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5,5′-Dibromo-2,2′-dihydroxy-3,3′-(piperazine-1,4-diyldimethylene)dibenzaldehyde

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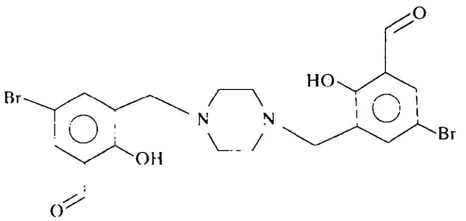
Abstract

The title molecule ($C_{20}H_{20}Br_2N_2O_4$) has crystallographic inversion symmetry. The piperazine ring adopts a chair conformation with the substituents at the N atoms lying in equatorial positions. The N atoms exhibit pyramidal coordination.

Comment

Synthetic binuclear ligands are capable of securing two metal ions in close proximity. There are many enzymes in which a bimetallic centre occurs (Fenton *et al.*, 1982). The role of the metals presented may be active or passive (structural), but as yet there is only limited X-ray structural information on these sites. The area of binuclear complexation has seen extensive growth, stimulated by interest in areas such as metalloenzymes, homogeneous catalysis and magnetic exchange processes (Kurtz, 1990). A number of facially-capping sterically-demanding ligands capable of generating mono- and multinuclear metal complexes have been synthesized and reported (Gunasekaran *et al.*, 1994, 1996).

Since the properties of binuclear complexes are controlled by the structure and stereochemistry of their ligands, we have structurally characterized the title ligand, (I). The asymmetric unit contains one half of the molecule and the other half is related by a centre of inversion (Fig. 1). The bond lengths and angles observed in the structure agree with those values reported in the literature (Domenicano *et al.*, 1975; Allen *et al.*, 1987). The bond angles around the N atom are indicative of sp^3 hybridization (Perales *et al.*, 1977). The piperazine ring adopts a chair conformation (Dupont *et al.*, 1992; Raves *et al.*, 1992). The plane through the C atoms of the piperazine ring makes a dihedral angle of 58.6 (1)° with the phenyl ring. An O—H···N intramolecular hydrogen bond is observed between the O2 and N atoms [O2—H1O2 0.78 (4), O2···N 2.608 (4), H1O2···N 1.89 (4) Å and O2—H1O2···N 153 (4)°]. The crystal structure is stabilized by van der Waals interactions.



(I)

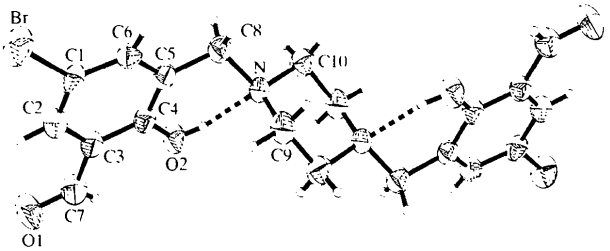


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

A mixture of piperazine (4.3 g, 0.05 mol), paraformaldehyde (3.3 g, 0.11 mol) and 3-bromo-6-hydroxybenzaldehyde (19.2 g, 0.1 mol) in ethanol/acetic acid (200 ml, 80:20 *v*/*v*) was stirred for 6 h at 323 K. This 1:2:2 mixture was subjected to Mannich base condensation to yield the title compound. The whole mixture was then neutralized using saturated aqueous Na_2CO_3 solution and the product was extracted using chloroform. The crude sample was purified on a silica-gel column using an *n*-hexane/chloroform solvent mixture (30:70 *v*/*v*) as the eluent. The title compound (m.p. 438 K) was crystallized by slow evaporation of an ethanol solution.

Crystal data

$C_{20}H_{20}Br_2N_2O_4$
$M_r = 512.20$
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

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Monoclinic
$P2_1/c$
$a = 8.825\,(2)$ Å
$b = 16.518\,(2)$ Å
$c = 7.368\,(2)$ Å
$\beta = 111.39\,(2)^\circ$
$V = 1000.1\,(4)$ Å^3
$Z = 2$
$D_x = 1.701$ Mg m^{-3}
D_m not measured

Cell parameters from 34 reflections
$\theta = 5.24$–12.55°
$\mu = 4.082$ mm^{-1}
$T = 293\,(2)$ K
Rectangular block
$0.48 \times 0.20 \times 0.18$ mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical ψ scans (Siemens, 1994)
$T_{\min} = 0.37$, $T_{\max} = 0.48$
3016 measured reflections
2304 independent reflections
1458 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 27.50^\circ$
$h = -11 \rightarrow 11$
$k = -21 \rightarrow 1$
$l = -1 \rightarrow 9$
3 standard reflections every 97 reflections intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.098$
$S = 0.935$
2303 reflections
167 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.293$ e Å^{-3}
$\Delta\rho_{\min} = -0.426$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Br—C1	1.895 (3)	O2—C4	1.353 (3)
N—C9	1.458 (4)	C1—C2	1.358 (4)
N—C10	1.471 (4)	C3—C7	1.467 (4)
N—C8	1.473 (3)	C9—C10ⁱ	1.497 (4)
O1—C7	1.195 (4)		
C9—N—C10	109.7 (2)	C10—N—C8	111.8 (2)
C9—N—C8	112.4 (3)	O1—C7—C3	125.4 (3)

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

Program used for data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1994); for structure solution and molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); for structure refinement: *SHELXL*93 (Sheldrick, 1993); for geometrical calculations: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1222). Services for accessing these data are described at the back of the journal.

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5-Amino-2,4-diphenyl-7-(pyrrolidin-1-yl)-1,6-naphthyridine-8-carbonitrile

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Abstract

In the title molecule, $C_{25}H_{21}N_5$, the naphthyridine ring system is almost planar. The phenyl-ring planes form dihedral angles of 28.00(5) and 84.80(5)° with the attached ring. Conformational disorder is observed in the pyrrolidine ring and both conformers adopt half-chair conformations. In the solid state, the molecules are linked to form centrosymmetrically-related hydrogen-bonded dimers.

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