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References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.

Bouwstra, J. A., Schouten, A. & Kroon, J. (1983). *Acta Cryst.* **C39**, 1121–1123.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.

Hall, S. R. & Stewart, J. M. (1990). Editors. *XTAL*3.0 *Users Manual.* Univs. of Western Australia, Australia, and Maryland, USA.

Hanson, A. W. (1973). *Acta Cryst.* **B29**, 454–460.

Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.

McCandlish, L. E., Stout, G. H. & Andrews, L. C. (1975). *Acta Cryst.* **A31**, 245–249.

Meetsma, A. (1991). *PLUTO*, extended version. Univ. of Groningen, The Netherlands. Unpublished.

Mostad, A. & Rømming, C. (1971). *Acta Chem. Scand.* **25**, 3561–3568.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Olthof-Hazekamp, R. (1990). *CRYLSQ. XTAL*3.0 *Users Manual,* edited by S. R. Hall & J. M. Stewart. Univs. of Western Australia, Australia, and Maryland, USA.

Prasad, J. S. (1979). *Acta Cryst.* **B35**, 1404–1407.

Shaikh, A. M., Shivaprakash, N. C., Abdoh, M. M. M. & Prasad, J. S. (1984). *Z. Kristallogr.* **169**, 109.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Snow, M. R. & Teikink, E. R. T. (1988). *Acta Cryst.* **B44**, 676–677.

Spek, A. L. (1988). *J. Appl. Cryst.* **21**, 578–579.

Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

Acta Cryst. (1993). C**49**, 292–294

Structure of (4-Bromophenyl)propiolic Acid and its Unusual Hydrogen-Bonding Pattern

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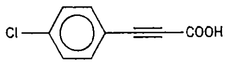
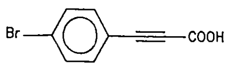
Abstract. $C_9H_5BrO_2$, $M_r = 225.04$, monoclinic, $P2_1/c$, $a = 3.913\ (20)$, $b = 6.141\ (2)$, $c = 34.444\ (27)$ Å, $\beta = 91.79\ (5)^\circ$, $V = 827.2\ (8)$ Å^3, $Z = 4$, $D_x = 1.81$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.870$ mm^{-1}, $F(000) = 440$, $T = 153$ K, $R = 0.030$, $wR = 0.030$ for 1469 independent reflections. The title compound exhibits unusual catemeric hydrogen bonding with both *syn* and *anti* arrangements of the carboxyl group. Such hydrogen bonding is also found in the corresponding chloro acid but the pattern of halogen–halogen contacts is different.

Introduction. We have previously reported that molecules of (4-chlorophenyl)propiolic acid (1) do not pack in the crystal according to the expected carboxylic dimer motif but in an unusual catemeric arrangment (Desiraju, Murty & Kishan, 1990). A possible reason could be the inability of the molecules to form C—H···O hydrogen bonds. Such bonds exist in other carboxylic acids which have the expected carboxylic dimer motif (Leiserowitz, 1976). There is not much crystallographic data on phenylpropiolic acids. The unsubstituted acid (Rollett, 1955) and several alkoxy derivatives examined by us (Desiraju & Kishan, 1989) adopt the dimer motif and it was not clear if the hydrogen-bond pattern exhibited by the chloro acid (1) is an uncommon variant or whether it would be observed in related derivatives. Accordingly, a crystallographic study of the title compound (2) was initiated.



(1)



(2)

Experimental. Acid (2) (m.p. 468–469 K) was prepared from 4-bromobenzaldehyde by literature procedures (Desiraju & Kishan, 1989) and recrystallized from 1:3 acetone–chloroform. Intensity data were collected on an irregularly shaped block 0.4 × 0.4 × 0.3 mm on a Nicolet *R*3*m* diffractometer. Unit-cell parameters were obtained from 25 reflections in the range $5 \leq 2\theta \leq 30^\circ$. The ω-scan method was used with a scan width of 1.20° and scan speed between 0.30 and 3.32° min^{-1}. 1974 reflections (1886 unique) were collected with $4 < 2\theta < 55^\circ$ and in the range $-5 \leq h \leq 5$, $0 \leq k \leq 8$, $0 \leq l \leq 45$. Of these,

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Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2 × 10^3)

For non-H atoms $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. H(9) was refined isotropically; H(2), H(3), H(5) and H(6) were allowed to ride with the corresponding C atoms C(2), C(3), C(5) and C(6).

	x	y	z	U_{eq}/U_{iso}
Br	0.4038 (1)	0.3585 (1)	0.2157 (1)	23 (1)
C(1)	0.0173 (8)	0.8445 (5)	0.1206 (1)	19 (1)
C(2)	0.1722 (9)	0.6497 (5)	0.1098 (1)	21 (1)
C(3)	0.2870 (8)	0.5038 (6)	0.1379 (1)	19 (1)
C(4)	0.2430 (8)	0.5579 (5)	0.1768 (1)	18 (1)
C(5)	0.0917 (8)	0.7482 (6)	0.1879 (1)	20 (1)
C(6)	−0.0230 (9)	0.8939 (5)	0.1598 (1)	19 (1)
C(7)	−0.0997 (9)	0.9932 (6)	0.0906 (1)	22 (1)
C(8)	−0.193 (1)	1.1138 (5)	0.0653 (1)	26 (1)
C(9)	−0.279 (1)	1.2401 (6)	0.0310 (1)	30 (1)
O(1)	−0.1768 (9)	1.1771 (5)	−0.0018 (1)	41 (1)
O(2)	−0.4536 (8)	1.4100 (4)	0.0342 (1)	42 (1)
H(9)	−0.09 (2)	1.09 (1)	0.01 (3)	4 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

Br—C(4)	1.907 (5)	C(1)—C(2)	1.397 (6)
C(1)—C(6)	1.398 (5)	C(1)—C(7)	1.442 (5)
C(2)—C(3)	1.384 (5)	C(3)—C(4)	1.398 (5)
C(4)—C(5)	1.370 (6)	C(5)—C(6)	1.383 (5)
C(7)—C(8)	1.192 (5)	C(8)—C(9)	1.445 (6)
C(9)—O(1)	1.270 (5)	C(9)—O(2)	1.253 (6)
O(1)—H(9)	0.67 (9)		
C(2)—C(1)—C(6)	120.4 (3)	C(2)—C(1)—C(7)	118.8 (3)
C(6)—C(1)—C(7)	120.7 (3)	C(1)—C(2)—C(3)	120.1 (3)
C(2)—C(3)—C(4)	118.1 (3)	Br—C(4)—C(3)	118.3 (3)
Br—C(4)— C(5)	119.2 (3)	C(3)—C(4)—C(5)	122.5 (3)
C(4)—C(5)—C(6)	119.3 (3)	C(1)—C(6)—C(5)	119.5 (3)
C(1)—C(7)—C(8)	178.6 (4)	C(7)—C(8)—C(9)	171.9 (4)
C(8)—C(9)—O(1)	119.4 (4)	C(8)—C(9)—O(2)	119.2 (3)
O(1)—C(9)—O(2)	121.3 (4)	C(9)—O(1)—H(9)	113 (1)

1469 unique reflections were found to be non-zero with $I \geq 3.0\sigma(I)$. Three standard reflections (0,0,12, 040 and 400) were measured every 97 reflections and showed less than 2% variation. Absorption corrections were applied with ψ scans. The structure was solved (by heavy-atom methods) and refined using the *SHELXTL* (Sheldrick, 1978) package. The non-H atoms were refined anisotropically and the aromatic H atoms H(2), H(3), H(5) and H(6) were allowed to ride with the corresponding C atoms. The carboxyl H atoms must be treated as $\frac{1}{2}$ H atoms since all O—H···O hydrogen bonds lie on inversion centres. Because both *syn* and *anti* arrangements occur, there are two non-equivalent centres of inversion. It was found that only one of the two non-equivalent $\frac{1}{2}$ H atoms (corresponding to the *anti* arrangement) could be refined isotropically [H(9)]. The other (*syn*) $\frac{1}{2}$ H atom was ignored. Refinement converged at $R = 0.030$, $wR = 0.030$, $S = 1.27$, $\Delta/\sigma_{max} = 0.028$. The minimum and maximum peaks in the final Fourier map were 0.56 and -0.66 e Å^{-3} (near the Br atom). The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic positions and equivalent isotropic temperature factors are listed in Table 1.* The bond lengths and angles are given in Table 2. The atom-numbering scheme is shown in Fig. 1. Except for the bond lengths and angles involving the halogen atom, all other bond lengths and angles are within 3 e.s.d.'s of each other in the chloro and bromo structures (1) and (2). The angle between the mean plane of the phenyl ring and the best plane of atoms C(1), C(7), C(8), C(9), O(1) and O(2) is 10.5° [corresponding angle in acid (1) is 9.6°]. A view of the crystal structure of acid (2) looking down the short axis is shown in Fig. 2. The carboxyl group is almost completely disordered [C(9)—O(1) 1.270 (5), C(9)—O(2) 1.253 (6) Å, C(8)—C(9)—O(1) 119.4 (4), C(8)—C(9)—O(2) 119.2 (3)°] but the environments

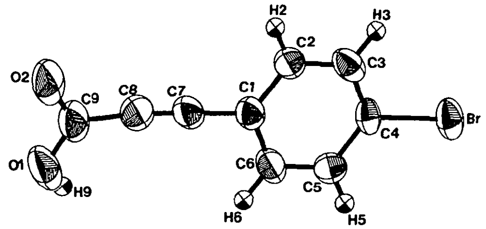

Fig. 1. *ORTEP* (Johnson, 1976) view of a molecule of (4-bromophenyl)propiolic acid (2), showing the atom-labelling scheme. Only the *anti* carboxyl H atom is shown.

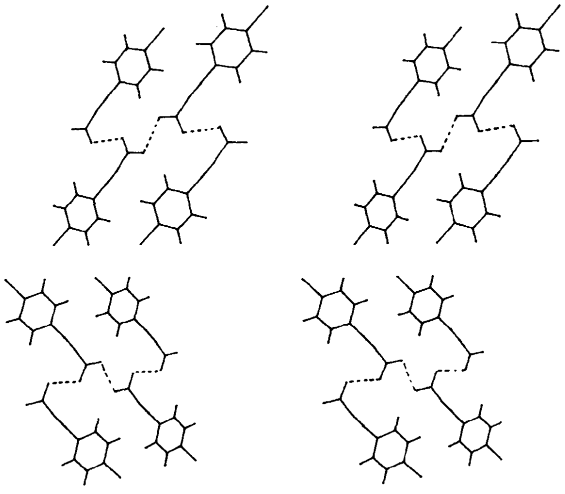

Fig. 2. Crystal structure of acid (2) viewed down [100] (y horizontal, z vertical) to show the hydrogen-bonded catemer network and Br···Br interactions. Notice the inclination of the hydrogen-bond ribbons.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55598 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR0206]

around the two O atoms, O(1) and O(2), are quite distinct. This is noteworthy because complete disorder of the carboxyl group is usually associated with nearly identical environments at the two O atoms (Leiserowitz, 1976). The hydrogen-bond network is of the catemeric type and is identical to that observed in the 4-chloro derivative (1) (Desiraju, Murty & Kishan, 1990). This catemer is generated by a combination of centres of inversion plus a translation along [010] and may be considered to be the primary structural motif in these crystals. The two O···O distances are 2.57 (8) and 2.61 (9) Å [corresponding distances in acid (1) are 2.59 (1) and 2.66 (1) Å]. It should be emphasized that the existence of both *syn* and *anti* O═C—O—H conformations in the structures of these two halogenated phenylpropiolic acids (1) and (2) is quite exceptional (Leiserowitz, 1976; Desiraju, 1989).

The catemer substructures in these two crystals are nearly identical but they are linked by short halogen···halogen contacts in distinctive ways to yield the secondary structure. In acid (1), inversion-related catemers are connected by short C—Cl···Cl—C interactions (Desiraju & Parthasarathy, 1989) [Cl···Cl 3.50 (1) Å] but, in the present structure, Br···Br contacts are found between 2_1-related molecules [Br···Br 3.93 (1) Å; Fig. 2]. In effect, catemers define molecular ribbons and adjacent ribbons are screw or glide related. These alternative secondary motifs may be considered to be triclinic and monoclinic variations of the same structural theme. The monoclinic variation found in this case may be preferred for overall close-packing reasons in that the tilt of the molecular ribbons promotes the formation of aromatic ring herringbone C···H interactions. In turn, tertiary structures are formed in both cases by stacking the secondary structure in the short-axis direction. Such stacking leads to solid-state thermal reactions of the Diels–Alder type for acid (2). Such reactivity has been previously reported (Desiraju & Kishan, 1989). To investigate these issues further, (4-iodophenyl)propiolic acid has been synthesized (m.p. 471 K) but crystals suitable for an X-ray diffraction study have not yet been obtained.

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References

Desiraju, G. R. (1989). *Crystal Engineering. The Design of Organic Solids*, pp. 115–173. Amsterdam: Elsevier.

Desiraju, G. R. & Kishan, K. V. R. (1989). *J. Am. Chem. Soc.* **111**, 4838–4843.

Desiraju, G. R., Murty, B. N. & Kishan, K. V. R. (1990). *Chem. Mater.* **2**, 447–449.

Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.

Rollett, J. S. (1955). *Acta Cryst.* **8**, 487–494.

Sheldrick, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Germany.

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Structure of Benfotiamine Hemihydrate

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Abstract. Benzenecarbothioic acid *S*-(2-{[(4-amino-2-methyl-5-pyrimidinyl)methyl]formylamino}-1-[2-(phosphonooxy)ethyl]-1-propenyl) ester hemihydrate, $C_{19}H_{23}N_4O_6PS.0.5H_2O$, $M_r = 475.5$, monoclinic, $P2_1/n$, $a = 16.822\,(5)$, $b = 18.556\,(6)$, $c = 14.429\,(5)$ Å, $\beta = 105.52\,(3)°$, $V = 4340\,(1)$ Å^3, $Z = 8$, $D_x = 1.359$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1.5418$ Å, $\mu = 24.1$ cm^{-1}, $F(000) = 1992$, $T = 295$ K, $R = 0.050$ for 4526 reflections with $I \geq 2\sigma(I)$. The two independent benfotiamine molecules, in the zwitterionic form, assume a similar conformation apart from the phosphonooxyethyl side chains, and maintain structural characteristics of the ring-opened derivatives of thiamin with the *N*-formyl and ethylenic groups nearly perpendicular to each other and the N(3)—C(4) bond retaining single-bond character. The conformation of benfotiamine is stabilized by an intramolecular N(4′α)—H···O(2α) hydrogen bond

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