Table 4. *Selected least-squares planes of molecules* (I) *and* (II)

E.s.d.'s of the interplanar angles = 0·1°. $\chi^2 = \sum(\Delta/\sigma)^2$.

Molecule	Plane	Atoms included in plane	χ^2		Interplanar angles 1	2	3	4	5
(I)	1	C9, C1, O1, N1, C3, C2, O2, O3	41591	1	0				
(I)	2	C3, C4, C5, C6, C7, C8	11	2	97·6	0			
(I)	3	C9, C10, C11, C12, C13, C14	99	3	107·1	26·9	0		
(II)	4	O1, C9, C1, N1, C3, C2, O2, O3, C10, C13	2730	4	—	—	—	0	
(II)	5	C3, C4, C5, C6, C7, C8	22	5	—	—	—	88·8	0

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Topochemical Studies. XII.* Structure of a Cinnamamide–Cinnamic Acid (1/1) Complex

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Abstract. $C_9H_9NO.C_9H_8O_2$, $M_r = 295{\cdot}24$, m.p. 377–379 K, monoclinic, $P2_1/a$, $a = 40{\cdot}183\,(3)$, $b = 9{\cdot}5084\,(6)$, $c = 4{\cdot}0569\,(5)$ Å, $\beta = 97{\cdot}540\,(9)°$, $V = 1536{\cdot}6\,(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}28\,(1)$, $D_x = 1{\cdot}277$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}72$ mm^{-1}, $F(000) = 624$, $T = 295$ K, $R = 0{\cdot}058$ for 2454 unique reflections. The molecules of cinnamamide (*A*) and cinnamic acid (*B*) are held together by two kinds of hydrogen bonds between the amide group and carboxyl group to form a dimer. The nearest C═C bonds are related by a *c* translation with a C···C distance of 4·057 (4) Å for both (*A*) and (*B*), the spacings between the planes through four C atoms involving the C═C bonds being 3·435 (4) Å for (*A*) and 3·394 (4) Å for (*B*). This fact suggests the possibility of the formation of β-type photodimers of (*A*) and (*B*) by topochemical reaction.

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* Part XI: Iwamoto, Kashino & Haisa (1989*b*).

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Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \beta_{ii}/a_{ii}^{*2}.$$

	x	y	z	B_{eq}
O(1*A*)	0·24599 (2)	0·2359 (1)	0·2466 (3)	5·05 (5)
O(1*B*)	0·18905 (2)	0·1871 (1)	0·4584 (4)	5·84 (6)
O(2*B*)	0·17088 (3)	0·3985 (1)	0·2838 (4)	6·45 (7)
N(1*A*)	0·23623 (3)	0·4592 (1)	0·0778 (5)	5·95 (8)
C(1*A*)	0·34879 (3)	0·2689 (1)	0·0824 (4)	3·51 (6)
C(2*A*)	0·36260 (4)	0·3787 (2)	−0·0832 (4)	4·03 (7)
C(3*A*)	0·39605 (4)	0·3775 (2)	−0·1253 (4)	4·68 (8)
C(4*A*)	0·41639 (4)	0·2675 (2)	−0·0043 (4)	4·65 (7)
C(5*A*)	0·40315 (4)	0·1584 (2)	0·1578 (4)	4·65 (8)
C(6*A*)	0·36971 (4)	0·1581 (2)	0·1995 (4)	4·20 (7)
C(7*A*)	0·31366 (4)	0·2663 (1)	0·1395 (4)	3·91 (7)
C(8*A*)	0·29055 (4)	0·3626 (2)	0·0527 (5)	4·39 (8)
C(9*A*)	0·25596 (4)	0·3475 (1)	0·1308 (4)	4·27 (7)
C(1*B*)	0·07115 (4)	0·2804 (1)	0·4512 (4)	3·75 (6)
C(2*B*)	0·06336 (4)	0·1621 (2)	0·6293 (4)	4·30 (7)
C(3*B*)	0·03048 (4)	0·1315 (2)	0·6681 (5)	5·31 (9)
C(4*B*)	0·00497 (4)	0·2185 (2)	0·5319 (5)	5·57 (9)
C(5*B*)	0·01211 (4)	0·3366 (2)	0·3587 (5)	5·28 (9)
C(6*B*)	0·04474 (4)	0·3678 (2)	0·3191 (4)	4·57 (8)
C(7*B*)	0·10549 (4)	0·3144 (1)	0·3957 (4)	3·96 (7)
C(8*B*)	0·13303 (4)	0·2407 (2)	0·4896 (4)	4·29 (7)
C(9*B*)	0·16576 (4)	0·2849 (2)	0·4008 (4)	4·32 (7)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Cinnamamide (*A*)	Cinnamic acid (*B*)
O(1)—C(9)	1·248 (2)	1·318 (2)
O(2)—C(9)		1·208 (3)
N(1)—C(9)	1·326 (3)	
C(1)—C(2)	1·395 (3)	1·395 (3)
C(1)—C(6)	1·392 (3)	1·398 (3)
C(1)—C(7)	1·460 (3)	1·463 (3)
C(2)—C(3)	1·377 (3)	1·382 (3)
C(3)—C(4)	1·378 (3)	1·375 (3)
C(4)—C(5)	1·372 (3)	1·375 (3)
C(5)—C(6)	1·376 (3)	1·374 (3)
C(7)—C(8)	1·319 (3)	1·323 (3)
C(8)—C(9)	1·473 (3)	1·470 (3)
O(1)—C(9)—O(2)		123·1 (2)
O(1)—C(9)—N(1)	121·8 (2)	
O(1)—C(9)—C(8)	121·5 (2)	113·1 (2)
O(2)—C(9)—C(8)		123·8 (2)
N(1)—C(9)—C(8)	116·6 (2)	
C(1)—C(2)—C(3)	120·7 (2)	120·8 (2)
C(1)—C(6)—C(5)	120·8 (2)	121·0 (2)
C(1)—C(7)—C(8)	127·4 (2)	127·5 (2)
C(2)—C(3)—C(4)	120·3 (2)	120·1 (2)
C(2)—C(1)—C(6)	118·0 (2)	117·9 (2)
C(2)—C(1)—C(7)	122·9 (2)	122·6 (2)
C(3)—C(4)—C(5)	119·7 (2)	120·1 (2)
C(4)—C(5)—C(6)	120·4 (2)	120·2 (2)
C(6)—C(1)—C(7)	119·1 (2)	119·6 (2)
C(7)—C(8)—C(9)	121·8 (2)	121·3 (2)

Introduction. Sarma & Desiraju (1985) have recently examined the crystal structure of a donor–acceptor complex of 3,4-dimethoxycinnamic acid and 2,4-dinitrocinnamic acid, and observed no photochemical reaction though the geometrical conditions permit it. On the other hand, a 1/1 complex of formic acid and formamide has been reported by Nahringbauer & Larsson (1969). In view of the crystal engineering of photoreactive crystals, we have attempted to form a hydrogen-bonded complex of cinnamamide and cinnamic acid which are similar in molecular shape and size, and examined the crystal structure.

Experimental. Crystals of the complex grown from an ethanol solution by slow evaporation. D_m measured by flotation in aqueous KI. A colourless plate developed {100}; 0·05 × 0·25 × 0·22 mm. Systematic absences *h*0*l* for *h* odd, 0*k*0 for *k* odd. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (Ni-filtered Cu *Kα*, at 40 kV, 200 mA). The lattice parameters determined with 20 reflections within $18 < 2\theta < 41°$. Intensity data collected within $2\theta_{max} = 125°$ ($-45 \le h \le 45$, $0 \le k \le 10$, $0 \le l \le 4$), ω–2θ scan method [scan speed 6° min^{-1} in ω, scan range $(1·2 + 0·15\tan\theta)°$], background measured for 4 s on either side of the peak; three standard reflections recorded every 97 reflections, fluctuations within 1%. Lorentz and polarization corrections; no absorption correction. 2454 reflections measured. 2196 unique reflections with $|F_o| > \sigma(|F_o|)$, $R_{int} = 0·014$ for 386 *hk*0 reflections. All reflections used in structure analysis. Structure solved by *MULTAN*78 and refined by block-diagonal least-squares method (non-H atoms anisotropically). H atoms determined from a difference Fourier map and refined isotropically; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1·0/[\sigma(F_o)^2 - 0·0684|F_o| + 0·0039|F_o|^2]$ for $|F_o| > 0$, $w = 1·3696$ for $|F_o| = 0$. Final $R = 0·058$ for 2454 reflections, $wR = 0·049$, $S = 1·4160$. $(\Delta/\sigma)_{max} = 0·07$ for non-H and 0·58 for H atoms. The residual electron density in the final difference map was within ±0·15 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *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 Research Center for Protein Engineering, Institute for Protein Research, Osaka University, and at the Okayama University Computer Center.

Discussion. The final atomic parameters are listed in Table 1.* The thermal ellipsoids of the molecules are shown in Fig. 1 with the atomic numbering. Bond lengths and bond angles are listed in Table 2. A stereoscopic view of the crystal structure is shown in Fig. 2.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been desposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52498 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the molecules of (*A*) and (*B*), the bond angles C(1)—C(7)—C(8) are widened by an intramolecular repulsion of C(2)···C(8) [3·021 (3) Å in (*A*); 3·022 (3) Å in (*B*)] and the lengths of C(7)═C(8) bonds are typical for cinnamic acids (Iwamoto, Kashino & Haisa, 1989*b*). The molecules are nearly planar; in (*A*) 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(1) are −0·9 (3), −179·1 (2) and −8·7 (3)°, respectively. The corresponding values for (*B*) are 2·4 (3), 176·9 (2) and 11·4 (3)°, respectively.

In the crystals the molecules of (*A*) and (*B*) are held together by hydrogen bonds N(1*A*)—H(N1*A*)···O(2*B*) [N···O 2·916 (3), H···O 2·01 (2) Å, N—H···O 166 (2)°] and O(1*B*)—H(O1*B*)···O(1*A*) [O···O 2·589 (1), H···O 1·57 (2) Å, O—H···O 173 (2)°] to form a dimer between the amide group and carboxyl group. The dimers related by a twofold screw axis are held together by the other hydrogen bond between the amide groups to form a ribbon {N(1*A*)—H(N2*A*)···O(1*A*)($\frac{1}{2}-x, \frac{1}{2}+y, -z$) [N···O 3·068 (2), H···O 2·14 (2) Å, N—H···O 176 (2)°]}. The ribbons are stacked along **c** by van der Waals interactions to form a sheet, and the sheets are stacked along **a**.

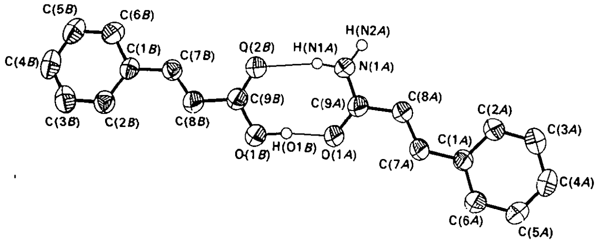

Fig. 1. The thermal ellipsoids of the molecules (*A*) and (*B*) with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms attached to the N and O atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2.

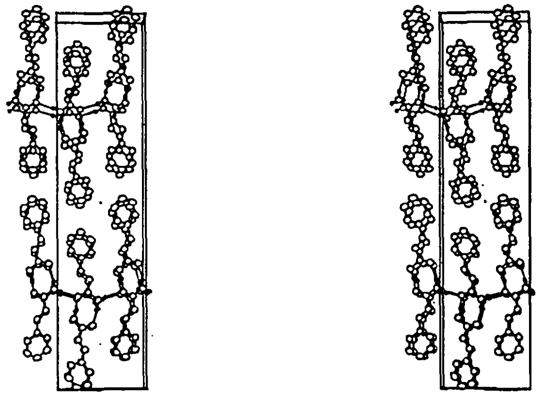

Fig. 2. Stereoscopic view of the crystal structure. The *a* axis points upwards, the *b* axis left to right and the *c* axis into the plane of the paper.

The crystal structure of the complex is more similar to that of *p*-chlorocinnamamide, $P2_1/c$ ($Z = 4$) (Rabinovich, 1969) than to that of cinnamamide, $P2_1/a$ ($Z = 4$) (Iwamoto, Kashino & Haisa, 1989*a*). The period of **a** is close to 39·95 Å, the period of [20$\bar{3}$] of *p*-chlorocinnamamide, because in both crystals the hydrogen-bonded dimers extend nearly along these directions. The periods of **b** of both crystals are also similar to each other, because of the formation of the hydrogen-bonded ribbons along **b**. On the other hand, the period of **c** is similar to those of **b** of the *β*-type of cinnamic acid, $P2_1/a$ ($Z = 4$) (Schmidt, 1964) and *p*-chlorocinnamic acid, $P2_1/a$ ($Z = 4$) (Glusker, Zacharias & Carrell, 1975), and the nearest C═C bonds are related by the *c* translation. The C···C distances between the C═C bonds are 4·057 (4) Å for (*A*) and (*B*), the spacings between the planes through C(1), C(7), C(8) and C(9) involving the C═C bonds being 3·435 (4) Å for (*A*) and 3·394 (4) Å for (*B*). Thus, the photoproducts may be a mixture of the *β*-photodimers of cinnamamide and cinnamic acid. The identification and crystallization of the products are in progress.

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