Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

A new polymorph of 2-bromo-5-hydroxybenzaldehyde

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.030
wR factor = 0.083
Data-to-parameter ratio = 12.7

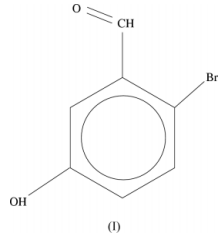
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 13 November 2003
Accepted 5 December 2003
Online 12 December 2003

A new polymorph of 2-bromo-5-hydroxybenzaldehyde, $C_7H_5BrO_2$, is reported. In this new form a pair of hydrogen bonds link molecules related by an inversion centre. The Br atom deviates significantly from the plane of the benzene ring and the aldehyde group is twisted by 10.0 (5)° around the Csp^2-C_{aryl} bond.

Comment

We have been studying halogen derivatives of *m*-hydroxybenzaldehyde used as precursors in the synthesis of *meso*-tetraaryl-substituted porphyrins (Matos Beja, Paixão, Ramos Silva, Alte da Veiga *et al.*, 1997; Matos Beja, Paixão, Ramos Silva, Rocha Gonsalves *et al.*, 1997; Matos Beja *et al.*, 2000). We have already reported the crystal structure of orthorhombic 2-bromo-5-hydroxybenzaldehyde (form I) (Matos Beja *et al.*, 2000). We report here a new monoclinic form of this compound.



(I)

The internal ring angles that deviate most from the ideal value of 120° are C1 [118.2 (4)°] and C6 [121.2 (4)°], while in form I the largest deviations were found at C1 and C2. The deviations of the substituents from the least-squares benzene ring are 0.041 (6) (Br), −0.067 (7) (C7), −0.251 (8) (O1) and −0.023 (7) Å (O2), which are similar to those found in form I. Again, the C7—C1 bond is slightly tilted out of the ring plane and there is also an in-plane twist as shown by the asymmetry between the C6—C1—C7 [118.4 (4)°] and C2—C1—C7 [123.4 (4)°] bond angles, although not so pronounced as in the monoclinic form. The rotation of the aldehyde group around the C1—C7 bond is larger in this form than in form I [10.0 (5)° instead of 7.1 (5)°]. The main differences between the two forms are the intermolecular interactions that result in different molecular packing. In form I, the molecules are joined together in chains running along the *b* axis by hydrogen bonds between the hydroxy and aldehyde group. In the new form, the molecules are linked as centrosymmetric dimers by a pair of similar hydrogen bonds [O2—H2···O1^{i} = 2.939 (5) Å and 167°; symmetry code:(i) $-x, -y, -z$].

Experimental

The title compound was prepared by slowly adding bromine to a solution of 3-hydroxybenzaldehyde in glacial acetic acid. After a few

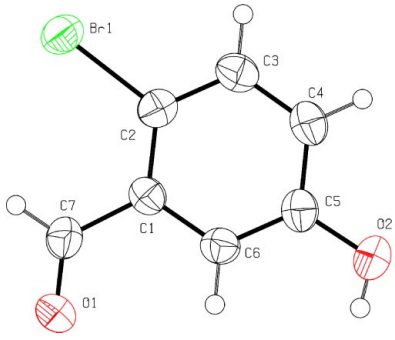


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

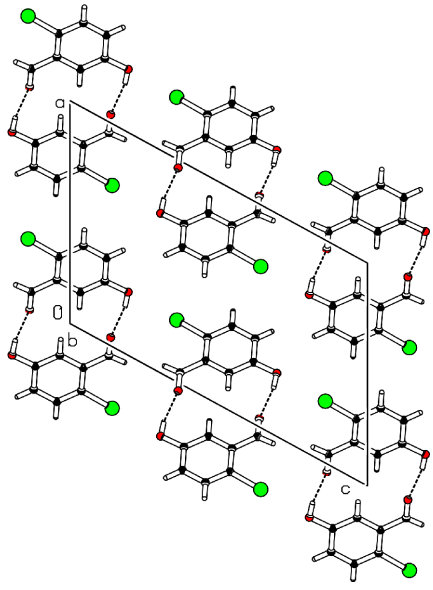


Figure 2
View of the unit-cell contents, projected along *b*. Hydrogen bonds are shown as dashed lines.

hours, water was added to precipitate a solid and the mixture was left overnight in a refrigerator. The solid was filtered off and recrystallized from ethanol.

Crystal data

$C_7H_5BrO_2$
M_r = 201.02
Monoclinic, $P2_1/c$
a = 11.235 (6) Å
b = 4.038 (5) Å
c = 17.057 (8) Å
β = 118.66 (3)°
V = 679 (1) Å^3
Z = 4
D_x = 1.966 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.4–16.9°
μ = 5.98 mm^{-1}
T = 293 (2) K
Pyramid, pink
0.35 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.52, T_{max} = 0.55
1228 measured reflections
1172 independent reflections
866 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 25.1°
$h = -13 \rightarrow 13$
$k = -4 \rightarrow 0$
$l = -13 \rightarrow 20$
3 standard reflections
frequency: 180 min
intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.04
1172 reflections
92 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 1.0851P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.87 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C2	1.905 (4)	O1—C7	1.209 (6)
O2—C5	1.367 (5)		
C3—C2—Br1	118.0 (3)	O1—C7—C1	123.3 (4)
C1—C2—Br1	121.4 (3)		
Br1—C2—C1—C6	−178.3 (3)	Br1—C2—C3—C4	179.0 (3)
Br1—C2—C1—C7	3.8 (6)	O2—C5—C6—C1	−178.4 (4)
C2—C1—C7—O1	170.0 (5)	C7—C1—C6—C5	177.3 (4)
C6—C1—C7—O1	−7.9 (7)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1^{i}	0.82	2.14	2.939 (5)	167

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

All H atoms were placed in idealized positions and constrained to ride on their parent atoms [C—H = 0.93 Å and O—H = 0.82 Å, and U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O)].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

This work was supported by Fundação para a Ciência e a Tecnologia (FCT) and FEDER under project SAPIENS-POCTI/QUI/33495/00.

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