

2,3-Dibromo-3-phenylpropanoic acid: a monoclinic polymorph

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Received 14 November 2016

Accepted 24 November 2016

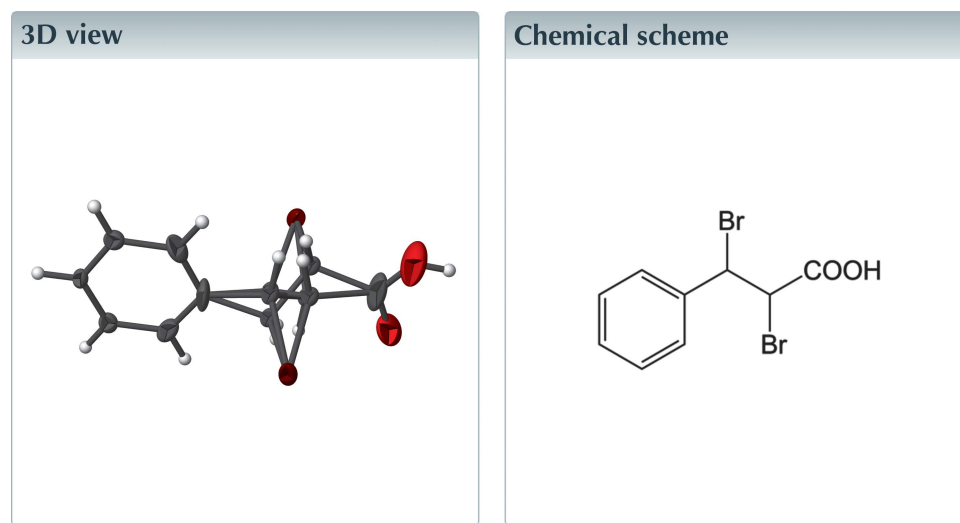
Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; bromination; hydrogen bonding; inversion dimers.

CCDC reference: 1519137

Structural data: full structural data are available from iucrdata.iucr.org

Bromination of *trans*-cinnamic acid resulted in the formation of 2,3-dibromo-3-phenylpropanoic acid, $C_9H_8Br_2O_2$. Crystallization from ethanol–water (1:1) gave crystals of different shapes. One is in the form of rods, that crystallized as the orthorhombic polymorph (*Pnma*), and whose structure has been described [Thong *et al.* (2008). *Acta Cryst.* **E64**, o1946]. The other are thin plate-like crystals which are the monoclinic polymorph ($P2_1/n$). The structure of this monoclinic polymorph is similar to that of the orthorhombic polymorph; here the aliphatic C atoms are disordered over three sets of sites (occupancy ratio 0.5:0.25:0.25). In the crystal, molecules are linked by pairs of O–H \cdots O hydrogen bonds, forming inversion dimers with an $R_2^2(8)$ ring motif. The dimers are linked by weak C–H \cdots Br hydrogen bonds, forming chains propagating along the *a*-axis direction.



Structure description

Addition of bromine in glacial acetic acid to *trans*-cinnamic acid yielded mostly *erythro*-2,3-dibromo-3-phenylpropanoic acid. Crystallization from ethanol–water (1:1, v:v), gave different-shaped crystals that proved to be two polymorphs of the title compound. The rod-shaped crystalline material was shown to be the orthorhombic polymorph (*Pnma*), reported on by Thong *et al.* (2008). The thin plate-like crystals have a monoclinic unit cell ($P2_1/n$), and herein we report on the crystal structure.

The aliphatic carbons, C1 and C2, are split over three positions, and were assigned an occupancy ratio of 0.5:0.25:0.25. The molecular structure of the major component is illustrated in Fig. 1.

In the crystal, molecules are linked by pairs of O–H \cdots O hydrogen bonds, forming a classical carboxylic acid inversion dimer with an $R_2^2(8)$ ring motif (Table 1 and Fig. 2).

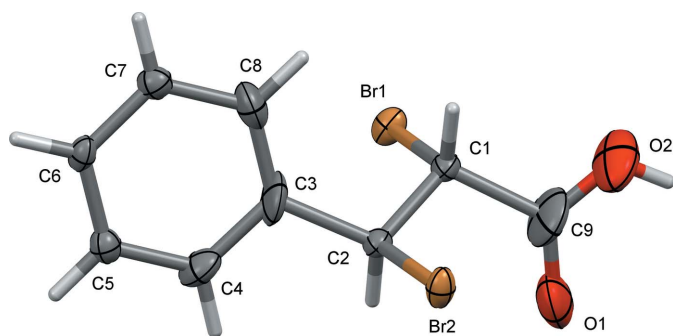


Figure 1
A view of the molecular structure of the title monoclinic polymorph, with the atom labelling and 50% probability displacement ellipsoids. Only the major component of the disordered aliphatic C atoms (C1 and C2) is shown.

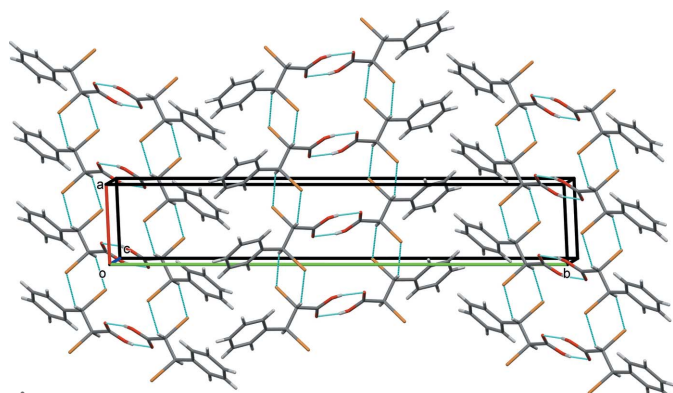


Figure 2
A view along the *c* axis of the crystal packing of the title monoclinic polymorph. The hydrogen bonds are shown as dashed lines (see Table 1), and only the major component of the disordered aliphatic C atoms (C1 and C2) is shown.

Neighboring dimers are linked by weak C—H···Br hydrogen bonds, forming chains propagating along the *a*-axis direction (Table 1 and Fig. 2).

Synthesis and crystallization

Excess bromine in glacial acetic acid was added to *trans*-cinnamic acid. The crude product was precipitated by addition of water. The crude product was recrystallized from a 1:1 ethanol–water solution at 277 K. Both colorless rod-like and plate-like crystals of the compound were obtained. The reaction scheme is shown in Fig. 3.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The aliphatic carbons, C1 and C2,

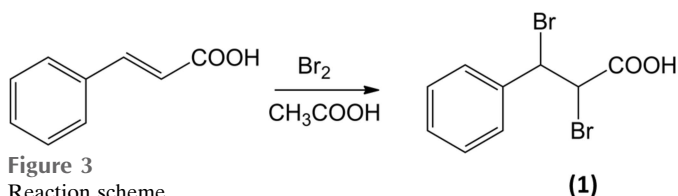


Figure 3
Reaction scheme.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H2O···O1 ⁱ	0.84	1.81	2.638 (5)	167
C1—H1···Br2 ⁱⁱ	1.00	2.96	3.845 (6)	148
C2—H2···Br1 ⁱⁱⁱ	1.00	3.01	3.884 (7)	147

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $x + 1, y, z$; (iii) $x - 1, y, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₉ H ₈ Br ₂ O ₂
<i>M</i> _r	307.97
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>
Temperature (K)	106
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.5382 (2), 28.8640 (13), 6.6112 (3)
β (°)	111.935 (1)
<i>V</i> (Å ³)	980.32 (7)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	8.23
Crystal size (mm)	0.48 × 0.35 × 0.09
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.456, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	32878, 2452, 2302
<i>R</i> _{int}	0.040
(sin θ/λ) _{max} (Å ⁻¹)	0.668
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.033, 0.093, 1.07
No. of reflections	2452
No. of parameters	126
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.04, −1.02

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2016* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009) and *SHELXL2016* (Sheldrick, 2015).

are split over three positions, and were assigned an occupancy ratio of 0.5:0.25:0.25.

Acknowledgements

The authors would like to thank the Chemistry and Biochemistry Department of the Fredonia State University of New York for funding this study and for the purchase of the diffractometer.

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full crystallographic data

IUCrData (2016). **1**, x161885 [https://doi.org/10.1107/S241431461601885X]

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2,3-Dibromo-3-phenylpropanoic acid

Crystal data

$C_9H_8Br_2O_2$	$F(000) = 592$
$M_r = 307.97$	$D_x = 2.087 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 5.5382 (2) \text{ \AA}$	Cell parameters from 9931 reflections
$b = 28.8640 (13) \text{ \AA}$	$\theta = 3.4\text{--}28.3^\circ$
$c = 6.6112 (3) \text{ \AA}$	$\mu = 8.23 \text{ mm}^{-1}$
$\beta = 111.935 (1)^\circ$	$T = 106 \text{ K}$
$V = 980.32 (7) \text{ \AA}^3$	Plate, colorless
$Z = 4$	$0.48 \times 0.35 \times 0.09 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	2452 independent reflections
φ and ω scans	2302 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2015)	$R_{\text{int}} = 0.040$
$T_{\text{min}} = 0.456$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 2.8^\circ$
32878 measured reflections	$h = -7 \rightarrow 6$
	$k = -38 \rightarrow 38$
	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 3.0256P]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2452 reflections	$\Delta\rho_{\text{max}} = 1.04 \text{ e \AA}^{-3}$
126 parameters	$\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$
0 restraints	Extinction correction: SHELXL2016 (Sheldrick, 2015),
Primary atom site location: structure-invariant direct methods	$Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0063 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	0.72796 (6)	0.36584 (2)	0.82102 (5)	0.02215 (13)	
Br2	-0.02058 (6)	0.43970 (2)	0.37555 (5)	0.02384 (13)	
C3	0.2346 (10)	0.34824 (16)	0.4013 (8)	0.0418 (10)	
C4	0.0636 (8)	0.31343 (15)	0.4024 (6)	0.0327 (8)	
H4	-0.021097	0.314523	0.503558	0.039*	
C5	0.0162 (7)	0.27744 (12)	0.2582 (6)	0.0220 (6)	
H5	-0.105009	0.254060	0.257170	0.026*	
C6	0.1431 (6)	0.27480 (12)	0.1139 (5)	0.0206 (6)	
H6	0.110182	0.249474	0.015500	0.025*	
C7	0.3178 (7)	0.30891 (13)	0.1124 (6)	0.0231 (7)	
H7	0.406474	0.306975	0.014352	0.028*	
C8	0.3625 (8)	0.34602 (14)	0.2555 (7)	0.0352 (9)	
H8	0.480065	0.369870	0.254135	0.042*	
C9	0.4667 (13)	0.4536 (2)	0.7928 (9)	0.0596 (15)	
O1	0.3550 (8)	0.44829 (11)	0.9260 (7)	0.0511 (9)	
O2	0.5956 (10)	0.48698 (15)	0.7794 (6)	0.0652 (12)	
H2O	0.622278	0.504415	0.887335	0.098*	
C1	0.4884 (13)	0.4126 (2)	0.6445 (10)	0.0191 (7)	0.5
H1	0.546193	0.424225	0.527342	0.023*	0.5
C2	0.2257 (13)	0.3899 (2)	0.5471 (11)	0.0191 (7)	0.5
H2	0.170807	0.378764	0.666760	0.023*	0.5
C1A	0.339 (3)	0.4271 (5)	0.554 (2)	0.0191 (7)	0.25
H1A	0.450625	0.432294	0.467135	0.023*	0.25
C2A	0.353 (3)	0.3769 (5)	0.622 (2)	0.0191 (7)	0.25
H2A	0.239337	0.372327	0.707530	0.023*	0.25
C1B	0.300 (3)	0.4015 (5)	0.477 (2)	0.0191 (7)	0.25
H1B	0.440311	0.414737	0.433276	0.023*	0.25
C2B	0.379 (3)	0.3982 (5)	0.715 (2)	0.0191 (7)	0.25
H2B	0.246721	0.384549	0.766877	0.023*	0.25

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02210 (19)	0.0249 (2)	0.01555 (18)	0.00575 (12)	0.00256 (13)	-0.00114 (11)
Br2	0.02141 (19)	0.01770 (19)	0.0258 (2)	0.00415 (11)	0.00120 (14)	-0.00336 (12)
C3	0.058 (3)	0.028 (2)	0.038 (2)	-0.0083 (19)	0.016 (2)	-0.0224 (18)
C4	0.035 (2)	0.040 (2)	0.0247 (17)	0.0049 (17)	0.0140 (15)	-0.0078 (16)
C5	0.0224 (15)	0.0185 (15)	0.0237 (15)	-0.0002 (12)	0.0068 (13)	0.0004 (12)
C6	0.0191 (14)	0.0196 (15)	0.0197 (14)	0.0012 (12)	0.0031 (12)	-0.0065 (12)
C7	0.0206 (15)	0.0261 (17)	0.0221 (15)	0.0001 (13)	0.0073 (13)	-0.0011 (13)
C8	0.035 (2)	0.0235 (18)	0.042 (2)	-0.0112 (16)	0.0081 (17)	-0.0039 (16)
C9	0.084 (4)	0.056 (3)	0.045 (3)	-0.008 (3)	0.031 (3)	-0.031 (3)
O1	0.055 (2)	0.0260 (15)	0.069 (2)	-0.0105 (15)	0.0196 (19)	-0.0064 (16)
O2	0.114 (4)	0.052 (2)	0.044 (2)	-0.013 (2)	0.047 (2)	-0.0139 (17)
C1	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)

C2	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)
C1A	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)
C2A	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)
C1B	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)
C2B	0.022 (2)	0.0174 (19)	0.020 (2)	-0.0008 (15)	0.0109 (15)	-0.0023 (14)

Geometric parameters (Å, °)

Br1—C1	1.946 (7)	C5—C6	1.382 (5)
Br1—C2B	2.019 (13)	C6—C7	1.383 (5)
Br1—C2A	2.026 (15)	C7—C8	1.389 (5)
Br2—C1A	1.931 (14)	C9—O2	1.222 (7)
Br2—C1B	1.984 (13)	C9—O1	1.261 (7)
Br2—C2	2.015 (7)	C9—C1	1.569 (8)
C3—C4	1.383 (6)	C9—C1A	1.658 (14)
C3—C8	1.394 (7)	C9—C2B	1.695 (14)
C3—C2	1.553 (7)	C1—C2	1.504 (9)
C3—C2A	1.589 (14)	C1A—C2A	1.51 (2)
C3—C1B	1.616 (14)	C1B—C2B	1.469 (18)
C4—C5	1.368 (5)		
C4—C3—C8	119.8 (3)	C2—C1—C9	108.0 (5)
C4—C3—C2	112.2 (4)	C2—C1—Br1	106.7 (5)
C8—C3—C2	127.4 (4)	C9—C1—Br1	110.0 (4)
C4—C3—C2A	114.9 (6)	C1—C2—C3	110.7 (5)
C8—C3—C2A	121.1 (6)	C1—C2—Br2	105.8 (4)
C4—C3—C1B	139.9 (6)	C3—C2—Br2	112.0 (4)
C8—C3—C1B	98.3 (6)	C2A—C1A—C9	101.7 (10)
C5—C4—C3	120.1 (4)	C2A—C1A—Br2	106.9 (9)
C4—C5—C6	120.5 (3)	C9—C1A—Br2	118.1 (7)
C5—C6—C7	120.2 (3)	C1A—C2A—C3	105.5 (10)
C6—C7—C8	119.4 (3)	C1A—C2A—Br1	105.7 (9)
C7—C8—C3	119.9 (4)	C3—C2A—Br1	119.1 (8)
O2—C9—O1	126.8 (4)	C2B—C1B—C3	102.3 (10)
O2—C9—C1	111.5 (5)	C2B—C1B—Br2	105.7 (9)
O1—C9—C1	121.2 (5)	C3—C1B—Br2	110.7 (7)
O2—C9—C1A	110.4 (6)	C1B—C2B—C9	101.5 (9)
O1—C9—C1A	117.6 (7)	C1B—C2B—Br1	105.4 (9)
O2—C9—C2B	146.2 (6)	C9—C2B—Br1	101.7 (7)
O1—C9—C2B	86.5 (6)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2O \cdots O1 ⁱ	0.84	1.81	2.638 (5)	167

C1—H1…Br2 ⁱⁱ	1.00	2.96	3.845 (6)	148
C2—H2…Br1 ⁱⁱⁱ	1.00	3.01	3.884 (7)	147

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