Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2-Bromo-5-hydroxybenzaldehyde

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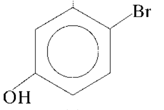
Received 16 November 1999
Accepted 24 November 1999

The molecules of the title compound, $C_7H_5BrO_2$, form zigzag chains running along the *b* axis and are stacked in layers perpendicular to the *a* axis. Intermolecular bonding occurs through hydrogen bonds linking the hydroxyl and carbonyl groups, with an O···O distance of 2.804 (4) Å. The Br atom deviates significantly from the plane of the ring and the aldehyde group is twisted by 7.1 (5)° around the Csp^2-C_{aryl} bond. The geometry of the molecule in the crystal is compared to that given by *ab initio* quantum mechanical calculations for the isolated molecule, using a molecular orbital Hartree–Fock method and density functional theory.

Comment

We have recently reported the structures of 2,4-dibromo and 2,4,6-tribromo derivatives of *m*-hydroxybenzaldehyde (Matos Beja, Paixão, Ramos Silva, Alte da Veiga *et al.*, 1997; Matos Beja, Paixão, Ramos Silva, Rocha Gonsalves *et al.*, 1997), compounds which we came across as precursors for the synthesis of *meso*-tetraaryl-substituted porphyrins. We report here the synthesis and the crystal structure of the monobromo derivative of *m*-hydroxybenzaldehyde.

Hodgson & Beard (1925) mention that monobromination of *m*-hydroxybenzaldehyde in chloroform occurs at positions 2 and 4 and isolated the 2-bromoderivative. Pandya *et al.* (1952) carried out the bromination in acetic acid and isolated a product with a very similar melting point to that obtained by Hodgson & Beard and identified it as the 4-bromoderivative. In order to clarify which isomer is obtained by monobromination of *m*-hydroxybenzaldehyde we followed Pandya's conditions as well as Hodgson & Beard's and have isolated the same compound in both conditions. This was identified by X-ray diffraction as the title compound, the 2-bromo-5-hydroxybenzaldehyde isomer, (I) (Fig. 1).



(I)

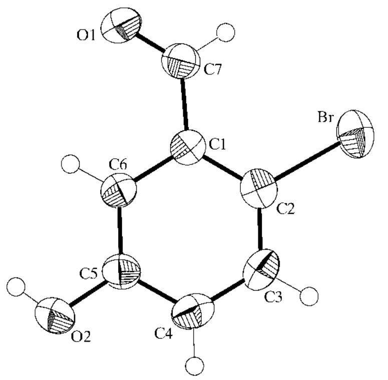


Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

The internal bond angles of the ring at C1 [118.3 (3)°] and C2 [121.1 (3)°] deviate significantly from the ideal value of 120°. While the hydroxyl-O2 atom is coplanar with the benzene ring within experimental uncertainty, both the aldehyde group and the Br atom are tilted out from this plane. The deviations from the least-squares benzene ring plane are Br 0.032 (5), C7 −0.042 (5) and O1 −0.181 (6) Å. The C7—C1 bond is slightly tilted out of the ring plane and there is also a pronounced in-plane twist as shown by the large asymmetry between the C6—C1—C7 [117.4 (3)°] and C2—C1—C7 [124.3 (3)°] bond angles. In addition, the aldehyde group is rotated by 7.1 (5)° around the C1—C7 bond. These effects may be due to a steric interaction between the formyl-H atom and the bulky Br atom, but may also reflect to some extent the involvement of the aldehyde group in intermolecular hydrogen-bond interactions. In order to distinguish between these two effects, we have performed an optimization of the geometry of the isolated molecule by *ab initio* quantum mechanical molecular orbital Hartree–Fock (MO–HF) calculations using the computer code *GAMESS* (Schmidt *et al.*, 1993). The atomic wave-functions of the light atoms were expanded on a standard 6-31G(d,p) basis set and for the Br atom the 'double zeta' basis set of Binning & Curtiss (1990) was used. The optimization was conducted starting from the experimental X-ray geometry without imposing any symmetry constraint on the molecule. Each self-consistent field calculation was iterated until a $\Delta\rho$ of less than 10^{-5} bohr^{-3} was achieved. The final equilibrium geometry at the minimum energy had a maximum gradient in internal coordinates of

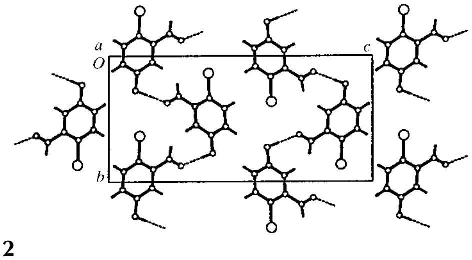


Figure 2
Projection of the crystal structure on the *bc* plane showing the hydrogen-bonding chains running along the *b* axis.

10^{-5} Hartree bohr^{-1} or 10^{-5} Hartree rad^{-1}. A similar geometry optimization was also performed using a density functional theory (DFT) hamiltonian, with similar results to the Hartree–Fock calculation. The DFT calculations were performed with the computer code *DeFT*2.2 (St-Amant *et al.*, 1998) employing a VWC exchange-correlation potential (Vosko *et al.*, 1980). Both methods reproduce well the in-plane twist of the C1—C7 bond [calculated values: C2—C1—C7 DFT 123.53°; MO–HF 123.55°, C6—C1—C7 DFT MO–HF 117.38°]. However, the minimum energy of the molecule occurs for a geometry close to C_s symmetry where all the substituent atoms are practically within the ring plane. We conclude that the observed twist of the aldehyde group around the C1—C7 bond is due to the intermolecular interaction between the aldehyde and hydroxyl groups.

The molecules are stacked in layers perpendicular to the short *a* axis. The hydroxyl and carbonyl group interact *via* a hydrogen bond [O2···O1 2.804 (4) Å] forming zigzag chains running along the *b* axis (Fig. 2). Similar chains were found in the crystal structure of 2,4,6-tribromo derivative in contrast with the situation found in the 2,4-dibromo derivative where the hydrogen bonds join pairs of molecules in dimers across a centre of symmetry. Judging by the O—H···O bond distances and angles, it appears that the strongest hydrogen bonds occur in the monobromo derivative.

Experimental

The title compound was prepared by slowly adding bromine (0.87 ml) to a solution of 3-hydroxybenzaldehyde (2.0 g) in glacial acetic acid (10 ml). After 3 h, water was added to precipitate a solid and the mixture was left overnight in the refrigerator. The solid was filtered and recrystallized in water to give 2.25 g of the title compound [η = 68%; m.p. 405–406 K, literature 406 K (Pandya *et al.*, 1952)]. MS (EI) 201 (M^+). ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6, p.p.m.): δ 10.1 (*s*, 1H, CHO), 9.7 (*s*, 1H, OH), 7.4 (*d*, 1H, *J* = 8.7 Hz, CH-aryl), 7.2 (*d*, 1H, *J* = 3.0 Hz, CH-aryl), 6.9 (*dd*, 1H, *J* = 8.7 and 3.0 Hz, CH-aryl); ^{13}C NMR (75.5 MHz, $CDCl_3$/DMSO-d_6, p.p.m.): 191.4, 157.1, 134.0, 133.3, 123.1, 115.3, 114.9; IR (KBr) cm^{-1} 3331 (*m*) (OH), 1684 (*s*, C=O), 1595, 1480 (*s*, C=C aromatic), 1305 (*s*), 1236 (*s*), 1170 (*m*, C—O), 866 (*m*), 831 (*m*), 763 (*m*), 586 (*m*) elemental analysis calculated for $C_7H_5O_2Br$: C 41.8, H 2.5%; found C 41.6, H 2.4%.

Crystal data

$C_7H_5BrO_2$
M_r = 201.01
Orthorhombic, $P2_12_12_1$
a = 3.974 (3) Å
b = 9.164 (8) Å
c = 19.172 (6) Å
V = 698.2 (8) Å^3
Z = 4
D_x = 1.912 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.51–17.13°
μ = 5.814 mm^{-1}
T = 293 (2) K
Block, light yellow
0.38 × 0.32 × 0.32 mm

Table 1
Selected geometric parameters (°).

C2—C1—C6	118.3 (3)	C3—C4—C5	120.1 (3)
C3—C2—C1	121.1 (3)	C6—C5—C4	120.0 (3)
C2—C3—C4	120.1 (3)	C5—C6—C1	120.4 (3)
C2—C1—C7—O1	−172.2 (4)	C6—C1—C7—O1	6.5 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1$^{\rm i}$	0.82	1.99	2.804 (4)	175

Symmetry code: (i) $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968) $T_{\rm min}$ = 0.126, $T_{\rm max}$ = 0.156
2879 measured reflections
762 independent reflections (plus 463 Friedel-related reflections)

925 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035
$\theta_{\rm max}$ = 24.97°
$h = 0 \rightarrow 4$
$k = -10 \rightarrow 10$
$l = -22 \rightarrow 22$
3 standard reflections frequency: 180 min intensity decay: 8.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.051$
S = 1.048
1225 reflections
92 parameters
H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.103P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max}$ = 0.38 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.014 (17)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); 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.

The authors are indebted to Dr J. C. Prata Pina for his invaluable assistance in the maintenance of the CAD-4 diffractometer. This work was supported by Fundação para a Ciência e Tecnologia (FCT) and Chymiotechnon.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1352). Services for accessing these data are described at the back of the journal.

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