Acta Cryst. (1990). C**46**, 2436–2438

Topochemical Studies. XIII.* Structures of 3-Bromocinnamic Acid and 3-Chlorocinnamic Acid

BY SHUICHI KANAO, SETSUO KASHINO† AND MASAO HAISA

Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan

(*Received* 7 *February* 1990; *accepted* 2 *April* 1990)

Abstract. 3-Bromocinnamic acid (1), $C_9H_7BrO_2$, M_r = 227·06, monoclinic, $C2/c$, a = 19·191 (6), b = 3·9879 (3), c = 24·798 (7) Å, β = 113·05 (2)°, V = 1746·3 (8) Å^3, Z = 8, D_m = 1·72, D_x = 1·728 Mg m^{-3}, μ = 6·11 mm^{-1}, $F(000)$ = 896, final R = 0·070 for 1232 non-zero reflections. 3-Chlorocinnamic acid (2), $C_9H_7ClO_2$, M_r = 182·60, triclinic, $P\bar{1}$, a = 8·618 (4), b = 13·627 (5), c = 3·909 (1) Å, α = 106·77 (3), β = 96·26 (3), γ = 75·71 (3)°, V = 425·9 (3) Å^3, Z = 2, D_m = 1·38, D_x = 1·424 Mg m^{-3}, μ = 3·65 mm^{-1}, $F(000)$ = 188, final R = 0·060 for 1309 non-zero reflections. T = 295 K, Cu $K\alpha$, λ = 1·54178 Å. The structures were determined with photoreactive crystals of (1) and (2). The C=C bond in (1) takes a *cis* conformation with respect to the 2 position of the phenyl ring, while that in (2) takes a *trans* conformation. The C=C double bonds of the nearest neighbours in (1) are related by a **b** translation and those in (2) are related by a **c** translation.

Introduction. The title compounds (1) and (2) have two kinds of polymorphs, the β and γ forms: their space groups and lattice parameters have been reported previously (Cohen & Schmidt, 1964; Schmidt, 1964). The photoproducts from the crystals of the β form of (1) and (2) have been chemically identified to be the β-type photodimers (Cohen, Schmidt & Sonntag, 1964). However, the crystal structures of the β forms of (1) and (2), and their photoproducts have not been investigated. As an extension of the preceding study (Kashino, Oka & Haisa, 1989), we report the crystal structures of the β forms of (1) and (2).

Experimental. Experimental details for (1) and (2) are listed in Table 1. Crystals of (1) were grown from a solution of acetic acid by slow evaporation. Crystals of (2) were grown by vapour diffusion of water into a solution of acetic acid. The densities were determined by the flotation method [aqueous $ZnCl_2$ for (1) and aqueous KC1 for (2)]. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (Ni-filtered Cu $K\alpha$, 40 kV, 200 mA); ω–2θ-scan method [scan speed 6° min^{-1} in ω: scan range $(1·2 + 0·15\tan\theta)°$ in ω], background measured for 4 s on either side of the peak; three standard reflections recorded every 97 reflections. Lorentz and polarization corrections, no absorption correction. Non-zero reflections were used in the structure analyses. The structure of (1) was solved by the Patterson heavy-atom method, and that of (2) was solved with *MULTAN*78. The positions of the H atoms were determined from difference Fourier maps. The structures were refined by block-diagonal least squares with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1·0/[\sigma(F_o)^2 + p|F_o| + q|F_o|^2]$.

For (1), disorder of the H atom of the carboxyl group was detected from a difference Fourier map. The occupancy factor of the disordered H atoms was fixed at 0·5. Rather high $\Delta\rho$ values in the final difference Fourier maps were observed around the Br and Cl atoms, but there were no significant peaks in the other regions.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs: *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *HBLS-V* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971). Computations were 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 2.‡ The thermal ellipsoids of the molecules are shown in Fig. 1. Bond lengths and angles are listed in Table 3. Stereoviews of the crystal structures are shown in Fig. 2.

* Part XII: Iwamoto & Kashino (1990).

† To whom correspondence should be addressed.

‡ 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 Supply Centre as Supplementary Publication No. SUP 53157 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/90/122436-03$03.00

Table 1. *Experimental details*

	(1)	(2)
M.p. (K)	437–439	455–456
Size of specimen (mm)	0·10 × 0·40 × 0·07	0·20 × 0·05 × 0·30
Range of 2θ (20 reflections) for lattice parameters (°)	20–46	27–33
Systematic absences	*hkl* for *h* + *k* odd *h*0*l* for *h*,*l* odd 0*k*0 for *k* odd	No condition
$2\theta_{max}$(°)	120	125
Range of *h*	−21 to 21	−9 to 9
k	0 to 4	−15 to 15
l	0 to 27	0 to 4
Fluctution of standard reflections (%)	0·8	1·3
No. of unique reflections	1301	1363
No. of non-zero reflections	1232	1309
No. of reflections with $\|F_o\| > \sigma\|F_o\|$	1180	1272
R_{int}	0·010 for 37 *hk*0 reflections	0·011 for 203 *hk*0 reflections
No. of parameters	142	138
p	0·0169	−0·1800
q	0·0069	0·0138
R/*wR*	0·070/0·080	0·060/0·056
S	1·29	2·12
$(\Delta/\sigma)_{max}$ for non-H/H	0·61/0·75	0·15/0·50
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1·82/−0·91	0·48/−0·31

Table 2. *Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

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

	x	*y*	*z*	B_{eq}(Å^2)
3-Bromocinnamic acid (1)				
Br	0·39913 (3)	0·9809 (1)	0·28609 (3)	5·74 (3)
O(1)	0·5306 (2)	0·141 (1)	0·0703 (2)	6·0 (2)
O(2)	0·4161 (2)	0·165 (1)	−0·0006 (2)	6·5 (2)
C(1)	0·3311 (3)	0·636 (1)	0·1150 (2)	4·1 (2)
C(2)	0·3745 (3)	0·720 (1)	0·1739 (2)	4·2 (2)
C(3)	0·3411 (3)	0·870 (1)	0·2065 (2)	4·3 (2)
C(4)	0·2641 (3)	0·951 (1)	0·1829 (3)	5·4 (3)
C(5)	0·2213 (3)	0·868 (1)	0·1259 (3)	5·3 (3)
C(6)	0·2534 (2)	0·718 (2)	0·0922 (2)	5·0 (2)
C(7)	0·3628 (2)	0·469 (1)	0·0778 (3)	4·7 (2)
C(8)	0·4350 (3)	0·391 (1)	0·0915 (2)	4·4 (2)
C(9)	0·4621 (3)	0·226 (1)	0·0515 (2)	4·6 (2)
3-Chlorocinnamic acid (2)				
Cl	0·25057 (7)	1·04880 (5)	0·8989 (2)	5·31 (2)
O(1)	0·8141 (2)	0·4770 (1)	−0·5164 (6)	6·4 (1)
O(2)	0·9013 (2)	0·6149 (1)	−0·1882 (6)	6·6 (1)
C(1)	0·4357 (3)	0·7628 (2)	0·2586 (6)	4·5 (1)
C(2)	0·4173 (3)	0·8645 (2)	0·4767 (6)	4·5 (1)
C(3)	0·2708 (3)	0·9205 (2)	0·6285 (6)	4·4 (1)
C(4)	0·1399 (3)	0·8762 (2)	0·5719 (7)	5·3 (1)
C(5)	0·1585 (3)	0·7742 (2)	0·3563 (8)	6·1 (1)
C(6)	0·3025 (3)	0·7180 (2)	0·2019 (7)	5·5 (1)
C(7)	0·5925 (3)	0·7066 (2)	0·0943 (7)	5·0 (1)
C(8)	0·6308 (3)	0·6139 (2)	−0·1372 (7)	5·4 (1)
C(9)	0·7909 (3)	0·5649 (2)	−0·2910 (7)	5·2 (1)

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

	3-Bromocinnamic acid (1) (*X* = Br)	3-Chlorocinnamic acid (2) (*X* = Cl)
X—C(3)	1·900 (6)	1·740 (2)
O(1)—C(9)	1·257 (6)	1·250 (4)
O(2)—C(9)	1·271 (7)	1·269 (4)
C(1)—C(2)	1·409 (7)	1·383 (4)
C(1)—C(6)	1·411 (8)	1·397 (4)
C(1)—C(7)	1·451 (8)	1·490 (4)
C(2)—C(3)	1·352 (8)	1·398 (4)
C(3)—C(4)	1·398 (9)	1·375 (4)
C(4)—C(5)	1·369 (10)	1·383 (4)
C(5)—C(6)	1·356 (9)	1·385 (4)
C(7)—C(8)	1·328 (8)	1·313 (4)
C(8)—C(9)	1·446 (7)	1·485 (4)
C(2)—C(1)—C(6)	117·6 (5)	117·1 (3)
C(2)—C(1)—C(7)	122·9 (5)	119·8 (3)
C(6)—C(1)—C(7)	119·5 (5)	123·1 (3)
C(1)—C(2)—C(3)	119·9 (5)	121·3 (3)
X—C(3)—C(2)	120·1 (4)	120·3 (2)
X—C(3)—C(4)	118·3 (5)	118·2 (2)
C(2)—C(3)—C(4)	121·5 (6)	121·4 (2)
C(3)—C(4)—C(5)	119·0 (6)	117·3 (3)
C(4)—C(5)—C(6)	120·6 (6)	121·9 (3)
C(1)—C(6)—C(5)	121·3 (6)	120·9 (3)
C(1)—C(7)—C(8)	126·9 (5)	129·1 (3)
C(7)—C(8)—C(9)	123·4 (5)	125·2 (3)
O(1)—C(9)—O(2)	122·3 (5)	121·7 (3)
O(1)—C(9)—C(8)	118·2 (5)	120·2 (3)
O(2)—C(9)—C(8)	119·4 (5)	118·2 (3)

Both molecules are planar, the maximum deviations from the mean molecular planes being 0·033 (5) Å at C(8) for (1) and 0·118 (2) Å at O(1) for (2). C(1)—C(7)—C(8) angles are widened as found in the other derivatives of cinnamic acid (Iwamoto, Kashino & Haisa, 1989). A difference in the conformations of molecules (1) and (2) is observed for the torsion angle C(2)—C(1)—C(7)—C(8): −4·2 (9)° for (1), but −174·7 (3)° for (2). *MM*2 calculations (Allinger & Yuh, 1985), taking the molecular-mechanics parameters for Br and Cl from Bowen, Reddy, Patterson & Allinger (1988), show that the rotational barrier between the *cis* and *trans* conformations is fairly low: 1·4 × 10^4 J mol^{-1} for (1), and 1·5 × 10^4 J mol^{-1} for (2). The differences in the conformational energies, $E_{trans} - E_{cis}$, are also small: −1·6 × 10^2 J mol^{-1} for (1) and −2·7 × 10^2 J mol^{-1} for (2). Thus, either of the conformations would be chosen for these molecules depending on the packing scheme in the crystals. In fact, a polymorphic form of (1) with the *trans* conformation has been suggested (Schmidt, 1964). The other torsion angles in (1) and (2) are similar to each other: C(1)—C(7)—C(8)—C(9) = −179·5 (5)° for (1), −181·0 (3)° for (2); C(7)—C(8)—C(9)—O(1) = −174·8 (5)° for (1), −178·4 (3)° for (2).

In both crystals the molecules form centrosymmetric dimers through hydrogen bonds between the carboxyl groups [O···O 2.628 (6) Å for (1); 2·680 (3) Å for (2)]. The dimers of (1) are stacked along the shortest axis, *b*, with an interplanar distance of 3·544 (9) Å and a displacement of the molecule by 1·83 Å parallel to the C(1)—C(7) bond. The dimers of (2) are also stacked along the shortest axis, *c*, with an interplanar distance of 3·468 (4) Å, but

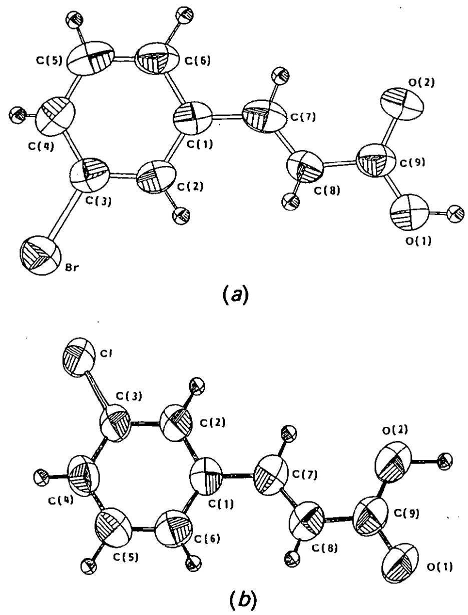

Fig. 1. The thermal ellipsoids of the molecules with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1{\cdot}0$ Å^2. (*a*) 3-Bromocinnamic acid (1); the disordered H atom of the carboxyl group is omitted. (*b*) 3-Chlorocinnamic acid (2).

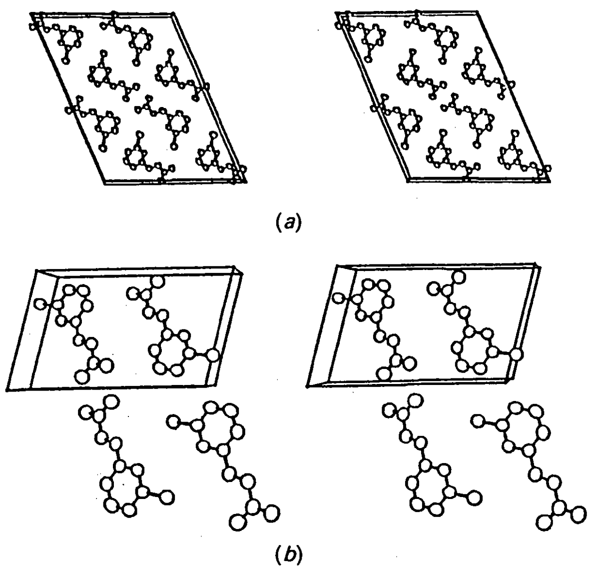

Fig. 2. Stereoviews of molecular packing. (*a*) 3-Bromocinnamic acid (1); the *a* axis points from left to right, the *b* axis into the plane of paper, and the *c* axis upward. (*b*) 3-Chlorocinnamic acid (2); the *a* axis points upward, the *b* axis left to right, and the *c* axis into the plane of paper.

with a displacement of the molecule by 1·52 Å parallel to and 0·97 Å perpendicular to the C(1)—C(7) bond. Thus, the C=C double bonds related by a translation along the shortest axis are displaced relative to each other by 0·93 Å for (1) and 1·71 Å for (2) in the direction parallel to the C(7)=C(8) bond, and by 1·57 Å for (1) and 0·56 Å for (2) perpendicular to this bond. The shortest contact between these double bonds is found between C(7) and C(8) [3·897 (8) Å for (1); 3·535 (4) Å for (2)]. However, no evidence was observed for reaction between these atoms to form a polymer. The next shortest contacts are found between the C(7) atoms and thus also between the C(8) atoms which are related by the translation along the shortest axis [3·9879 (3) Å for (1); 3·909 (1) Å for (2)]. Photodimerization occurred between these double bonds in both crystals (Kanao, Kashino & Haisa, 1990). The structure of 4-chloro-*trans*-cinnamic acid, which is similar to (2), has been reported (Glusker, Zacharias & Carrell, 1975).

The authors thank the Research Center for Protein Engineering, Institute for Protein Research, Osaka University, for the use of the facility.

References

Allinger, N. L. & Yuh, Y. H. (1985). *MM*2. Program for molecular-mechanics calculations. Quantum Chemistry Program Exchange, Indiana Univ., Indiana, USA.

Ashida, T. (1973). *HBLS-V* and *DAPH. The Universal Crystallographic Computing System, Osaka.* The Computation Center, Osaka Univ., Japan.

Bowen, J. P., Reddy, V. V., Patterson, D. G. Jr & Allinger, N. L. (1988). *J. Org. Chem.* **53**, 5471–5475.

Cohen, M. D. & Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 1996–2000.

Cohen, M. D., Schmidt, G. M. J. & Sonntag, F. I. (1964). *J. Chem. Soc.* pp. 2000–2013.

Fujii, S. (1979). *MOLCON. The Universal Crystallographic Computing System, Osaka.* The Computation Center, Osaka Univ., Japan.

Glusker, J. P., Zacharias, D. E. & Carrell, H. L. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 68–74.

Iwamoto, T. & Kashino, S. (1990). *Acta Cryst.* C**46**, 686–688.

Iwamoto, T., Kashino, S. & Haisa, M. (1989). *Acta Cryst.* C**45**, 1753–1758.

Johnson, C. K. (1971). *ORTEP.* Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Kanao, S., Kashino, S. & Haisa, M. (1990). *Acta Cryst.* C**46**, 2439–2442.

Kashino, S., Oka, H. & Haisa, M. (1989). *Acta Cryst.* C**45**, 154–157.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Schmidt, G. M. J. (1964). *J. Chem. Soc.* pp. 2014–2021.