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2,4-Dibromo-5-hydroxybenzaldehyde

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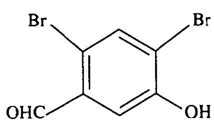
Abstract

The title compound, $C_7H_4Br_2O_2$, crystallizes as centrosymmetric dimers in which two molecules are linked by two hydrogen bonds between the hydroxyl and carbonyl groups, with an O···O distance of 2.839 (5) Å. Other intermolecular interactions are weak. There are no unusual intramolecular bond distances or angles. The atoms of the aldehyde group and the Br atoms, however, are found to deviate significantly from the plane of the benzene ring.

Comment

During the course of a research program aimed at the synthesis and structural investigation of tetrapyrrol macrocycles in order to prepare biomimetic catalysts and photodynamic therapy agents, we synthesized the title compound, (I), as a precursor for *meso*-tetraryl-substituted porphyrins.



(I)

According to a search of the April 1996 version of the Cambridge Structural Database (Allen *et al.*, 1991), this is the first reported crystal structure of a halogen-substituted hydroxybenzaldehyde. The structure of *p*-hydroxybenzaldehyde has been determined by Iwasaki (1977), but those of *m*-hydroxybenzaldehyde and *o*-hydroxybenzaldehyde have not been reported (the latter is a liquid at room temperature). Only a limited number of derivatives of hydroxybenzaldehyde have been investigated, namely those involving a methoxy substituent, *i.e.* *o*-vanillin (Iwasaki, Tanaka & Aihara, 1976), isovanillin (Iwasaki, 1973) and vanillin-I (Velavan, Sureshkumar, Sivakumar & Natarajan, 1995). The average aromatic C—C bond length is 1.386 (3) Å [1.384 (13) Å; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987] and the weighted average torsion angle of the benzene ring (Domenicano, Vaciago & Coulson, 1975) is 1.0 (4)° (Fig. 1). The ring is planar to within 0.01 Å and the length of the hydroxyl bond [1.356 (5) Å] is close to that of *p*-hydroxybenzaldehyde [1.357 (4) Å; Iwasaki, 1977], *o*-vanillin [1.354 (8) Å; Iwasaki, Tanaka & Aihara, 1976] and isovanillin [1.359 (7) Å; Iwasaki, 1973], but larger than that found in the vanillin-I molecules (1.344–1.350 Å; Velavan, Sureshkumar, Sivakumar & Natarajan, 1995). The geometry of the aldehyde group is close to that found in those compounds.

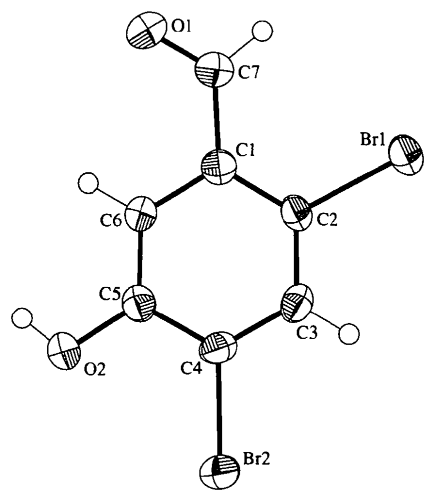


Fig. 1. View of the 2,4-dibromo-5-hydroxybenzaldehyde molecule showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

The internal bond angles of the benzene ring deviate significantly from the ideal value of 120°. The overall pattern of distortions conform qualitatively with the additive effects of the individual substituents (Domenicano, Vaciago & Coulson, 1975; Domenicano & Murray-Rust, 1979). While the hydroxyl O atom is coplanar within experimental error with the benzene ring, both Br atoms and the aldehyde group are significantly tilted out of the ring plane. The deviations from the least-squares plane are Br1 0.061 (6), Br2 −0.061 (6), C7 −0.085 (8) and O1 −0.185 (9) Å. The large deviation found for the aldehyde group can be explained as a twist around the C1—C7 bond as a result of an intermolecular interaction between this group and the hydroxyl group of a neighbouring molecule.

The strongest intermolecular interaction is the hydrogen bond between the hydroxyl and aldehyde groups (Fig. 2). This bond links two neighbouring molecules as dimers and is longer than the bond in *p*-hydroxybenzaldehyde (O2···O1 2.684 Å), where the molecules are linked forming a zigzag chain. A weaker intramolecular interaction possibly exists between the H atom of the aldehyde group and the Br1 atom [Br1···C7 3.211 (5) Å].

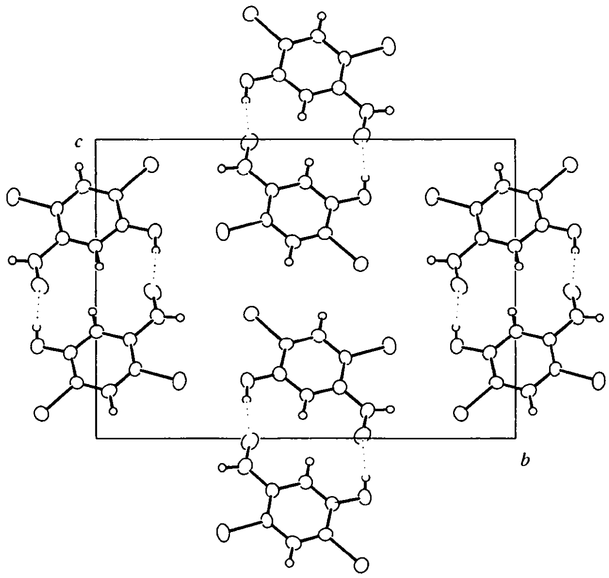


Fig. 2. Projection of the crystal structure along the shortest axis showing the hydrogen-bonding scheme.

Experimental

The title compound, (I), was synthesized by adding bromine (0.087 mol) to a suspension of 3-hydroxybenzaldehyde (0.041 mol) in 140 ml of chloroform. The mixture was stirred for 6 d at room temperature. The solvent was then evaporated and the residue recrystallized from dilute acetic acid to obtain 8.9 g of the title compound as a white crystalline solid [η = 73%; m.p. 411–412 K, literature 412 K (Hodgson & Beard, 1925)]. ^{1}H NMR (300 MHz, $CDCl_3/DMSO$-d_6): δ 10.21 (*s*, 1H, CHO), 9.58 (*s*, 1H, OH), 7.81 (*s*, 1H, aryl-CH), 7.47 (*s*, 1H, aryl-CH); ^{13}C NMR (75.5 MHz, $CDCl_3/DMSO$-d_6): δ 190.5 (CO), 153.7 (COH), 136.5 (CH—CBr), 132.3 (C—CO), 117.7 (CBr—CHO), 115.2 (CH), 114.8 (CBr); elemental analysis calculated for $C_7H_4Br_2O_2$: C 30.04, H 1.44%; found C 29.96, H 1.64%.

Crystal data

$C_7H_4Br_2O_2$	Mo $K\alpha$ radiation
M_r = 279.92	λ = 0.71073 Å
Monoclinic	Cell parameters from 25 reflections
$P2_1/n$	θ = 8.33–16.62°
a = 3.9851 (5) Å	μ = 10.337 mm^{-1}
b = 16.547 (3) Å	T = 293 (2) K
c = 11.841 (2) Å	Parallelepiped
β = 93.20 (1)°	0.15 × 0.15 × 0.10 mm
V = 779.6 (2) Å^3	Colourless
Z = 4	
D_x = 2.385 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1031 reflections with $I > 2\sigma(I)$
Profile data from ω–2θ scans	R_{int} = 0.0858
Absorption correction:	θ_{max} = 29.97°
ψ scan (North, Phillips	h = −4 → 4
& Mathews, 1968)	k = −19 → 20
T_{min} = 0.237, T_{max} = 0.356	l = −16 → 14
5148 measured reflections	3 standard reflections
1800 independent reflections	frequency: 120 min
	intensity decay: 2.7%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F)$ = 0.0279	$\Delta\rho_{max}$ = 0.479 e Å^{-3}
$wR(F^2)$ = 0.0681	$\Delta\rho_{min}$ = −0.920 e Å^{-3}
S = 1.013	Extinction correction: none
1800 reflections	Scattering factors from
101 parameters	*International Tables for*
H atoms riding	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 0.4639P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Br1—C2	1.895 (4)	O2—C5	1.356 (5)
Br2—C4	1.887 (4)	C1—C7	1.479 (6)
O1—C7	1.205 (6)		
C2—C1—C6	118.7 (4)	C3—C4—Br2	118.4 (3)
C2—C1—C7	123.2 (4)	C5—C4—Br2	119.9 (3)
C6—C1—C7	118.0 (4)	O2—C5—C6	123.6 (4)
C1—C2—C3	120.8 (4)	O2—C5—C4	118.6 (4)
C1—C2—Br1	121.7 (3)	C6—C5—C4	117.8 (4)
C3—C2—Br1	117.5 (3)	C5—C6—C1	121.8 (4)
C4—C3—C2	119.1 (3)	O1—C7—C1	122.7 (4)
C3—C4—C5	121.7 (4)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.82 (3)	2.04 (4)	2.839 (5)	166 (3)

Symmetry code: (i) $-x, 1-y, -z$.

The structure was solved by direct methods (*MULTAN*11/82; Main *et al.*, 1982). The H atoms were placed at calculated positions and refined as riding using *SHELXL*93 (Sheldrick, 1993) defaults; O—H = 0.82, C—H = 0.93 Å and U(H) = 1.5U(parent atom). Examination of the crystal structure with *PLATON*92 (Spek, 1990) showed that there were no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running the LINUX operating system.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Molecular graphics: *ORTEP*II (Jonhson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1276). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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13-Phenyl-11,13,15-triazatricyclo-[8.5.2.0^{11,15}]heptadec-16-ene-12,14-dione

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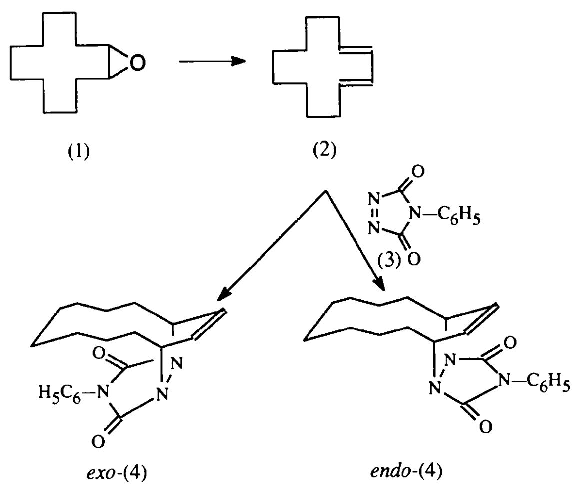
Abstract

The title compound, $C_{20}H_{25}N_3O_2$, has been assigned an *endo* structure on the basis of its X-ray analysis. In the *N*-phenyl-1,2,4-triazoline-3,5-dione moiety, the N—N and average C—O bond distances have values of 1.424 (3) and 1.208 (2) Å, respectively. The closest intermolecular contact of 3.306 (4) Å is between a phenyl C atom and an O atom of the 1,2,4-triazoline-3,5-dione moiety.

Comment

The Diels–Alder reaction of 1,3-cyclooctadiene with *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) results in a cyclo-adduct with an almost planar hydrazine moiety (Brock, Demir & Watt, 1995). The molecule is one of the most planar of the 1,3-diene adducts of PTAD found in version 5.07 of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). The dihedral angle between the triazoline ring and the bridging moiety increases with increasing length of the bridge (Agmon, Kaftory, Nelson & Blakstock, 1986). By a conversion reaction of epoxide to 1,3-diene, we obtained a 1,3-cyclododecadiene. The Diels–Alder adduct with *N*-phenyl-1,2,4-triazoline-3,5-dione was identified as the title compound, but it was impossible to identify the structure as *endo* or *exo* on the basis of ^1H and ^{13}C NMR spectral data. The present X-ray crystal structure determination resolved this ambiguity and showed it to be the *endo* product, *i.e.* *endo*-(4).



In the cyclododecene part of the molecule, there is only one C=C double bond, namely, C10=C11; all the other C—C bond lengths have values in the single-bond range, with C9—C10 and C11—C12 being C_{sp^2}—C_{sp^3} bonds, while the rest are C_{sp^3}—C_{sp^3} (Table 1). The C12—N2 and C9—N3 bonds are C_{sp^3}—N_{sp^3}, and are longer than the other C—N bonds. The dihedral angle between the phenyl and triazoline-3,5-dione rings is 57.8 (1)°. The ring N3—C9—C10—C11—C12—N2 is in a boat conformation, with the C9 and C12 atoms −0.378 (3) and −0.607 (3) Å, respectively, from the least-squares plane through atoms N2, N3, C10 and C11.