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Single-crystal-to-single-crystal photodimerization of 4-chlorocinnamoyl-*O*,*O*′-dimethyldopamine

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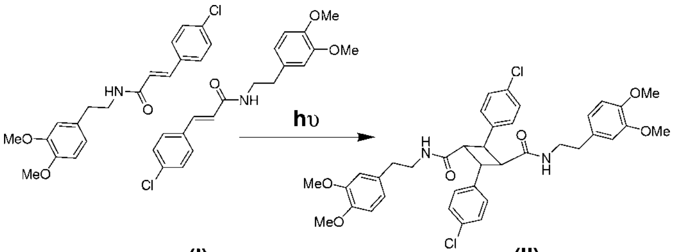
[2+2]Photodimerization of the title compound, $C_{19}H_{20}ClNO_3$, has been observed *in situ* by single-crystal X-ray diffraction. Pairs of monomers related by centers of symmetry have parallel C=C bonds at a C···C distance of 4.155 (17) Å. Irradiation of a single crystal with a mercury lamp achieves 100% conversion to the dimer. Redetermination of the structure during the course of the reaction revealed a linear correlation between the percent conversion to the dimer and the decrease in the cell volume. The displacement parameters for the pure dimer structure are substantially smaller than those for the pure monomer structure. The dimerization reaction is also induced by irradiation with X-rays, the induction being stronger with Cu $K\alpha$ than with Mo $K\alpha$ radiation.

1. Introduction

Topochemical principles, the basic concepts in organic solid-state reactions, were first established by Schmidt and co-workers (Cohen & Schmidt, 1964; Cohen, Schmidt & Sonntag, 1964; Schmidt, 1964). It is known that the separation distance, mutual orientation and local symmetry of space around reactive functional groups are crucial (Ramamurthy & Venkatesan, 1987). If the reaction proceeds in a single-crystal-to-single-crystal manner, the process can be observed *in situ* by X-ray diffraction (Ohashi, 1998; Hosomi, Ohba *et al.*, 2000 and references therein). One of the main challenges in such studies is to protect the single crystal from degradation by the reaction. Possible methods to achieve homogeneous photoreaction in single crystals are irradiation far into the long wavelength absorption tail (Enkelmann *et al.*, 1993; Novak *et al.*, 1993) and two-photon excitation (Harada *et al.*, 1999). However, these methods are not always successful, and even in fortunate cases where the crystal lattice remains intact the crystals may still decompose gradually. Photoreaction without any degradation of the crystal is rare: here we report one such case.

N-Cinnamoyl-substituted dopamines and *O*,*O*′-dimethyldopamines were prepared and their photoreactivities in the solid state were investigated by Ito *et al.* (2001). In the reaction of the title compound (I) to give the α-truxillic amide dimer (II) the chemical yield was quantitative and the quantum yield (Φ = 0.75) was very high (Ito *et al.*, 2001). In the present study, the X-ray structure analysis of a long-shelved crystal (I*b*) unexpectedly indicated disorder as the result of partial reaction. This observation suggested the possibility of single-crystal-to-single-crystal transformation. We have performed photoirradiation of a single crystal and determined the structure of the pure photodimer (II).



(I) (II)

2. Experimental

The title compound (I) was prepared by Ito *et al.* (2001). Thin acicular crystals of (I) were grown by slow evaporation from benzene solution. Crystal data, experimental conditions and refinement details are listed in Table 1.[1]

(I*a*): The monomer crystals grown from solution were stored in the dark. No significant amount of dimer was detectable in solutions of these crystals by high-pressure liquid chromatography (HPLC) or proton NMR spectra. X-ray diffraction data were collected at room temperature in the dark on a Rigaku AFC7R four-circle diffractometer using Mo $K\alpha$ radiation. Because the high-order reflections were weak, only 27% of the unique reflections to 25.0° in θ were observed. H atoms were placed geometrically and allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent). The final difference synthesis did not show any peaks that corresponded to the cyclobutane ring of the photodimer.

(I*b*): Monomer crystals were packed loosely in a small sample tube and exposed to ambient light for about half a year. X-ray intensity measurements on this crystal were initially carried out at 250 K using Cu $K\alpha$ radiation from a Rigaku 18 kW rotating anode operating at 54 kV, 250 mA. During the period of the data collection (over 73 h), the standard reflections showed variations of −1.6, −8.4 and +6.8% in $|F|$ for 404, 311 and 515, respectively, and the unit-cell volume decreased by *ca.* 25 Å^3 (0.7%). These phenomena were attributed (see below) to a dimerization reaction induced in the crystal by Cu $K\alpha$ radiation.

The X-ray intensity data of this crystal specimen were then re-collected at 298 K using Mo $K\alpha$ radiation from a Rigaku 18 kW rotating anode operating at 54 kV, 250 mA. The intensity variations of the same standard reflections were small (from −2.9 to −0.4% in $|F|$). The X-ray analysis indicated that the structure is disordered as the result of a partial reaction. If the only atoms of the product molecule included in the refinement model were C12* and C13* we obtained $R(F)[I > 2\sigma(I)]$ and $wR(F^2)$ values of 0.070 and 0.184, respectively. The determination of the crystal structure of the pure photodimer (II) afforded atomic parameters for (II), which could be used as initial parameters of the product molecule in (I*b*). The positional parameters of the 4-chlorophenyl group of the product (Cl*, C6*—C11*) were refined with atomic displacement parameters fixed at their values in (II), while C12* and C13* were refined anisotropically. The (dimethoxyphenyl)ethylaminocarbonyl fragments of the substrate and product molecules were treated as fully overlapping. The occupancy of the dimer in (I*b*) was 34.2 (8)%. The final $R(F)$ and $wR(F^2)$ values were 0.057 and 0.158, respectively.

(I*c*, I*d*, I*e*, I*f*): In order to ascertain the extent of the reaction induced in the crystal by Mo $K\alpha$ radiation, another crystal was picked up from the same batch of (I*b*), and four sequential sets of X-ray intensity measurements were carried out with the room light off, each set requiring 60 h. The structures were refined in the same manner as (I*b*). The variations in the lattice constants and occupation factors of the dimer are shown in Table 2.

(II): After the Mo $K\alpha$ data collection in (I*b*), the same crystal was irradiated for 3 h with the tungsten lamp that is normally employed for crystal centering, then for 6 h with a fluorescent lamp in the diffractometer housing. During this period the lattice constants did not show any significant changes. The crystal was then irradiated with light from a 250 W ultra-high-pressure Hg lamp, which had been filtered through a BP365 band-pass filter ($T = 50\%$ at 365 nm, half-height width 10 nm). Changes in the lattice constants indicated process of the reaction. After 3 h the lattice constants showed no further changes, but irradiation was continued for a further 3 h. No decrease in the diffraction power of the crystal was observed, and the reflection profiles showed no broadening of their typical peak half-width (0.35°). Diffraction intensities were measured and structure refinement indicated 100% conversion. The variations of the structure factors $|F|$ for 404, 311 and 515 from (I*b*) to (II) were −25, −56 and +17%, respectively.

3. Discussion

3.1. Molecular structure

In crystals of the pure monomer, (I*a*), the nearest contacts between the C=C bonds are observed for pairs of molecules related by centers of symmetry (Fig. 1*a*, Table 3). The C12=C13 bond axis is parallel to that in the neighboring molecule and the C12$\cdots$C13$^{\rm i}$ (i: $1 - x, 1 - y, -z$) distance is 4.155 (17) Å. This is insignificantly shorter than Schmidt's critical distance (4.2 Å; Ramamurthy & Venkatesan, 1987). However, the π–π overlapping is excellent, and the C9—C12$\cdots$C13$^{\rm i}$, C13=C12$\cdots$C13$^{\rm i}$, C12=C13$\cdots$C12$^{\rm i}$ and C14—C13$\cdots$C12$^{\rm i}$ angles are in the range 80.0 (8)–99.0 (8)°. The displacement ellipsoids of some C atoms exhibit poor shapes, which may be due to the insufficient number of reflections observed $[I > 2\sigma(I)]$. This lack of observations is the result of the extensive vibration and the loose packing of the molecules in (I*a*) (see below).

Fig. 1(*b*) shows the molecular structure in the crystal (I*b*), which was illuminated by ambient room light for half a year

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0063). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(I*a*)	(I*b*)	(II)
Crystal data			
Chemical formula	$C_{19}H_{20}ClNO_3$	$C_{19}H_{20}ClNO_3$	$C_{38}H_{40}Cl_2N_2O_6$
M_r	345.81	345.81	691.62
Cell setting, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*
a, *b*, *c* (Å)	21.499 (4), 5.003 (1), 33.542 (5)	21.150 (4), 4.972 (1), 33.620 (5)	20.835 (3), 4.966 (1), 33.352 (3)
β (°)	91.518 (13)	91.298 (14)	92.166 (9)
V (Å^3)	3606.6 (13)	3534.8 (11)	3448.1 (9)
Z	8	8	4
D_x (Mg m^{-3})	1.274	1.300	1.332
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	25	25	25
θ range (°)	7.0–11.6	10.1–11.8	10.1–13.9
μ (mm^{-1})	0.23	0.23	0.24
Temperature (K)	298	297	297
Crystal form, color	Needle, colorless	Needle, colorless	Needle, colorless
Crystal size (mm)	0.80 × 0.10 × 0.05	0.45 × 0.20 × 0.07	0.45 × 0.20 × 0.07
Data collection			
Diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
Data collection method	ω	ω	ω
Absorption correction	Integration	Integration	Integration
$T_{\min}$	0.970	0.950	0.948
$T_{\max}$	0.989	0.984	0.984
No. of measured, independent and observed parameters	3664, 3165, 865	6042, 4079, 1136	5877, 3951, 1805
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.035	0.021	0.017
$\theta_{\max}$	25.0	27.5	27.5
Range of *h*, *k*, *l*	$0 \Rightarrow h \Rightarrow 25$ $0 \Rightarrow k \Rightarrow 5$ $-39 \Rightarrow l \Rightarrow 39$	$-14 \Rightarrow h \Rightarrow 27$ $-6 \Rightarrow k \Rightarrow 3$ $-43 \Rightarrow l \Rightarrow 43$	$-14 \Rightarrow h \Rightarrow 27$ $-6 \Rightarrow k \Rightarrow 3$ $-43 \Rightarrow l \Rightarrow 43$
No. and frequency of standard reflections	3 every 150 reflections	3 every 150 reflections	3 every 150 reflections
Intensity decay (%)	0.2	2.6	0.8
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.142, 0.277, 2.03	0.057, 0.158, 1.08	0.043, 0.125, 0.99
No. of reflections	3165	4079	3951
No. of parameters	217	263	217
H-atom treatment	Not refined	Not refined	Not refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.03P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 1.86P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	<0.001	<0.001	<0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.37, −0.41	0.12, −0.12	0.19, −0.23
Extinction method	None	None	None
Occupation factor of the dimer	0	0.342 (8)	1
Absorption correction	Integration (Coppens *et al.*, 1965)	Integration (Coppens *et al.*, 1965)	Integration (Coppens *et al.*, 1965)

Computer programs: *WinAFC Diffractometer Control Software* (Rigaku, 1999); *TEXSAN* (Molecular Structure Corporation, 2001); *SIR*92 (Altomare *et al.*, 1994); *ORTEPII* (Johnson, 1976); *SHELXL*97 (Sheldrick, 1997).

Table 2
Additional X-ray data collection repeated four times with the room light off.

Crystal size 0.4 × 0.2 × 0.05 mm; $\theta_{\max}$(Mo $K\alpha$) = 27.5°.

	(I*c*)	(I*d*)	(I*e*)	(I*f*)
Crystal data				
a, *b*, *c* (Å)	21.233 (5), 4.983 (1), 33.664 (5)	21.210 (4), 4.982 (1), 33.657 (4)	21.195 (3), 4.978 (1), 33.646 (4)	21.180 (4), 4.977 (1), 33.642 (4)
β (°)	91.313 (14)	91.313 (12)	91.292 (10)	91.290 (11)
V (Å^3)	3560.6 (14)	3554.7 (12)	3549.3 (10)	3545.3 (11)
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.160, 1.04	0.053, 0.190, 0.94	0.053, 0.195, 0.93	0.052, 0.201, 0.93
Occupation factor of the dimer	0.220 (6)	0.256 (7)	0.280 (8)	0.295 (7)

Table 3
Selected geometric parameters (Å, °).

	(I*a*)	(I*b*)	(II)
Cl—C6	1.720 (16)	1.718 (19)	1.741 (3)
C12—C13	1.306 (17)	1.326 (11)	1.538 (3)
C12···C13$^{\rm i}$	4.155 (17)	3.891 (11)	1.587 (3)
C12*—C13*	–	1.534 (14)	–
C12*—C13*$^{\rm i}$	–	1.534 (14)	–

Symmetry code: (i) $1 - x, 1 - y, -z$.

after crystallization and then irradiated with Cu $K\alpha$ radiation for 75 h. The α-type photodimer was observed with an occupancy factor of 34.2 (8)%. Another crystal (I*c*) picked up from the same batch of (I*b*) showed a dimer content of 22.0 (6)%. These results suggest that the crystals had undergone gradual photoreaction under room lighting over about six months. A similar highly sensitive [2+2]-photodimerization was reported for single crystals of 2-benzyl-5-benzylidenecyclopentanone (BBCP), where exposure to daylight provided a similarly slow conversion (Nakanishi *et al.*, 1981).

The shifts of the ethane C atoms in (I*b*) during dimerization are comparable to those observed in photodimerization of *trans*-cinnamamides (Hosomi, Ito & Ohba, 2000). The C12—C12* and C13—C13* atom shifts in (I*b*) are 1.22 (1) and 1.16 (1) Å, respectively. The distance between the reaction points of the substrate molecules, C12···C13$^{\rm i}$, is 3.891 (11) Å, which is shorter by 0.26 (2) Å than the distance in (I*a*). This shortening may be due to the contraction of the cell volume as discussed below. Fig. 1(*c*) shows the structure of the pure photodimer (II) after the single-crystal-to-single-crystal transformation. The C12—C13^{i} (i: $1 - x$, $1 - y$, $-z$) bond distance is 1.587 (3) Å. The atomic coordinates in the pure monomer (I*a*) and the pure dimer (II) are compared in Fig. 2. The product molecules in (I*b*) adopt approximately the same positions as the molecules in the final pure dimer (II), in contrast to the translational and rotational movement of the product molecules in a BBCP crystal during the transformation (Turowska-Tyrk, 2001). In the present crystal structure, the orientation of the substrate and product molecules has been fixed by the intermolecular N—H$\cdots$O hydrogen bonds (Fig. 3).

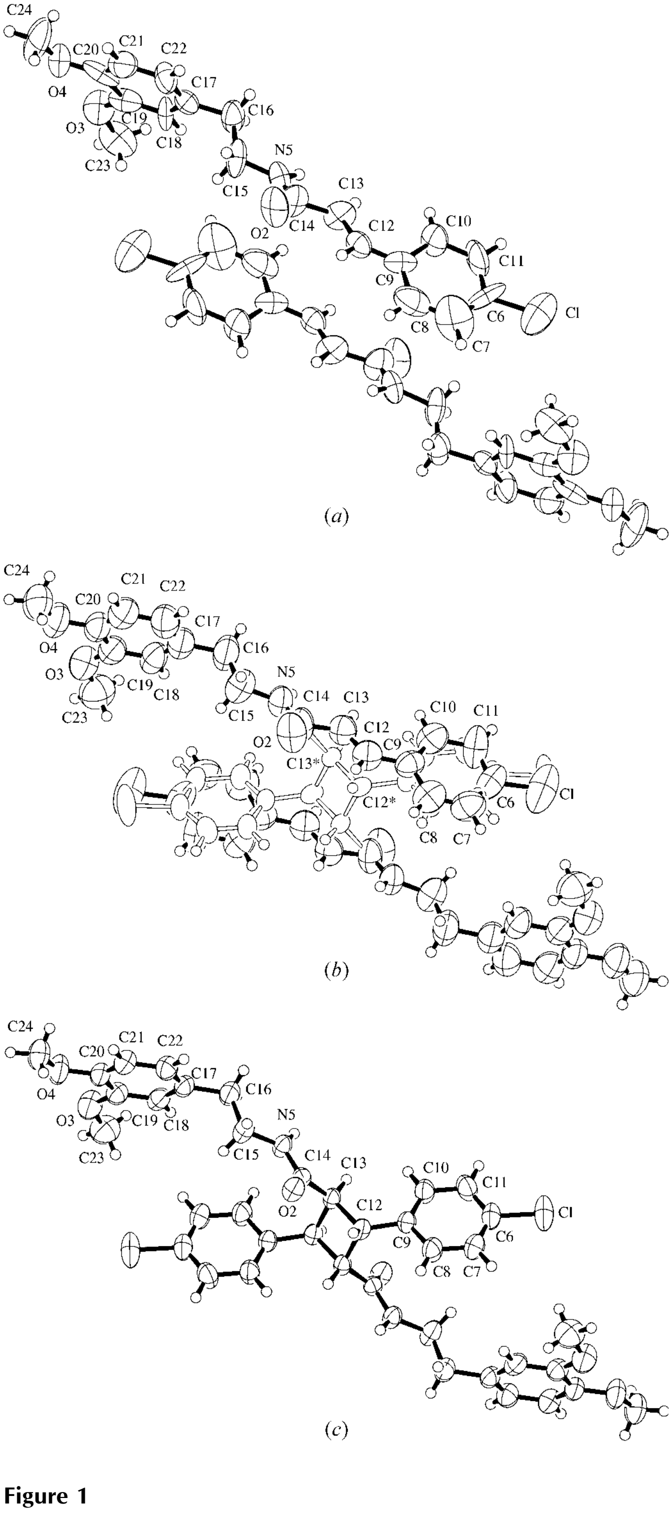

Figure 1
(*a*) The structure of a pair of monomer molecules in (I*a*), which are related by a center of symmetry. (*b*) The disordered structure in (I*b*), which consists of the monomer (solid bonds) 65.8 (8)% and the dimer (open bonds) 34.2 (8)%. (*c*) The structure of the dimer molecule in (II). Displacement ellipsoids are plotted at the 50% probability level.

3.2. Crystal structure

The amide moiety is involved in intermolecular N—H$\cdots$O hydrogen bonding that forms a chain along *b* (Fig. 3 and Table 4). These hydrogen bonds were retained after the reaction. The crystal structures of the monomer (I*a*) and the dimer (II) are compared in Fig. 4. The atomic displacement parameters $U_{\rm eq}$ of (II) average *ca.* two-thirds of those of (I*a*), which indicates that the initial structure had loose packing and that dimerization led to a more compact structure with lower atomic vibration. The main changes in lattice constants in the course of the reaction consisted of a shrinkage of the *a* axis

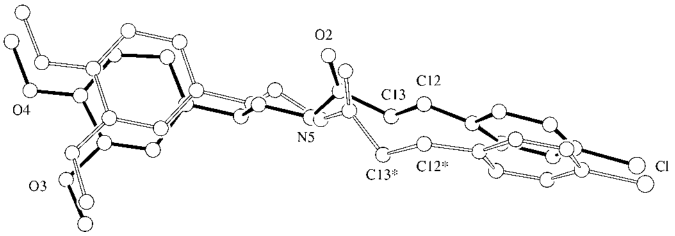

Figure 2
A comparison of the atomic positions in (I*a*) (solid bonds) and (II) (open bonds). The lattice constants of (I*a*) were used with the atomic coordinates for both of (I*a*) and (II).

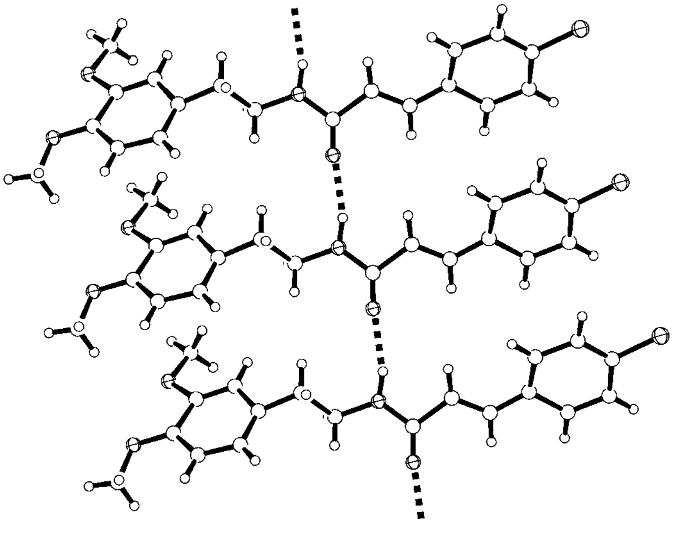

Figure 3
A chain of N—H$\cdots$O hydrogen bonds running along the *b* axis in (I*a*).

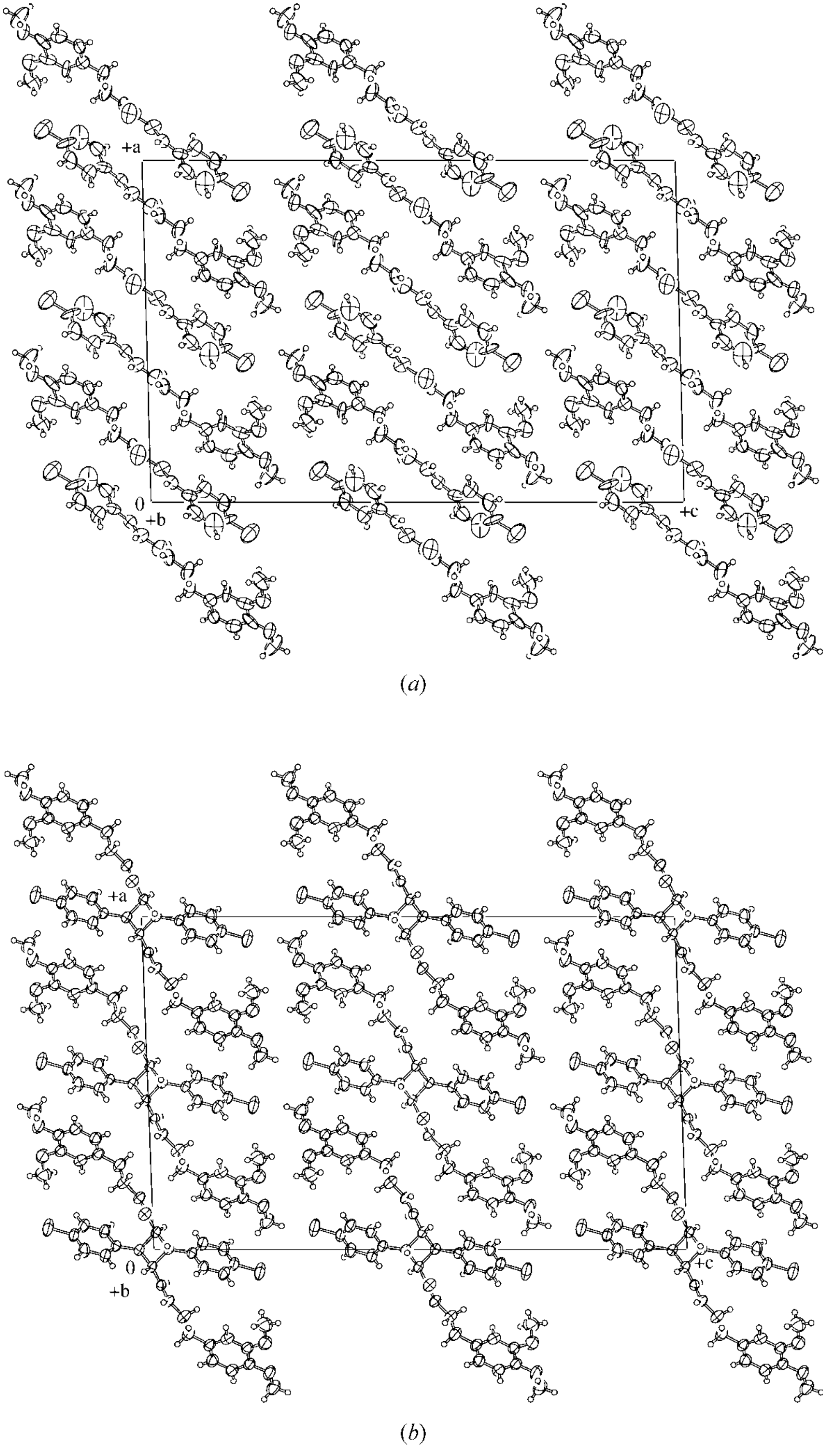

Figure 4
Projection of crystal structures of (*a*) (I*a*) and (*b*) (II) along the *b* axis.

and a decrease in the unit-cell volume. A linear correlation was observed between the cell volume and the degree of conversion (Fig. 5). There have been very few reports of photoreaction that achieves 100% conversion in a single crystal (Nakanishi *et al.*, 1981; Enkelmann *et al.*, 1993; Novak *et al.*, 1993; Suzuki *et al.*, 1994; Hosomi *et al.*, 1998; Leibovitch *et al.*, 1998; Tanaka *et al.*, 2000). In general the cell volume increases during the photoreaction and the crystallinity is degraded by the effects of strain, as reported for the [2+2]dimerization of *trans*-cinnamamides (Hosomi, Ito & Ohba, 2000), and this degradation prevents the *in situ* observation of the complete conversion by diffraction techniques.

The unsubstituted cinnamoyl-*O*,*O*′-dimethyldopamine, (III), is photostable (Ito *et al.*, 2001). The crystal structure was determined in order to reveal the geometrical factors that prevent [2+2] photodimerization (Ohba & Ito, 2002). The crystal structures of the photoactive 4-chloro derivative (I*a*) and the photostable non-substituted compound (III) have some similarities. The space group of (III) is $P2_1/a$, which is one of the maximal non-isomorphic subgroups of $A2/a$ [a non-standard setting of the space group $C2/c$ observed for (I*a*)]. In (III), the chain of N—H···O hydrogen bonds lies in the direction of the *b* axis [5.2431 (5) Å] as observed in (I*a*), and the close contacts are observed in a pair of molecules related by a center of symmetry (Fig. 6). However, the C═C double bonds in the cinnamoyl moieties lie far apart and the amido groups are close to each other. The introduction of the 4-chloro group to the cinnamoyl moiety increases the overall length of the molecule, with the result that the C═C bonds in crystals of (I*a*) are brought closer together.

3.3. Reaction by X-ray radiation

The occupancy factors of the dimer in (I*b*) and (I*c*) are 34.2 (8)% and 22.0 (6)%, respectively. The larger conversion in (I*b*) may be a result of the irradiation with Cu $K\alpha$ radiation for 75 h before the data re-collection with Mo $K\alpha$. The decrease in the cell volume of *ca.* 25 Å^3 during the data collection with Cu $K\alpha$ radiation corresponds closely to the difference in the cell volume between (I*b*) and (I*c*). Further evidence that the reaction is induced by X-radiation can be found in the variation in the three standard reflections (from −8.4% to +6.8% in $|F_o|$) during the Cu $K\alpha$ data collection: this variation matches the change in structure factors from (I*b*) to (II) that is caused by photodimerization.

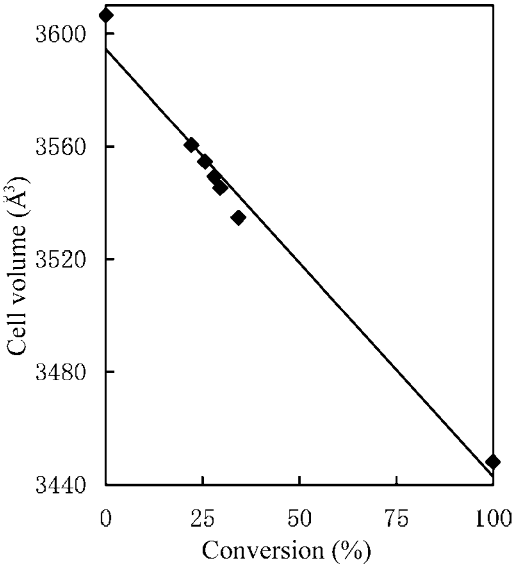

Figure 5
Cell volume (Å^3) *versus* degree of conversion (%) during the photodimerization.

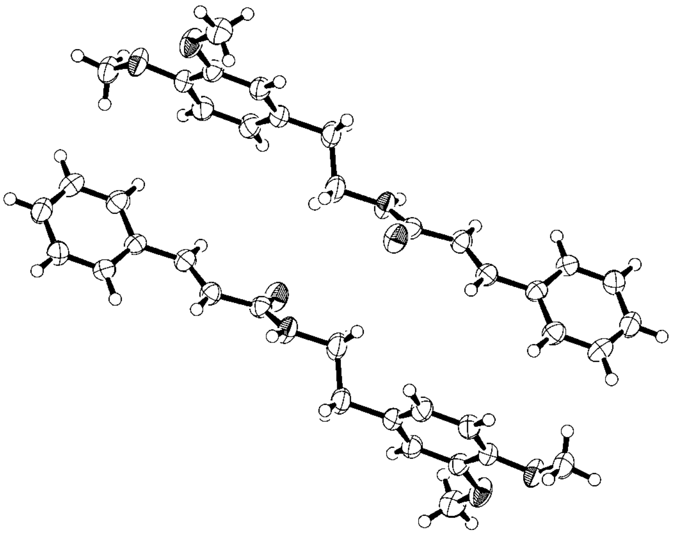

Figure 6
The structure of a pair of molecules in (III) that are related by a center of symmetry (Ohba & Ito, 2002).

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

	D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
(I*a*)	N5—H5$\cdots$O2$^{\rm i}$	0.95	2.05	2.942 (13)	155
(I*b*)	N5—H5$\cdots$O2$^{\rm i}$	0.95	2.14	3.013 (3)	152
(II)	N5—H5$\cdots$O2$^{\rm i}$	0.95	2.36	3.171 (2)	143

Symmetry code: (i) $x, y-1, z$.

The effect on the crystals of Mo $K\alpha$ radiation was found to be less than that of Cu $K\alpha$ radiation. X-ray intensity measurements on (I*c*) were repeated four times in the absence of room light to quantify the influence of Mo $K\alpha$ radiation (Table 2). The occupation factor of the dimer increased on average by 2.5 (8)% during the 60 h required for the collection of each data set. The stronger induction of the reaction by Cu $K\alpha$ than by Mo $K\alpha$ may be due to the greater absorption efficiency of Cu $K\alpha$, although the intensity of the incident X-ray beam for Cu $K\alpha$ was stronger than that for Mo $K\alpha$ by a factor of *ca.* 1.5 because of the lower threshold excitation voltage for Cu $K\alpha$.

Although reactions induced by X-ray irradiation of a single crystal were reported for the molecular rearrangement of hirsutic acid (Comer & Trotter, 1966), retro[2+2]cycloaddition of a *syn*-tricyclooctane derivative (Mori *et al.*, 1994), polymerization of diethyl *cis*,*cis*-muconate (Matsumoto *et al.*, 1998; Tashiro *et al.*, 1999), polymerization of 2,4-hexadiynylene bis(*p*-toluenesulfonate) (Enkelmann *et al.*, 1979) and polymerization of other diacetylene derivatives (Kai & Yamamoto, 1993), the dependence of the reaction rate on the X-ray wavelength has not previously been noted.

4. Concluding remarks

Photodimerization of 4-chlorocinnamoyl-*O*,*O*′-dimethyldopamine has been observed by a single-crystal-to-single-crystal transformation, and we have shown that the cell volume decreases linearly as a function of the extent of conversion. This solid-state reaction was about 22% complete after half a year under ambient room lighting. The high photosensitivity of the crystal is attributed to the loose packing of the monomer molecules and to the excellent π–π overlap of their C═C bonds, which are related pairwise by a center of symmetry. This solid-state reaction was also induced by X-ray radiation, the influence of Cu $K\alpha$ being greater than that of Mo $K\alpha$ radiation.

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