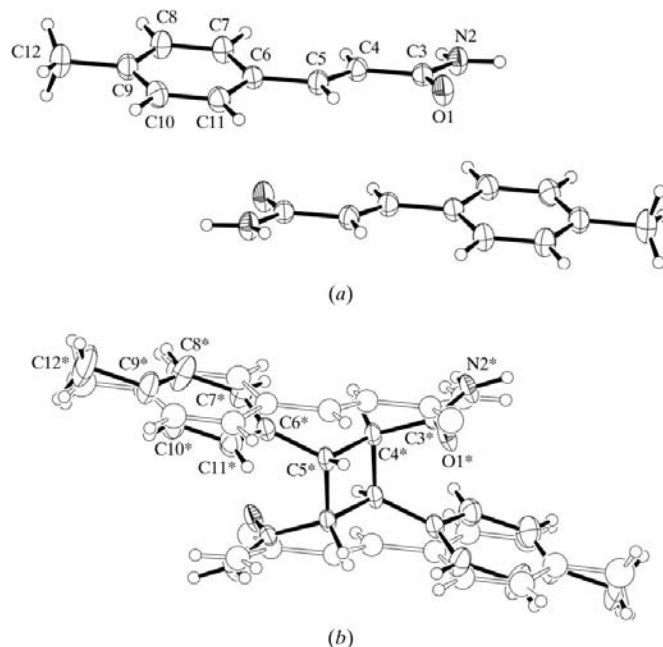
Structure (I): There is a rotational disorder of the methyl-H atoms. Two sets of positions [H12A/H12C and H12\*A/H12\*C] were assumed with site occupancy factor 50% each. Structure

(III): An orientational disorder of the thiophene ring was treated according to the convenient method by Pelletier & Brisse (1994), assuming that the S1 and C10\* atoms (and the S1\* and C10 atoms) share the same positional and displacement parameters. The site occupation factor of S1 was refined to 0.825 (3). The positional parameters of the H10 and H10\* atoms were calculated and fixed with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ .

Other H atoms were refined isotropically.

Structure (I'): A single crystal of (I) was photoirradiated with the 250 W ultra high-pressure Hg lamp through a band-pass filter BP365 ( $T = 50\%$  at 365 nm, half-height width 10 nm). The photoreaction was followed by measuring the lattice constants repeatedly on a four-circle diffractometer. The  $\beta$  value increased continuously and became obtuse from acute [87.69 (2)°]. The X-ray diffraction ability of the crystal decreased as the reaction proceeded and the X-ray measurement became impossible after photoirradiation for 10 h. To ensure sufficient resolution of the structure analysis, several crystals were photoirradiated for 5 h and X-ray intensities were measured on a crystal whose typical peak half-width was 0.45°. The population of the dimer was converged to 86.2 (4)%, and that of the monomer to 13.8 (4)%. The positional and isotropic displacement parameters of the atoms of the monomer were fixed to the corresponding values of (I). For the dimer, the non-H atoms were refined anisotropically.

Structure (II'): A single crystal of (II) was photoirradiated for 6 h with a 250 W ultra-high-pressure Hg lamp through a



**Figure 1**

(a) The structure of a pair of molecules in (I) related by a center of symmetry; (b) the disordered structure in (I') which consists of the monomer (open bonds) 13.8 (4)% and the dimer (solid bonds) 86.2 (4)%. Displacement ellipsoids are plotted at the 30% probability level. H atoms are shown as spheres of arbitrary size.

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA0024). Services for accessing these data are described at the back of the journal.

**Table 2**

Experimental details.

Atomic scattering factors were taken from *International Tables for Crystallography* (1992, Vol. C). For all compounds, data collection and cell refinement: *MSCI/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program used to solve structure: *SIR92* (Altomare *et al.*, 1994); program used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN* and *ORTEPII* (Johnson, 1976).

	(I)	(I')	(II)	(II')	(III)
<b>Crystal data</b>					
Chemical formula	C <sub>10</sub> H <sub>11</sub> NO	C <sub>10</sub> H <sub>11</sub> NO	C <sub>9</sub> H <sub>8</sub> ClNO	C <sub>9</sub> H <sub>8</sub> ClNO	C <sub>7</sub> H <sub>7</sub> NOS
Chemical formula weight	161.20	161.20	181.62	181.62	153.20
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	C2/c	C2/c	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c	Pbca
<i>a</i> (Å)	23.599 (3)	22.444 (1)	11.037 (1)	11.398 (3)	20.243 (3)
<i>b</i> (Å)	9.148 (3)	9.557 (2)	9.075 (2)	9.330 (4)	9.087 (2)
<i>c</i> (Å)	8.208 (3)	8.632 (1)	9.042 (2)	8.698 (3)	8.137 (2)
$\beta$ (°)	87.69 (2)	94.50 (1)	108.42 (1)	108.95 (2)	90
<i>V</i> (Å <sup>3</sup> )	1770.5 (8)	1845.9 (5)	859.3 (2)	874.8 (5)	1496.9 (4)
<i>Z</i>	8	8	4	4	8
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.209	1.160	1.404	1.379	1.359
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25	25
$\theta$ range (°)	13.2–15.0	12.0–14.6	12.2–14.8	10.7–14.8	14.3–14.9
$\mu$ (mm <sup>-1</sup> )	0.079	0.075	0.390	0.383	0.357
Temperature (K)	298 (1)	298 (1)	298 (1)	298 (1)	298 (1)
Crystal form	Plate-like	Plate-like	Plate-like	Plate-like	Plate-like
Crystal size (mm)	0.8 × 0.5 × 0.2	0.7 × 0.4 × 0.2	0.6 × 0.6 × 0.1	0.6 × 0.6 × 0.1	0.7 × 0.3 × 0.05
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colorless
<b>Data collection</b>					
Diffractometer	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R
Data collection method	$\theta$ - $2\theta$ scans	$\theta$ - $2\theta$ scans	$\theta$ - $2\theta$ scans	$\omega$ scans	$\theta$ - $2\theta$ scans
Absorption correction	None	None	Integration	Integration	Integration
<i>T</i> <sub>min</sub>	—	—	0.799	0.812	0.735
<i>T</i> <sub>max</sub>	—	—	0.961	0.962	0.975
No. of measured reflections	2080	2404	2101	2138	2476
No. of independent reflections	2034	2128	1977	2006	2188
No. of observed reflections	1420	1294	1360	1148	1074
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.030	0.017	0.015	0.026	0.024
$\theta$ <sub>max</sub> (°)	27.5	27.5	27.5	27.5	30
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 31 -12 → <i>k</i> → 0 -11 → <i>l</i> → 11	0 → <i>h</i> → 29 -12 → <i>k</i> → 5 -11 → <i>l</i> → 11	-14 → <i>h</i> → 14 0 → <i>k</i> → 12 -12 → <i>l</i> → 0	-14 → <i>h</i> → 14 0 → <i>k</i> → 12 -12 → <i>l</i> → 0	-14 → <i>h</i> → 28 0 → <i>k</i> → 12 0 → <i>l</i> → 11
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
<b>Refinement</b>					
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.038	0.062	0.038	0.049	0.049
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.116	0.212	0.115	0.145	0.142
<i>S</i>	1.03	1.19	1.02	1.11	0.99
No. of reflections used in refinement	2034	2128	1977	2006	2188
No. of parameters used	165	110	141	218	116
H-atom treatment	All H-atom parameters refined	H-atom parameters not refined	All H-atom parameters refined	H-atom parameters not refined	H atoms: see text
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.6818P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 2.4674P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.3386P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.2095P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.5253P]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.0001	0.0001	0.0001	0.0001	0.0001
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.16	0.30	0.27	0.15	0.21
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	-0.16	-0.22	-0.21	-0.14	-0.17
Extinction method	None	None	None	None	None

band-pass filter BP365. A peak half-width of X-ray diffraction increased gradually from 0.47 to 0.70°. The populations of the dimer and monomer were refined to 48.4 (6) and 51.6 (6)%, respectively. The positional parameters of all the

non-H atoms of the dimer and monomer were refined anisotropically.

Structure (IV'): Photoirradiation for several hours through BP365 or UV36 (*T* = 15% at 350 nm) did not cause a signifi-

Table 2 (continued)

	(IV)	(IV')	(V)
Crystal data			
Chemical formula	C <sub>9</sub> H <sub>9</sub> NO	C <sub>9</sub> H <sub>9</sub> NO	C <sub>18</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
Chemical formula weight	147.18	147.18	363.24
Cell setting	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	16.047 (2)	16.191 (2)	8.733 (3)
<i>b</i> (Å)	5.084 (2)	5.079 (2)	18.578 (9)
<i>c</i> (Å)	9.584 (2)	9.509 (2)	5.210 (3)
$\alpha$ (°)	90	90	91.86 (4)
$\beta$ (°)	94.06 (1)	93.37 (2)	93.04 (4)
$\gamma$ (°)	90	90	93.21 (3)
<i>V</i> (Å <sup>3</sup> )	779.9 (3)	780.7 (4)	842.2 (7)
<i>Z</i>	4	4	2
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.253	1.252	1.432
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25
$\theta$ range (°)	12.2–14.8	12.2–14.6	10.8–14.4
$\mu$ (mm <sup>-1</sup> )	0.083	0.083	0.398
Temperature (K)	298 (1)	298 (1)	298 (1)
Crystal form	Prism	Prism	Needle
Crystal size (mm)	0.8 × 0.3 × 0.2	0.8 × 0.3 × 0.2	0.4 × 0.1 × 0.05
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Rigaku AFC-7R	Rigaku AFC-7R	Rigaku AFC-7R
Data collection method	$\theta$ -2 $\theta$ scans	$\theta$ -2 $\theta$ scans	$\theta$ -2 $\theta$ scans
Absorption correction	None	None	$\psi$ scan
<i>T</i> <sub>min</sub>	—	—	0.868
<i>T</i> <sub>max</sub>	—	—	0.980
No. of measured reflections	1857	1859	3320
No. of independent reflections	1790	1793	2961
No. of observed reflections	1259	1163	1393
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.007	0.008	0.029
$\theta$ <sub>max</sub> (°)	27.5	27.5	25.0
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 21 -7 → <i>k</i> → 0 -12 → <i>l</i> → 12	0 → <i>h</i> → 21 -7 → <i>k</i> → 0 -12 → <i>l</i> → 12	0 → <i>h</i> → 10 -22 → <i>k</i> → 22 -6 → <i>l</i> → 6
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
Intensity decay (%)	0.8	1.3	0
Refinement			
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.040	0.051	0.091
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.121	0.160	0.221
<i>S</i>	1.02	1.05	1.60
No. of reflections used in refinement	1790	1793	2961
No. of parameters used	137	137	217
H-atom treatment	All H-atom parameters refined	H atoms: see text	H-atom parameters not refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0639P)^2 + 0.0958P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2 + 0.0444P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.0001	0.0001	0.0001
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.12	0.20	0.85
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	-0.15	-0.18	-0.39
Extinction method	SHELXL97 (Sheldrick, 1997)	None	None
Extinction coefficient	0.066 (8)	—	—

cant change in lattice constants of (IV). The irradiation through a long-pass filter UV34 (*T* = 10% at 330 nm) caused the reaction, although the crystal easily decomposed. After several trials, the X-ray intensities were measured using the crystal irradiated through the UV34 for 2 h. The typical peak

half-width increased from 0.38 to 0.45° without splitting. At first, the non-H atoms of the monomer constituent were refined anisotropically and the H atoms were refined isotropically. Then, the C4\* and C5\* atoms of the photodimer were located on a difference synthesis. The C4\*—C5\* and C4\*—

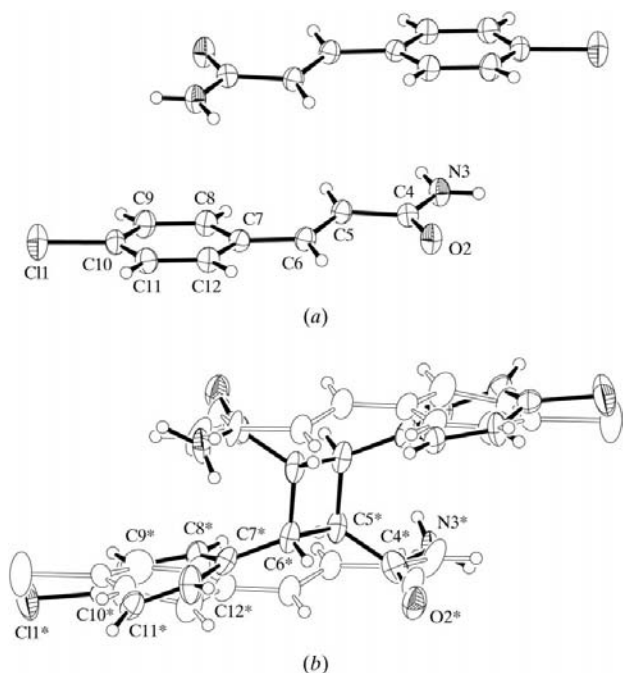
$C5^{*iv}$  bond lengths were reasonable for a cyclobutane ring. Positional parameters of the  $O1^*$ ,  $N2^*$ ,  $C3^*$ ,  $C6^*$ ,  $C7^*$  and  $C11^*$  atoms were derived by the method of trial and error based on difference syntheses, adjustment of bond lengths, and refinements with restraint on bond distances. The positional parameters of the  $C8^*$ ,  $C9^*$ ,  $C10^*$  and H atoms were calculated geometrically. All the positional parameters of the dimer were finally fixed using the isotropic displacement parameters of the corresponding atoms of the monomer. By the introduction of the dimer of 4.5 (2)% population, the  $R$  value reduced from 0.062 to 0.051.

Crystals of (I)–(IV) changed instantly into opaque by photoirradiation without a filter. Plate-like crystals of (III) were deformed and curled soon after photoirradiation even through the band pass filter BP365. The lowest-energy absorption maxima of the  $CH_3CN$  solutions are (I) 278, (II) 273, (III) 302 and (IV) 269 nm.

### 3. Discussion

#### 3.1. Molecular structure

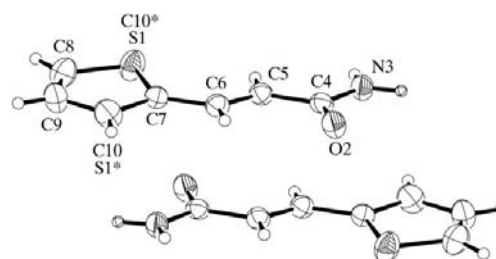
Fig. 1*a* shows a pair of monomers in *trans*-4-methylcinnamide (I) related by a center of symmetry. The distance between the  $C=C$  double bonds,  $C4 \cdots C5'$ , is 3.670 (2) Å. Fig. 1*b* is a disordered structure of (I) after photoirradiation for 5 h. The population of the dimer is 86.2 (4)%. The atom labels of the dimer correspond to those of the monomer with an asterisk. Fig. 2*a* shows a pair of monomers in *trans*-4-chlorocinnamide (II). The  $C5 \cdots C6'$  distance is 3.632 (2) Å.



**Figure 2**  
(*a*) The structure of a pair of molecules in (II) related by a center of symmetry; (*b*) the disordered structure in (II') which consists of the monomer (open bonds) 51.6 (6)% and the dimer (solid bonds) 48.4 (6)%. Displacement ellipsoids are plotted at the 30% probability level. H atoms are shown as spheres of arbitrary size.

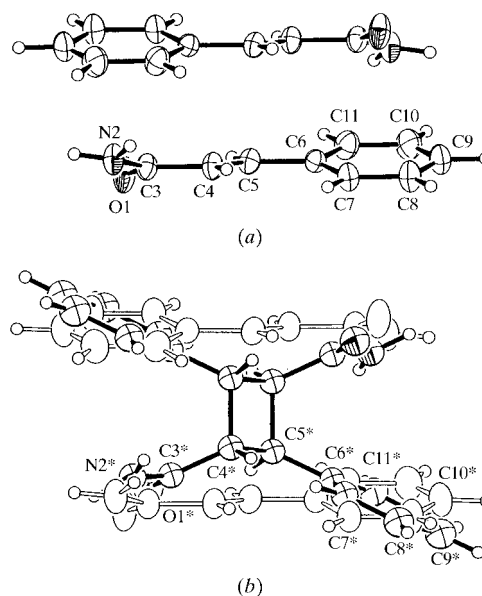
Fig. 2(*b*) shows the disordered structure of (II') after photoirradiation for 6 h. The population of the dimer is 48.4 (6)%. Fig. 3 shows a pair of monomers of *trans*-3-(2-thienyl)acrylamide (III). The  $C5 \cdots C6'$  distance is 3.762 (3) Å. *trans*-Cinnamide (IV) is less photoreactive than (I)–(III) and the  $C4 \cdots C5'$  distance in Fig. 4(*a*) is 4.120 (2) Å, which is longer than the corresponding distances in (I)–(III) by 0.358 (4)–0.488 (3) Å. Fig. 4(*b*) shows the structure of (IV') after photoirradiation for 2 h. The population of the dimer is 4.5 (2)%.

In (I') and (II'), the ethene C atoms are moved nearly perpendicular to the molecular plane to form a cyclobutane ring. The length of the movement of the ethene C atom is longer in the phenyl side than in the amido side. In (I') the  $C5-C5^*$  and  $C4-C4^*$  distances are 1.20 (1) and 0.91 (1) Å,



**Figure 3**

The structure of a pair of molecules in (III) related by a center of symmetry. The positional and anisotropic displacement parameters of  $C10^*$  and  $S1^*$  were assumed to be the same as those of  $S1$  and  $C10$ , respectively. The site occupation factors of  $S1$  and  $C10$  are 0.808 (4), and those of  $S1^*$  and  $C10^*$  are 0.192. Displacement ellipsoids are plotted at the 30% probability level. H atoms are shown as spheres of arbitrary size.



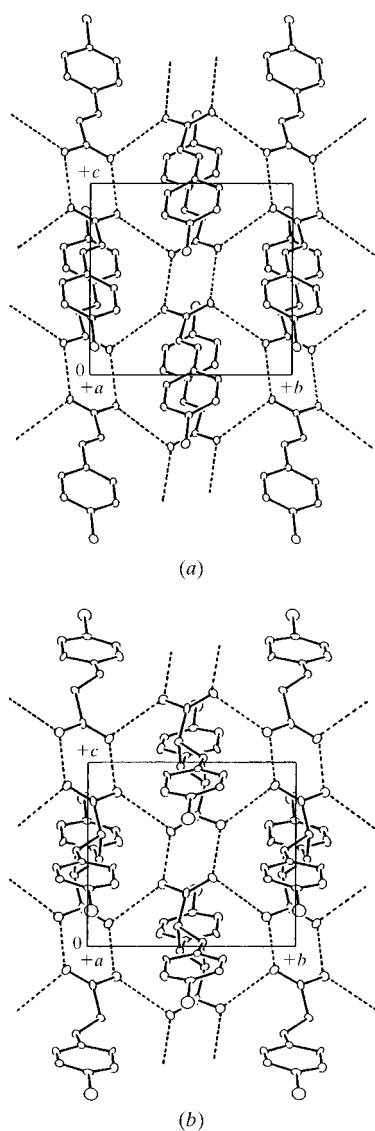
**Figure 4**

(*a*) The structure of a pair of molecules in (IV) related by a center of symmetry; (*b*) the disordered structure in (IV') which consists of the monomer (open bonds) 95.5 (2)% and the dimer (solid bonds) 4.5 (2)%. Displacement ellipsoids are plotted at the 30% probability level. H atoms are shown as spheres of arbitrary size.

respectively. In (II') the C6—C6\* and C5—C5\* distances are 1.26 (1) and 0.86 (1) Å, respectively. Although the orientation of the amido plane altered by 17–25° in (I') and (II'), the N—H···O intermolecular hydrogen bonds were kept after the reaction (Table 4). In (IV'), the ethene C atoms moved for dimerization not only perpendicular to the molecular plane, but also along the C=C bond direction. The C4—C4\* and C5—C5\* distances are *ca* 1.3 Å. As can be seen from Table 4 and Fig. 6(b), the cyclic N—H···O hydrogen bonds were broken between the monomer and dimer, and between the dimers.

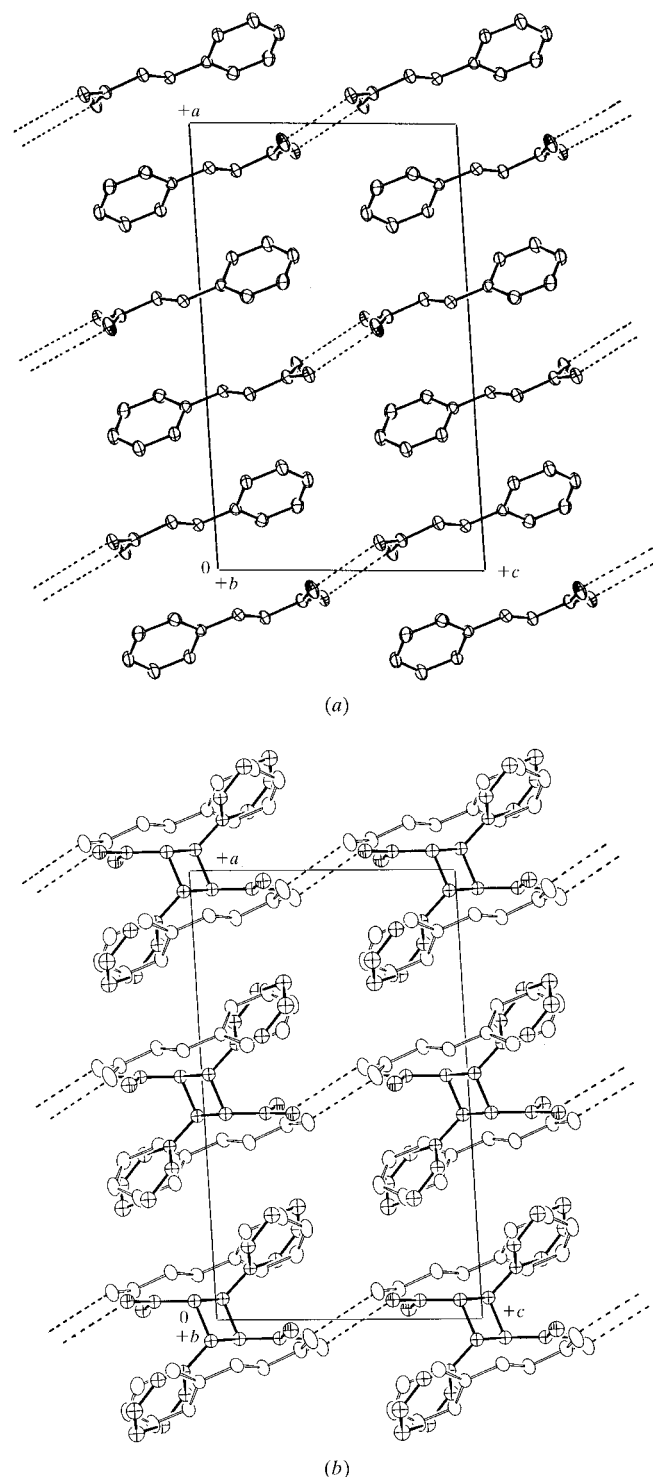
### 3.2. Crystal structure

Structures of the hydrogen-bond networks in (I)–(III) are similar to each other. Projections of the crystal structures of (II) and (II') are shown in Fig. 5. Both H atoms of the NH<sub>2</sub>



**Figure 5**  
Projection of the crystal structure of (a) (II) and (b) (II') along *a*. Dashed lines represent hydrogen bonds. The monomer component in (II') is omitted for clarity.

group are involved in the intermolecular N—H···O hydrogen bonds to form a two-dimensional pleated sheet, and photodimerization occurs within the sheet. According to the notation proposed by Leiserowitz & Schmidt (1969), the crystal structures of (I)–(III) belong to a screw-axis related packing. A twofold screw axis parallel to *b* lies on the two-dimensional

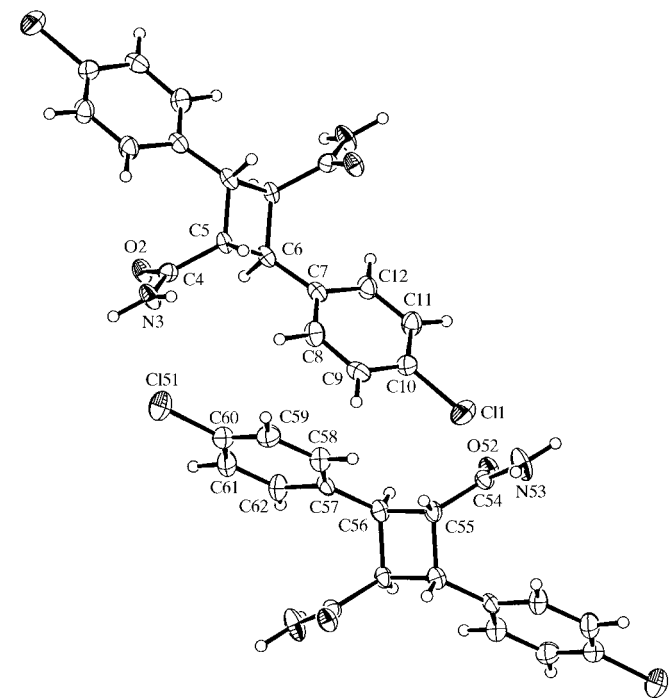


**Figure 6**  
Projection of crystal structure of (a) (IV) and (b) (IV') along *b*. Dashed lines represent hydrogen bonds.

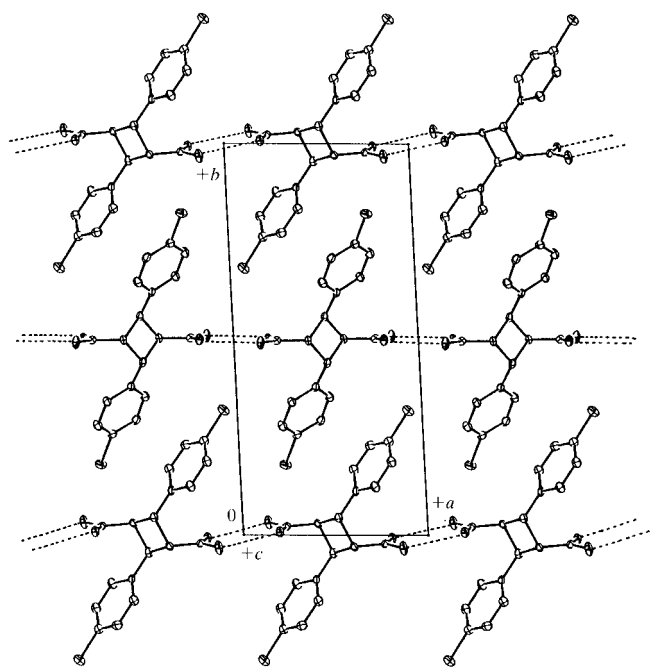
**Table 3**  
Selected geometric parameters (Å, °).

(I)		(I')	
C4=C5	1.325 (2)	C4*—C5*	1.540 (4)
C4...C5 <sup>i</sup>	3.670 (2)	C4*—C5* <sup>i</sup>	1.595 (4)
C5=C4...C5 <sup>i</sup>	108.9 (1)	C5*—C4*—C5* <sup>i</sup>	90.9 (2)
C3—C4...C5 <sup>i</sup>	80.2 (1)	C3*—C4*—C5* <sup>i</sup>	112.0 (2)
O1=C3—C4=C5	−1.7 (2)	O1*—C3*—C4*—C5*	14.6 (4)
N2—C3—C4=C5	179.5 (1)	N2*—C3*—C4*—C5*	−168.0 (3)
C3—C4=C5—C6	177.5 (1)	C3*—C4*—C5*—C6*	123.9 (3)
(II)		(II')	
C5=C6	1.326 (3)	C5*—C6*	1.548 (9)
C5...C6 <sup>ii</sup>	3.632 (2)	C5*—C6* <sup>ii</sup>	1.582 (8)
C6=C5...C6 <sup>ii</sup>	107.3 (1)	C6*—C5*—C6* <sup>ii</sup>	90.2 (4)
C4—C5...C6 <sup>ii</sup>	96.0 (1)	C4*—C5*—C6* <sup>ii</sup>	117.7 (8)
O2=C4—C5=C6	−6.6 (3)	O2*—C4*—C5*—C6*	−10 (2)
N3—C4—C5=C6	172.7 (2)	N3*—C4*—C5*—C6*	−177.1 (7)
C4—C5=C6—C7	−179.0 (2)	C4*—C5*—C6*—C7*	−118.3 (8)
(III)		(IV)	
C5=C6	1.321 (3)	C4=C5	1.316 (2)
C5...C6 <sup>iii</sup>	3.762 (3)	C4...C5 <sup>iv</sup>	4.120 (2)
C6=C5...C6 <sup>iii</sup>	117.4 (1)	C5=C4...C5 <sup>iv</sup>	65.7 (1)
C4—C5...C6 <sup>iii</sup>	81.2 (1)	C3—C4...C5 <sup>iv</sup>	101.6 (1)
O2=C4—C5=C6	2.5 (3)	O1=C3—C4=C5	14.2 (2)
N3—C4—C5=C6	−177.1 (2)	N2—C3—C4=C5	−166.5 (1)
C4—C5=C6—C7	178.6 (2)	C3—C4=C5—C6	−178.8 (1)
(IV')		(V)	
C4*—C5*	1.519	C5—C6	1.57 (1)
C4*—C5* <sup>iv</sup>	1.582	C5—C6 <sup>v</sup>	1.56 (1)
C5*—C4*—C5* <sup>iv</sup>	86.6	C6—C5—C6 <sup>v</sup>	89.0 (5)
		C55—C56	1.54 (1)
		C55—C56 <sup>vi</sup>	1.59 (1)
		C56—C55—C56 <sup>vi</sup>	89.5 (5)

Symmetry codes: (i)  $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $-x, 1-y, 1-z$ ; (iv)  $2-x, 1-y, 2-z$ ; (v)  $1-x, 1-y, 1-z$ ; (vi)  $1-x, -y, 1-z$ .



**Figure 7**  
The structure of two independent molecules in (V). Displacement ellipsoids are plotted at the 30% probability level. H atoms are shown as spheres of arbitrary size.



**Figure 8**  
Projection of crystal structure of (V) along *c*. Dashed lines represent hydrogen bonds.

hydrogen-bond sheet with  $b = 9.148 (3)$ ,  $9.075 (2)$  and  $9.087 (2)$  Å for (I), (II) and (III), respectively.

On the other hand, the hydrogen-bond network in (IV) is a one-dimensional flat ribbon, where the cyclic hydrogen-bonded dimers of the amido moieties are linked side by side along the *b* axis (Fig. 6*a*). According to the notation of Leiserowitz & Schmidt (1969), the crystal structure of (IV) belongs to translation packing. On photodimerization, the cyclic hydrogen bonds were broken not only between the photodimers, but also between the monomer and the photodimer (Fig. 6*b* and Table 4).

Figs. 7 and 8 show the molecular and crystal structure of (V), which was prepared by a photodimerization of (II) and was recrystallized from a chloroform solution. There are two independent molecules and the hydrogen-bond network is composed of a one-dimensional flat ribbon along *c*. The crystal structure of (V) was different from that of (II'), which was derived from the crystal-to-crystal transformation. The cell volumes of (I') and (II') became greater than those of (I) and (II), indicating the decrease in packing efficiency on photodimerization.

**Table 4**  
Hydrogen-bonding geometry (Å, °).

	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(I)	$N2-H2A\cdots O1^i$	0.95 (2)	1.99 (2)	2.932 (2)	169 (2)
	$N2-H2B\cdots O1^{ii}$	0.92 (2)	2.04 (2)	2.956 (2)	170 (2)
(I')	$N2-H2A\cdots O1^i$	0.96	2.03	2.961	162
	$N2-H2B\cdots O1^{ii}$	0.96	2.19	3.117	161
	$N2^*-H2^*A\cdots O1^{*i}$	0.95	2.01	2.946 (3)	166
	$N2^*-H2^*B\cdots O1^{*ii}$	0.95	2.12	3.049 (3)	166
(II)	$N3-H3A\cdots O2^{iii}$	0.88 (3)	2.09 (2)	2.941 (3)	163 (2)
	$N3-H3B\cdots O2^{iv}$	0.87 (2)	2.18 (2)	3.050 (2)	178 (2)
(II')	$N3-H3A\cdots O2^{iii}$	0.96	2.10	2.98 (2)	153
	$N3-H3B\cdots O2^{iv}$	0.96	2.30	3.06 (1)	135
	$N3^*-H3^*A\cdots O2^{*iii}$	0.96	2.04	2.94 (2)	157
	$N3^*-H3^*B\cdots O2^{*iv}$	0.96	2.05	3.00 (2)	171
(III)	$N3-H3A\cdots O2^v$	0.91 (3)	2.01 (3)	2.916 (3)	169 (2)
	$N3-H3B\cdots O2^{vi}$	0.96 (3)	2.02 (3)	2.970 (3)	173 (2)
(IV)	$N2-H2A\cdots O1^{vii}$	0.90 (2)	2.07 (2)	2.960 (2)	176 (2)
	$N2-H2B\cdots O1^{viii}$	0.89 (2)	2.14 (2)	2.943 (2)	151 (1)
(IV')	$N2-H2A\cdots O1^{vii}$	0.93 (2)	2.02 (2)	2.943 (2)	172 (2)
	$N2-H2A\cdots O1^{*vii}$	0.93 (2)	2.48	3.404 †	171
	$N2-H2B\cdots O1^{viii}$	0.88 (2)	2.15 (2)	2.939 (2)	149 (1)
	$N2-H2B\cdots O1^{*viii}$	0.88 (2)	2.31	3.122	153
	$N2^*-H2^*A\cdots O1^{*vii}$	0.96	2.46	3.257 †	141
	$N2^*-H2^*A\cdots O1^{*vii}$	0.96	2.94	3.809 †	151
	$N2^*-H2^*B\cdots O1^{*viii}$	0.96	2.13	3.025	155
	$N2^*-H2^*B\cdots O1^{*viii}$	0.96	2.10	3.049	168
(V)	$N3-H3A\cdots O2^{ix}$	0.99	1.94	2.925 (7)	173
	$N3-H3B\cdots O2^x$	0.96	2.11	3.007 (8)	156
	$N53-H53A\cdots O52^{xi}$	0.97	2.06	3.005 (7)	164
	$N53-H53B\cdots O52^x$	0.97	2.32	3.163 (9)	146

Symmetry codes: (i)  $\frac{1}{2}-x, \frac{3}{2}-y, -z$ ; (ii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $1-x, -y, 2-z$ ; (iv)  $1-x, \frac{1}{2}+y, \frac{3}{2}-z$ ; (v)  $-x, 1-y, 2-z$ ; (vi)  $-x, y-\frac{1}{2}, \frac{3}{2}-z$ ; (vii)  $2-x, 1-y, 3-z$ ; (viii)  $x, y-1, z$ ; (ix)  $2-x, 1-y, 1-z$ ; (x)  $x, y, z-1$ ; (xi)  $-x, -y, 1-z$ . † These data indicate a breaking of the hydrogen bond involving the photodimer.

Crystal structures of the photodimer of (IV) have been reported for monohydrate (Iwamoto & Kashino, 1990), anhydrate monoclinic (Vaida *et al.*, 1989) and anhydrate triclinic forms (Iwamoto & Kashino, 1992). The mode of hydrogen bonding in the latter crystal is similar to that in (V) with the relationship of lattice constants  $a' \cong b/2$ ,  $b' \cong 2a$  and  $c' \cong c$ .

#### 4. Concluding remarks

Photodimerization in crystals of *trans*-4-methylcinnamamide, *trans*-4-chlorocinnamamide and *trans*-cinnamamide was observed by crystal-to-crystal transformations. The lower photoreactivity of *trans*-cinnamamide is not only due to longer C··C distances between the nearest neighbor C=C double bonds, but also due to partial breakdown of the N—H··O hydrogen-bond network by the photodimerization.

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