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4,4′-Dibromo-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol

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Key indicators

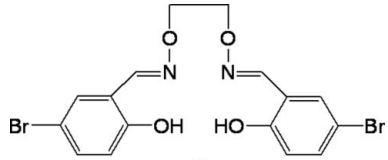
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.030
wR factor = 0.083
Data-to-parameter ratio = 14.0

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

The title compound, $C_{16}H_{14}Br_2N_2O_4$, has been synthesized by the reaction of 1,2-bis(aminooxy)ethane with 5-bromo-2-hydroxybenzaldehyde in ethanol. The molecule is centrosymmetric. Intramolecular O—H···N hydrogen bonding is observed between hydroxy groups and oxime N atoms.

Comment

(*N*,*N*′-Disalicylideneethylenediamine) (salen) and its analogues are versatile chelating ligands in inorganic chemistry with metal complexes used as catalysts in organic reactions (Katsuki, 1995), non-linear optical materials (Lacroix, 2001), or with interesting magnetic properties (Costes *et al.*, 2000). Although most complexes containing salen ligands are stable in solution and in the solid state, C=N bonds can undergo exchange reactions (Koehler *et al.*, 1964) as well as hydrolysis (Cordes & Jencks, 1962). Reversible C=N bond formation (Rowan *et al.*, 2002) is sometimes useful for the synthesis of thermodynamically stable macrocyclic (Akine *et al.*, 2004) and interlocked compounds (Cantrill *et al.*, 1999) in high yields. In some cases, a macrocyclic imine is formed *via* C=N bond recombination of an acyclic diamine (Houjou *et al.*, 2001). Rate constants of oxime formation are smaller than those of imine formation and the equilibrium constants are larger by several orders of magnitude (Korpela & Makela, 1981). Hence, oxime-type ligands should be stable enough to resist metathesis of the C=N bonds. To explore this, we have synthesized a new series of salen-type chelating ligands, based on *O*-alkyl oxime instead of the imine group. Linear derivatives bearing two salicylaldoxime units at both ends have been reported in preliminary studies (van Veggel *et al.*, 1989; Akine *et al.*, 2006) and in this paper, we report the structure of the new oxime-type chelating ligand 4,4′-dibromo-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol, (I).



(I)

The structure of (I) is shown in Fig. 1. The molecule is centrosymmetric. For comparison, the parent 1,2-bis(salicylideneaminooxy)ethane crystallizes in the triclinic system, with two crystallographically independent molecules in the unit cell (Akine *et al.*, 2005). An intramolecular O—H···N hydrogen bond is observed between the hydroxy group and the oxime N atom.

Generally, salicylaldimine derivatives exist as a mixture of two tautomers, *viz*. the imine-OH and keto-NH forms. The present results indicate that the oxime-OH form is more favorable in the crystalline state of (I).

Experimental

To an ethanol solution (10 ml) of 5-bromo-2-hydroxybenzaldehyde (201.0 mg, 1.00 mmol) was added an ethanol solution (5 ml) of 1,2-bis(aminooxy)ethane (46.1 mg, 0.50 mmol). After the solution had been stirred at 328 K for 3 h, the mixture was filtered and washed successively with ethanol and hexane. The product was dried under reduced pressure and purified by recrystallization from ethanol to yield 179.12 mg of a colorless crystalline solid (yield 78.2%; m.p. 417.5–418.5 K). Analysis calculated for $C_{16}H_{14}Br_2N_2O_4$: C 41.95, H 3.08, N 6.125%; found: C 41.78, H 3.04, N 6.065%. Single crystals suitable for X-ray diffraction studies were obtained after several weeks by slow evaporation of an acetone solution.

Crystal data

$C_{16}H_{14}Br_2N_2O_4$
M_r = 458.12
Monoclinic, $P2_1/c$
a = 19.249 (3) Å
b = 5.7607 (8) Å
c = 7.6200 (10) Å
β = 96.312 (2)°
V = 839.82 (19) Å^3
Z = 2
D_x = 1.812 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 4.85 mm^{-1}
T = 293 (2) K
Block, colorless
0.37 × 0.27 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
T_{min} = 0.266, T_{max} = 0.596
(expected range = 0.250–0.559)
4208 measured reflections
1544 independent reflections
1297 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 25.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.05
1544 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.2088P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N	0.82	1.94	2.658 (3)	146

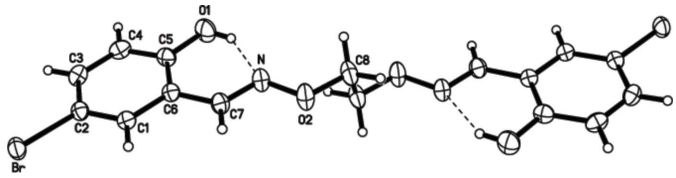


Figure 1
The molecular structure of (I) with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Unlabeled atoms are related to labeled atoms by (−x, 1 − y, 1 − z). Dashed lines indicate hydrogen bonds.

H atoms were treated as riding atoms, with C—H = 0.97 (CH_2) or 0.93 Å (CH), O—H = 0.82 Å and U_{iso}(H) = 1.2U_{eq}(C) or 1.5 U_{eq}(O).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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