

2,2'-[1,1'-(Propane-1,3-diylidioxy-dinitrilo)diethylidyne]diphenol

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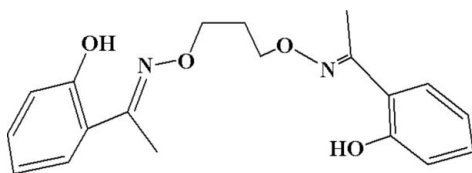
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.053; wR factor = 0.163; data-to-parameter ratio = 7.7.

The title compound, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$, was synthesized by the reaction of 2'-hydroxyacetophenone with 1,3-bis(aminooxy)propane in ethanol. Intramolecular $\text{O}-\text{H}\cdots\text{N}$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds stabilize the three-dimensional structure. A twofold rotation axis passes through the molecule.

Related literature

For related literature, see: Atkins *et al.* (1985); Atwood (1997); Costes *et al.* (2000); Dong & Feng (2006); Dong *et al.* (2006*a,b*, 2007*a,b,c,d*); Duan *et al.* (2007); Katsuki (1995); Lacroix (2001); Venkataramanan *et al.* (2005); Yu *et al.* (2008); Zhang *et al.* (2007).



Experimental

Crystal data

$\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$ $V = 872.4$ (2) Å³
 $M_r = 342.39$ $Z = 2$
 Orthorhombic, $Pba2$ Mo $K\alpha$ radiation
 $a = 7.4595$ (15) Å $\mu = 0.09$ mm⁻¹
 $b = 25.459$ (2) Å $T = 298$ (2) K
 $c = 4.5938$ (8) Å $0.40 \times 0.19 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer 3761 measured reflections
 Absorption correction: multi-scan 880 independent reflections
 (SADABS; Sheldrick, 1996) 601 reflections with $I > 2\sigma(I)$
 $T_{\min} = 0.964$, $T_{\max} = 0.985$ $R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$ 1 restraint
 $wR(F^2) = 0.162$ H-atom parameters constrained
 $S = 1.12$ $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 880 reflections $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³
 114 parameters

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{N1}$	0.82	1.85	2.570 (5)	146
$\text{C3}-\text{H3A}\cdots\text{O1}$	0.96	2.17	2.603 (6)	106

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2386).

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Acta Cryst. (2008). E64, o1098 [doi:10.1107/S1600536808012701]

2,2'-[1,1'-(Propane-1,3-diyl)dioxydinitrilo]diethylidyne]diphenol

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Comment

Salen-type compounds have been intensively used as versatile chelating ligands in the formation of transition metal complexes (Yu *et al.*, 2008). Some of them or their metal complexes are used in various organic reaction processes as catalysts (Venkataramanan *et al.*, 2005), models of reaction centers of metalloenzymes (Katsuki *et al.*, 1995), have fascinating magnetic properties (Costes *et al.*, 2000) and are nonlinear optical materials (Lacroix *et al.*, 2001). They can also be used as biological models in understanding the structure of biomolecules and biological processes (Atkins *et al.*, 1985, Atwood *et al.*, 1997). Most of their important features of these compounds are their preparative accessibility, diversity and structural variability, which make them more attractive.

In recent years, we have been very much interested in the synthesis and study of salen-type bisoxime derivatives, such as 2,2'-[(1,4-butylene)dioxybis(nitrilomethylidyne)]dinaphthol (Dong *et al.*, 2006a), 4,4'-dibromo-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (Dong & Feng, 2006), 4,4'-dibromo-2,2'-[(1,3-propylene)dioxybis(nitrilomethylidyne)]diphenol (Dong *et al.*, 2006b), 2,2'-[(1,4-butylene)dioxybis(nitrilomethylidyne)]diphenol (Dong *et al.*, 2007a), 4,4'-dichloro-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidyne)]diphenol (Dong *et al.*, 2007b), 4,4',6,6'-tetra(*tert*-butyl)-2,2'-[(1,4-butylene)dioxybis(nitrilomethylidyne)]diphenol (Dong *et al.*, 2007c), 2,2'-[(1,4-butylene)dioxybis(nitriloethylidyne)]diphenol (Dong *et al.*, 2007d), 2,2'-[(propane-1,3-diyl)dioxy]bis(nitrilomethylidyne)]diphenol (Duan *et al.*, 2007), and 5,5'-bis(diethylamino)-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (Zhang *et al.*, 2007). In this paper, a novel bisoxime ligand, 2,2'-[(propane-1,3-diyl)dioxy]bis(nitriloethylidyne)]diphenol (I) was designed and synthesized, and shown in Fig. 1.

The single-crystal structure of (I) is built up by discrete $C_{19}H_{22}N_2O_4$ molecules (Fig. 1), in which all bond lengths are in normal ranges. There is a crystallographic twofold rotation axis passing through the middle point (symmetry code: $-x, -y, z$) of the C—C—C unit. The molecule adopts a trans conformation in which two phenoldoxime moieties adopt an extended form, where the oxime, methyl groups and phenolic alcohols lie in trans positions relative to the C2 atom in the N—O—CH₂—CH₂—CH₂—O—N linkage, which is similar to what is observed in our previously reported salen-type bisoxime of 2,2'-[(propane-1,3-diyl)dioxy]bis(nitrilomethylidyne)]diphenol (Duan *et al.*, 2007). There is an intramolecular O—H...N hydrogen bond between the N1 atom and the hydroxy proton (Table 1) generating a six membered ring, which with weak C—H...O intermolecular hydrogen bonds, stabilizes the three-dimensional structure of (I).

Experimental

2,2'-[(Propane-1,3-diyl)dioxy]bis(nitriloethylidyne)]diphenol was synthesized according to an analogous method reported earlier (Dong *et al.*, 2007d). To an ethanol solution (5 ml) of 2'-hydroxyacetophenone (280.9 mg, 2.01 mmol) was added an ethanol (3 ml) solution of 1,3-bis(aminoxy)propane (105.5 mg, 1.00 mmol). The mixture solution was stirred at 328 K for 3 h. After cool to room temperature, the precipitate was formed, which was filtered, and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum and to yield 64.90 mg of the title compound.

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Yield, 19.1%. mp. 363–363.5 K. Anal. Calc. for $C_{19}H_{22}N_2O_4$: C, 66.65; H, 6.48; N, 8.18. Found: C, 66.76; H, 6.39; N, 7.97. Colorless needle-shaped single crystals suitable for X-ray diffraction studies were obtained after three months by slow evaporation from an ethanol solution (10 ml) of 2,2'-[(propane-1,3-diylldioxy)bis(nitriloethylidyne)]diphenol.

Refinement

H atoms were treated as riding atoms with distances C—H = 0.97 (CH₂), or 0.93 Å (CH), O—H = 0.82 Å, and $U_{iso}(H) = 1.2 U_{eq}(C)$ and $1.5 U_{eq}(O)$. The hydroxyl protons were located directly from a Fourier map.

Figures

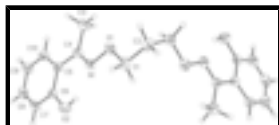


Fig. 1. Molecule structure of (I) possessing a crystallographic twofold rotation axis passing through the middle point of the C—C—C unit (symmetry code: $-x+1, -y, z$), Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

2,2'-[1,1'-(Propane-1,3-diylldioxydinitrilo)diethylidyne]diphenol

Crystal data

$C_{19}H_{22}N_2O_4$

$M_r = 342.39$

Orthorhombic, *Pba*2

Hall symbol: P 2 -2ab

$a = 7.4595$ (15) Å

$b = 25.459$ (2) Å

$c = 4.5938$ (8) Å

$V = 872.4$ (2) Å³

$Z = 2$

$F_{000} = 364$

$D_x = 1.303$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1047 reflections

$\theta = 2.4$ – 22.9°

$\mu = 0.09$ mm⁻¹

$T = 298$ (2) K

Needle-shaped, colorless

$0.40 \times 0.19 \times 0.17$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{min} = 0.964$, $T_{max} = 0.985$

3761 measured reflections

880 independent reflections

601 reflections with $I > 2\sigma(I)$

$R_{int} = 0.080$

$\theta_{max} = 25.0^\circ$

$\theta_{min} = 1.6^\circ$

$h = -8 \rightarrow 4$

$k = -30 \rightarrow 28$

$l = -5 \rightarrow 5$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.052$$

$$wR(F^2) = 0.162$$

$$S = 1.12$$

880 reflections

114 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.09P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.7665 (5)	0.07883 (13)	0.2794 (9)	0.0424 (10)	
O1	0.6235 (4)	0.06405 (11)	0.0997 (8)	0.0497 (10)	
O2	1.0675 (4)	0.06514 (11)	0.5410 (10)	0.0613 (12)	
H2	0.9857	0.0579	0.4284	0.092*	
C1	0.6621 (6)	0.01443 (16)	-0.0329 (12)	0.0447 (13)	
H1A	0.6845	-0.0120	0.1148	0.054*	
H1B	0.7671	0.0171	-0.1564	0.054*	
C2	0.5000	0.0000	-0.2107 (16)	0.0479 (18)	
H2A	0.5305	-0.0294	-0.3353	0.058*	0.50
H2B	0.4695	0.0294	-0.3353	0.058*	0.50
C3	0.5696 (7)	0.15361 (18)	0.3585 (17)	0.0660 (17)	
H3A	0.5088	0.1406	0.1891	0.099*	
H3B	0.5989	0.1900	0.3308	0.099*	
H3C	0.4931	0.1500	0.5254	0.099*	
C4	0.7390 (6)	0.12265 (17)	0.4060 (10)	0.0406 (12)	
C5	0.8802 (6)	0.14197 (16)	0.5999 (11)	0.0380 (11)	
C6	1.0350 (6)	0.11254 (15)	0.6663 (11)	0.0396 (12)	
C7	1.1585 (6)	0.1310 (2)	0.8622 (13)	0.0540 (15)	
H7	1.2586	0.1107	0.9065	0.065*	
C8	1.1363 (6)	0.1787 (2)	0.9934 (16)	0.0582 (15)	
H8	1.2207	0.1908	1.1263	0.070*	

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C9	0.9884 (8)	0.2086 (2)	0.9277 (16)	0.0649 (18)
H9	0.9733	0.2414	1.0135	0.078*
C10	0.8645 (7)	0.19013 (18)	0.7369 (13)	0.0521 (15)
H10	0.7646	0.2108	0.6966	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.038 (2)	0.047 (2)	0.043 (2)	-0.0020 (17)	-0.005 (2)	0.002 (2)
O1	0.0458 (18)	0.0516 (19)	0.052 (2)	-0.0039 (14)	-0.0123 (19)	-0.0063 (18)
O2	0.053 (2)	0.054 (2)	0.077 (3)	0.0138 (15)	-0.018 (2)	-0.0045 (19)
C1	0.048 (3)	0.041 (2)	0.045 (3)	-0.004 (2)	0.005 (3)	-0.001 (2)
C2	0.068 (5)	0.046 (3)	0.030 (4)	-0.007 (3)	0.000	0.000
C3	0.051 (3)	0.060 (3)	0.087 (5)	0.009 (2)	-0.021 (4)	-0.015 (3)
C4	0.038 (2)	0.042 (2)	0.042 (3)	0.000 (2)	-0.005 (2)	0.004 (2)
C5	0.035 (2)	0.045 (2)	0.034 (3)	-0.001 (2)	-0.001 (2)	0.004 (2)
C6	0.035 (2)	0.042 (2)	0.042 (3)	-0.002 (2)	-0.002 (2)	0.010 (2)
C7	0.036 (3)	0.066 (3)	0.060 (4)	0.002 (2)	-0.015 (3)	0.009 (3)
C8	0.046 (3)	0.072 (3)	0.057 (4)	-0.015 (3)	-0.011 (3)	-0.001 (3)
C9	0.057 (3)	0.056 (3)	0.082 (5)	-0.003 (3)	-0.017 (4)	-0.016 (3)
C10	0.043 (3)	0.056 (3)	0.057 (4)	0.006 (2)	-0.004 (3)	0.003 (3)

Geometric parameters (\AA , $^\circ$)

N1—C4	1.275 (5)	C3—H3B	0.9600
N1—O1	1.400 (5)	C3—H3C	0.9600
O1—C1	1.432 (5)	C4—C5	1.464 (6)
O2—C6	1.359 (5)	C5—C10	1.383 (6)
O2—H2	0.8200	C5—C6	1.410 (6)
C1—C2	1.505 (6)	C6—C7	1.370 (7)
C1—H1A	0.9700	C7—C8	1.366 (7)
C1—H1B	0.9700	C7—H7	0.9300
C2—C1 ⁱ	1.505 (6)	C8—C9	1.374 (7)
C2—H2A	0.9700	C8—H8	0.9300
C2—H2B	0.9700	C9—C10	1.358 (8)
C3—C4	1.505 (6)	C9—H9	0.9300
C3—H3A	0.9600	C10—H10	0.9300
C4—N1—O1	112.4 (3)	N1—C4—C5	117.1 (4)
N1—O1—C1	109.5 (3)	N1—C4—C3	121.8 (4)
C6—O2—H2	109.5	C5—C4—C3	121.1 (4)
O1—C1—C2	106.5 (3)	C10—C5—C6	116.2 (4)
O1—C1—H1A	110.4	C10—C5—C4	120.9 (4)
C2—C1—H1A	110.4	C6—C5—C4	122.8 (4)
O1—C1—H1B	110.4	O2—C6—C7	117.6 (4)
C2—C1—H1B	110.4	O2—C6—C5	121.7 (4)
H1A—C1—H1B	108.6	C7—C6—C5	120.7 (4)
C1—C2—C1 ⁱ	114.3 (6)	C8—C7—C6	120.8 (5)
C1—C2—H2A	108.7	C8—C7—H7	119.6

C1 ⁱ —C2—H2A	108.7	C6—C7—H7	119.6
C1—C2—H2B	108.7	C7—C8—C9	119.6 (5)
C1 ⁱ —C2—H2B	108.7	C7—C8—H8	120.2
H2A—C2—H2B	107.6	C9—C8—H8	120.2
C4—C3—H3A	109.5	C10—C9—C8	119.7 (5)
C4—C3—H3B	109.5	C10—C9—H9	120.1
H3A—C3—H3B	109.5	C8—C9—H9	120.1
C4—C3—H3C	109.5	C9—C10—C5	122.9 (5)
H3A—C3—H3C	109.5	C9—C10—H10	118.5
H3B—C3—H3C	109.5	C5—C10—H10	118.5
C4—N1—O1—C1	-179.4 (4)	C4—C5—C6—O2	3.6 (7)
N1—O1—C1—C2	177.5 (4)	C10—C5—C6—C7	1.7 (7)
O1—C1—C2—C1 ⁱ	-70.3 (3)	C4—C5—C6—C7	-176.2 (4)
O1—N1—C4—C5	180.0 (3)	O2—C6—C7—C8	178.9 (5)
O1—N1—C4—C3	-0.3 (7)	C5—C6—C7—C8	-1.3 (8)
N1—C4—C5—C10	177.4 (5)	C6—C7—C8—C9	-0.1 (9)
C3—C4—C5—C10	-2.3 (7)	C7—C8—C9—C10	1.1 (10)
N1—C4—C5—C6	-4.9 (6)	C8—C9—C10—C5	-0.7 (9)
C3—C4—C5—C6	175.4 (5)	C6—C5—C10—C9	-0.7 (8)
C10—C5—C6—O2	-178.6 (4)	C4—C5—C10—C9	177.2 (5)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots N1	0.82	1.85	2.570 (5)	146
C3—H3A \cdots O1	0.96	2.17	2.603 (6)	106

Fig. 1

