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3,3'-Dibromo-1,1'-[ethylenedioxy-bis(nitrilomethylidene)]dibenzene

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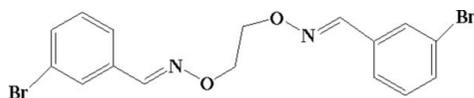
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.037; wR factor = 0.098; data-to-parameter ratio = 14.0.

In the centrosymmetric title compound, $\text{C}_{16}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2$, the intramolecular interplanar distance between the parallel benzene rings is 1.305 (3) Å, while the intermolecular interplanar distance (between neighbouring molecules) is 3.463 (3) Å, exhibiting obvious strong intermolecular $\pi-\pi$ stacking interactions.

Related literature

For related literature, see: Akine *et al.* (2006); Atwood & Harvey (2001); Dong & Duan (2008); Dong *et al.* (2007); Dong, Duan *et al.* (2008); Dong, Shi *et al.* (2008); Katsuki (1995); Sun *et al.* (2004).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_2$
 $M_r = 426.11$
 Monoclinic, $P2_1/n$

$a = 4.5072$ (7) Å
 $b = 7.615$ (2) Å
 $c = 23.180$ (3) Å

$\beta = 93.523$ (2)°
 $V = 794.1$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 5.11$ mm⁻¹
 $T = 298$ (2) K
 $0.42 \times 0.27 \times 0.15$ mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.223$, $T_{\max} = 0.514$
 (expected range = 0.201–0.464)

3840 measured reflections
 1400 independent reflections
 1168 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.097$
 $S = 1.04$
 1400 reflections

100 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

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: WW2122).

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supporting information

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3,3'-Dibromo-1,1'-[ethylenedioxybis(nitrilomethylidyne)]dibenzene

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S1. Comment

Schiff base compounds have played an important role in the development of coordination chemistry as they can readily form stable complexes with most metal ions (Dong & Duan, 2008; Dong, Duan *et al.*, 2008; Dong, Shi *et al.*, 2008; Atwood & Harvey, 2001). These complexes are very interesting in many fields, such as catalysis and enzymatic reactions (Akine *et al.*, 2006), magnetism and molecular architectures (Sun *et al.*, 2004; Katsuki, 1995). However, to the best of our knowledge, the complexes derived from the Schiff base 3,3'-dibromo-1,1'-[ethylenedioxybis(nitriloethylidyne)]dibenzene have never been reported so far. Information on the structure of the Schiff base compound will help us understand the interactions in the molecule so as to further design and synthesize complexes derived from this ligand. As a further investigation on such compounds, we report herein the synthesis and crystal structure of the Schiff base bisoxime compound 3,3'-dibromo-1,1'-[ethylenedioxybis(nitriloethylidyne)]dibenzene, shown in Fig. 1.

The X-ray crystallography reveals the title compound crystallizes in the monoclinic system, space group P2(1)/n with $a = 4.5072(7)$ Å, $b = 7.615(2)$ Å, $c = 23.180(3)$ Å, $\beta = 93.523(2)^\circ$ and $Z = 2$. The structure of the title compound consists of discrete $C_{16}H_{14}Br_2N_2O_2$ molecules in which all bond lengths are in normal ranges.

The molecule is disposed about a crystallographic centre of symmetry at the mid-point of the (CH₂—CH₂) linkage adopting an anti-symmetrized conformation in which two benzaldoxime moieties adopt an extended form. Both intra- and inter-molecular hydrogen bonds are not observed in the title compound. The intramolecular plane-to-plane distance of the benzene rings was found to be 1.305 Å, while that of the intermolecular plane-to-plane distance (between neighbouring molecules) was found to be 3.463(3) Å, exhibiting obvious strong intermolecular π - π stacking interactions.

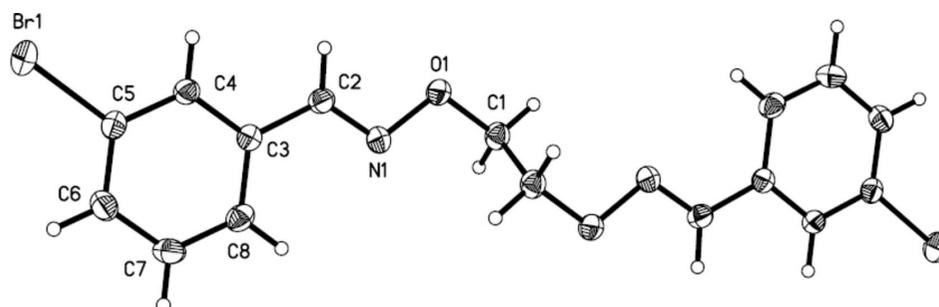
S2. Experimental

3,3'-Dibromo-1,1'-[ethylenedioxybis(nitriloethylidyne)]dibenzene was synthesized according to our previous work (Dong *et al.*, 2007). To an ethanol solution (3 ml) of 3-bromo-benzaldehyde (398.7 mg, 2.15 mmol) was added dropwise an ethanol solution (2 ml) of 1,2-bis(aminoxy)ethane (96.2 mg, 1.04 mmol). The mixture solution was stirred at 328 K for 4 h. After cooling to room temperature, the precipitate was filtered off, and washed successively with ethanol and ethanol-hexane mixture (1:4), respectively. The product was dried *in vacuo* to yield 366.0 mg (Yield, 82.3%) of colorless microcrystals; m.p. 363.5 - 365.5 K. Anal. Calcd. for $C_{16}H_{14}Br_2N_2O_2$: C, 45.10; H, 3.31; N, 6.57. Found: C, 45.01; H, 3.20; N, 6.43%.

Single crystals were obtained by slow evaporation from a ethanol-acetone mixed solution of the title compound at room temperature.

S3. Refinement

Non-H atoms were refined anisotropically. H atoms were treated as riding atoms with distances C—H = 0.97 (CH₂), 0.93 Å (CH), and $U_{iso}(H) = 1.2 U_{eq}(C)$.

**Figure 1**

The molecular structure of the title compound with atom numbering scheme [Symmetry codes: $-x - 1, -y, -z$]. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level.

3,3'-Dibromo-1,1'-[ethylenedioxybis(nitrilomethylidyne)]dibenzene

Crystal data

$C_{16}H_{14}Br_2N_2O_2$

$M_r = 426.11$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2yn$

$a = 4.5072$ (7) Å

$b = 7.615$ (2) Å

$c = 23.180$ (3) Å

$\beta = 93.523$ (2)°

$V = 794.1$ (3) Å³

$Z = 2$

$F(000) = 420$

$D_x = 1.782$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2000 reflections

$\theta = 2.6$ – 26.7 °

$\mu = 5.11$ mm⁻¹

$T = 298$ K

Needle-shaped, colorless

$0.42 \times 0.27 \times 0.15$ mm

Data collection

Siemens SMART 1000 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.223$, $T_{\max} = 0.514$

3840 measured reflections

1400 independent reflections

1168 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.043$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 1.8$ °

$h = -5 \rightarrow 5$

$k = -8 \rightarrow 9$

$l = -19 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.097$

$S = 1.04$

1400 reflections

100 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.3108P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.28$ e Å⁻³

$\Delta\rho_{\min} = -0.49$ e Å⁻³

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.56056 (10)	0.86904 (5)	0.160074 (19)	0.0576 (2)
N1	-0.2668 (6)	0.2442 (4)	0.05861 (13)	0.0381 (7)
O1	-0.4716 (6)	0.2385 (3)	0.00969 (11)	0.0422 (6)
C1	-0.6114 (8)	0.0710 (5)	0.00676 (17)	0.0396 (8)
H1A	-0.7723	0.0722	-0.0230	0.048*
H1B	-0.6952	0.0452	0.0434	0.048*
C2	-0.1591 (8)	0.3960 (4)	0.06447 (16)	0.0373 (8)
H2	-0.2198	0.4837	0.0384	0.045*
C3	0.0595 (7)	0.4362 (4)	0.11157 (15)	0.0324 (8)
C4	0.1868 (8)	0.6001 (4)	0.11401 (15)	0.0350 (8)
H4	0.1337	0.6827	0.0857	0.042*
C5	0.3929 (8)	0.6427 (4)	0.15821 (16)	0.0369 (8)
C6	0.4796 (9)	0.5227 (5)	0.19990 (16)	0.0449 (9)
H6	0.6198	0.5523	0.2294	0.054*
C7	0.3545 (9)	0.3565 (5)	0.19728 (18)	0.0485 (10)
H7	0.4098	0.2741	0.2256	0.058*
C8	0.1504 (9)	0.3121 (5)	0.15356 (16)	0.0412 (9)
H8	0.0719	0.1992	0.1517	0.049*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0701 (4)	0.0416 (3)	0.0597 (3)	-0.0158 (2)	-0.0076 (2)	-0.00700 (18)
N1	0.0374 (16)	0.0381 (17)	0.0381 (18)	-0.0031 (13)	-0.0038 (13)	-0.0018 (13)
O1	0.0438 (14)	0.0346 (13)	0.0468 (15)	-0.0078 (11)	-0.0083 (12)	0.0016 (11)
C1	0.037 (2)	0.0389 (19)	0.043 (2)	-0.0032 (16)	-0.0004 (16)	-0.0033 (16)
C2	0.0387 (19)	0.0329 (19)	0.040 (2)	0.0004 (15)	0.0022 (16)	0.0032 (15)
C3	0.0310 (18)	0.0343 (18)	0.0323 (19)	0.0008 (14)	0.0061 (14)	-0.0021 (14)
C4	0.039 (2)	0.0322 (18)	0.0337 (19)	0.0024 (15)	0.0026 (15)	-0.0001 (14)
C5	0.038 (2)	0.0344 (19)	0.038 (2)	-0.0041 (15)	0.0036 (16)	-0.0037 (15)
C6	0.047 (2)	0.049 (2)	0.037 (2)	0.0008 (18)	-0.0054 (18)	-0.0027 (17)
C7	0.052 (2)	0.046 (2)	0.047 (2)	0.0059 (19)	-0.0024 (19)	0.0120 (18)
C8	0.048 (2)	0.0334 (19)	0.043 (2)	-0.0055 (17)	0.0102 (18)	0.0027 (16)

Geometric parameters (Å, °)

Br1—C5	1.881 (3)	C3—C8	1.399 (5)
N1—C2	1.258 (4)	C4—C5	1.379 (5)
N1—O1	1.418 (4)	C4—H4	0.9300
O1—C1	1.423 (4)	C5—C6	1.369 (5)
C1—C1 ⁱ	1.521 (7)	C6—C7	1.386 (5)
C1—H1A	0.9700	C6—H6	0.9300
C1—H1B	0.9700	C7—C8	1.368 (5)
C2—C3	1.457 (5)	C7—H7	0.9300
C2—H2	0.9300	C8—H8	0.9300
C3—C4	1.373 (5)		
C2—N1—O1	110.0 (3)	C3—C4—H4	119.8
N1—O1—C1	109.3 (3)	C5—C4—H4	119.8
O1—C1—C1 ⁱ	110.5 (4)	C6—C5—C4	121.1 (3)
O1—C1—H1A	109.5	C6—C5—Br1	119.9 (3)
C1 ⁱ —C1—H1A	109.5	C4—C5—Br1	119.0 (3)
O1—C1—H1B	109.5	C5—C6—C7	118.8 (3)
C1 ⁱ —C1—H1B	109.5	C5—C6—H6	120.6
H1A—C1—H1B	108.1	C7—C6—H6	120.6
N1—C2—C3	120.8 (3)	C8—C7—C6	120.7 (4)
N1—C2—H2	119.6	C8—C7—H7	119.6
C3—C2—H2	119.6	C6—C7—H7	119.6
C4—C3—C8	118.7 (3)	C7—C8—C3	120.2 (4)
C4—C3—C2	118.9 (3)	C7—C8—H8	119.9
C8—C3—C2	122.3 (3)	C3—C8—H8	119.9
C3—C4—C5	120.4 (3)		
C2—N1—O1—C1	-174.7 (3)	C3—C4—C5—Br1	-179.8 (3)
N1—O1—C1—C1 ⁱ	-67.7 (5)	C4—C5—C6—C7	-0.5 (6)
O1—N1—C2—C3	-179.6 (3)	Br1—C5—C6—C7	-179.5 (3)
N1—C2—C3—C4	175.5 (3)	C5—C6—C7—C8	0.7 (6)
N1—C2—C3—C8	-2.8 (5)	C6—C7—C8—C3	-1.6 (6)
C8—C3—C4—C5	-2.1 (5)	C4—C3—C8—C7	2.3 (6)
C2—C3—C4—C5	179.6 (3)	C2—C3—C8—C7	-179.4 (4)
C3—C4—C5—C6	1.2 (5)		

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