

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# 5,5'-Bis(benzyloxy)-2,2'-[hydrazine-diydilenebis(methanylylidene)]diphenol

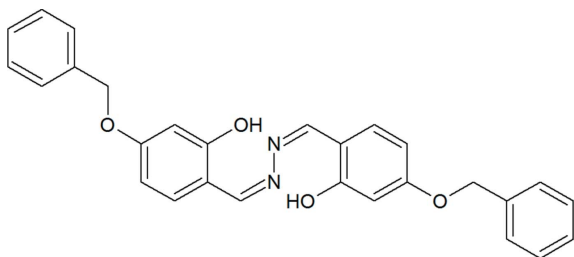
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Received 29 October 2013; accepted 4 November 2013

 Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.122; data-to-parameter ratio = 17.2.

 The title azine molecule,  $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$ , lies about a center of inversion. The dihedral angle between the phenyl ring and the hydroxy-substituted ring is  $70.3$  (5)°. The phenolic O–H group forms an intramolecular hydrogen bond to the azine N atom.

## Related literature

 For the biological activity of azines, see: Gul *et al.* (2003); Kumaraswamy & Vaidya (2005). For related structures, see: Acrovito *et al.* (1969); Sithambaresan & Kurup (2011). For a related synthesis, see: Karmakar *et al.* (2007).


## Experimental

### Crystal data

 $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$   
 $M_r = 452.49$   
 Monoclinic,  $P2_1/n$   
 $a = 12.4748$  (17) Å  
 $b = 5.3630$  (6) Å  
 $c = 17.021$  (2) Å  
 $\beta = 90.699$  (5)°

 $V = 1138.7$  (2) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.40 \times 0.20 \times 0.20$  mm

### Data collection

 Bruker Kappa APEXII CCD  
 diffractometer  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2004)  
 $T_{\min} = 0.965$ ,  $T_{\max} = 0.982$ 

 6320 measured reflections  
 2738 independent reflections  
 1593 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.122$   
 $S = 1.01$   
 2738 reflections  
 159 parameters  
 1 restraint

 H atoms treated by a mixture of  
 independent and constrained  
 refinement  
 $\Delta\rho_{\text{max}} = 0.13$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.15$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}'\cdots\text{N1}$	0.87 (2)	1.84 (2)	2.625 (2)	148 (2)

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg, 2010); software used to prepare material for publication: SHELXL97 and publCIF (Westrip, 2010).

NRS thanks the Council of Scientific and Industrial Research (India) for a Junior Research Fellowship. MRPK thanks the University Grants Commission, New Delhi, for a UGC–BSR one-time grant to faculty. The authors thank the Sophisticated Analytical Instruments Facility, Cochin University of S &amp; T, for the diffraction measurements.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5346).

## References

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## supporting information

*Acta Cryst.* (2013). E69, o1755 [doi:10.1107/S1600536813030171]

**5,5'-Bis(benzyloxy)-2,2'-[hydrazinediylidenebis(methanylylidene)]diphenol**

**N. R. Sajitha, M. Sithambaresan and M. R. Prathapachandra Kurup**

**S1. Comment**

Azines are 2,3-diaza analogous compounds of 1,3-butadiene. Compounds containing azine moiety exhibit a broad spectrum of biological activity such as antitumor (Gul *et al.*, 2003), antibacterial (Kumaraswamy & Vaidya, 2005) and many others.

The present compound is analogous to salicylaldehyde azine, in which the fourth position is substituted. The salicylaldehyde azine was characterized previously (Acrovito *et al.*, 1969) as luminescent and thermochromic substance in the solid state.

The title compound (Fig. 1) adopts an *E* configuration with respect to C14=N1 (bond distance: 1.288 (21) Å) and is close to the formal C=N bond [1.2758 (19) Å] (Sithambaresan & Kurup, 2011) confirming the azomethine bond formation and the presence of benzylidene moiety. The azomethine and benzaldehyde moieties are nearly planar with interplanar dihedral angle of 2.396 (7)°. The dihedral angle between benzene ring and benzaldehyde ring is 70.329 (46)°. The phenolic O–H forms an intramolecular O–H⋯N hydrogen bond with a D⋯A distance of 2.6245 (18) Å (Table 1, Fig. 2). There are very few weak short ring interactions found in the crystal system, but they are not significant to support the network since centroid-centroid distances are above 4 Å. Fig. 3 shows a packing diagram of the title compound viewed along *b* axis.

**S2. Experimental**

The title compound was prepared by adapting a reported procedure (Karmakar *et al.*, 2007). 4-Benzyloxy-2-hydroxybenzaldehyde (0.4564 g, 2 mmol) was dissolved in methanol (30 ml). The solution was acidified with 5 drops of glacial acetic acid and hydrazine monohydrate (0.501 g, 1 mmol). The mixture was stirred for 1 h at room temperature. A yellow solution obtained was kept for crystallization for 3 days and the crystalline substance formed was separated and washed with hexane and dried over P<sub>4</sub>O<sub>10</sub> *in vacuo*. This crystalline substance was recrystallized from dimethylformamide (20 ml) to give yellow needles of 4-benzyloxy-2-hydroxybenzaldehyde azine. The compound was obtained in 65% yield (0.181 g).

IR (KBr,  $\nu$  in cm<sup>-1</sup>): 1183, 1277, 1213, 1455, 1614, 2945, 3032. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  in p.p.m.): 8.583 (s, 1H), 5.103 (s, 2H), 7.224 (s, 1H), 7.333–7.446 (m, 5H), 6.585–6.618 (m, 3H).

**S3. Refinement**

All H atoms on C were placed in calculated positions, guided by difference maps, with C—H bond distances of 0.93 Å. H atoms were assigned  $U_{\text{iso}}(\text{H})$  values of 1.2U<sub>eq</sub>(carrier). Omitted owing to bad disagreement were reflections (1 0 1) and (-1 0 1). H atom of O2—H2' bond was located from difference maps and the bond distance is restrained to 0.84±0.02 Å.

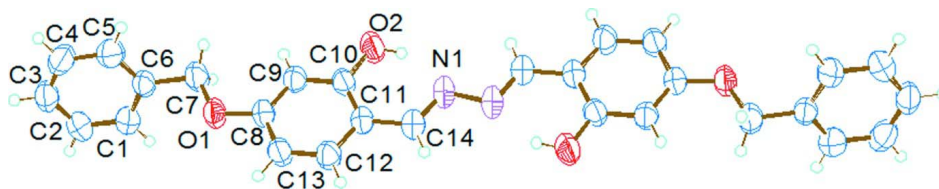


Figure 1

ORTEP view of the title compound drawn with 50% probability displacement ellipsoids for the non-H atoms.

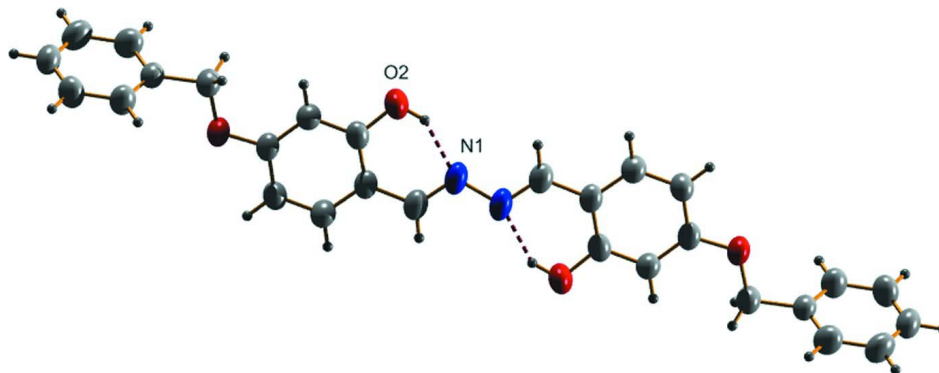


Figure 2

Hydrogen-bonding interactions in the crystal structure of  $C_{28}H_{24}N_2O_4$ .

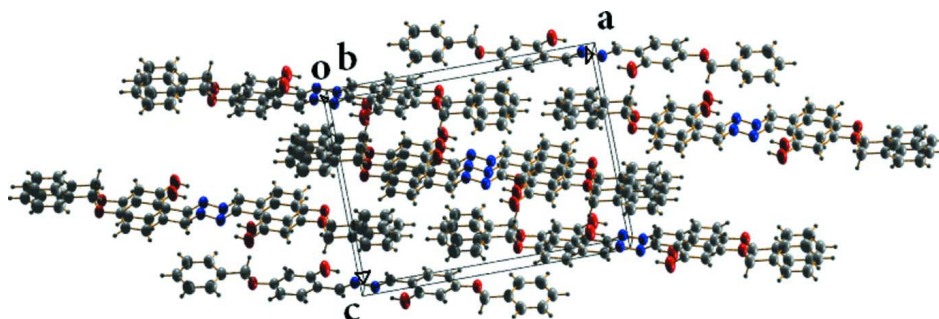


Figure 3

Packing diagram of the compound along the  $b$  axis

### 5,5'-Bis(benzyloxy)-2,2'-[hydrazinediylidenebis(methanylylidene)]diphenol

#### Crystal data

$C_{28}H_{24}N_2O_4$

$M_r = 452.49$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 12.4748$  (17) Å

$b = 5.3630$  (6) Å

$c = 17.021$  (2) Å

$\beta = 90.699$  (5)°

$V = 1138.7$  (2) Å<sup>3</sup>

$Z = 2$

$F(000) = 476$

$D_x = 1.320$  Mg m<sup>-3</sup>

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

Cell parameters from 1647 reflections

$\theta = 3.3$ – $27.3$ °

$\mu = 0.09$  mm<sup>-1</sup>

$T = 296$  K

Needle, yellow

$0.40 \times 0.20 \times 0.20$  mm

*Data collection*

Bruker Kappa APEXII CCD  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\omega$  and  $\varphi$  scan  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2004)  
 $T_{\min} = 0.965$ ,  $T_{\max} = 0.982$

6320 measured reflections  
2738 independent reflections  
1593 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\max} = 28.2^\circ$ ,  $\theta_{\min} = 2.4^\circ$   
 $h = -16 \rightarrow 14$   
 $k = -7 \rightarrow 6$   
 $l = -22 \rightarrow 17$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.122$   
 $S = 1.01$   
2738 reflections  
159 parameters  
1 restraint  
Primary atom site location: structure-invariant  
direct methods  
Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites  
H atoms treated by a mixture of independent  
and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.1778P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$   
Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kFc[1 + 0.001x \text{Fc}^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.0115 (19)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.38498 (9)	0.6629 (2)	0.90134 (6)	0.0614 (4)
O2	0.36761 (13)	0.8385 (2)	0.62715 (7)	0.0803 (4)
N1	0.47835 (11)	0.5470 (3)	0.53460 (7)	0.0601 (4)
C1	0.23742 (16)	0.7056 (3)	1.04210 (9)	0.0663 (5)
H1	0.2071	0.5745	1.0138	0.080*
C2	0.22037 (16)	0.7219 (4)	1.12153 (10)	0.0699 (5)
H2	0.1786	0.6028	1.1464	0.084*
C3	0.26443 (16)	0.9118 (4)	1.16380 (10)	0.0665 (5)
H3	0.2522	0.9238	1.2175	0.080*
C4	0.32641 (17)	1.0844 (4)	1.12737 (11)	0.0742 (6)
H4	0.3573	1.2133	1.1563	0.089*
C5	0.34358 (16)	1.0684 (3)	1.04737 (11)	0.0706 (5)
H5	0.3862	1.1868	1.0228	0.085*
C6	0.29828 (14)	0.8791 (3)	1.00385 (9)	0.0553 (4)
C7	0.31240 (16)	0.8630 (3)	0.91687 (9)	0.0675 (5)

H7A	0.2439	0.8320	0.8911	0.081*
H7B	0.3410	1.0185	0.8970	0.081*
C8	0.40808 (13)	0.6150 (3)	0.82489 (9)	0.0505 (4)
C9	0.37165 (14)	0.7540 (3)	0.76205 (9)	0.0565 (4)
H9	0.3261	0.8887	0.7701	0.068*
C10	0.40315 (14)	0.6925 (3)	0.68662 (9)	0.0539 (4)
C11	0.46947 (13)	0.4874 (3)	0.67316 (8)	0.0512 (4)
C12	0.50273 (14)	0.3498 (3)	0.73856 (10)	0.0611 (5)
H12	0.5461	0.2110	0.7310	0.073*
C13	0.47411 (14)	0.4112 (3)	0.81321 (9)	0.0594 (5)
H13	0.4986	0.3173	0.8557	0.071*
C14	0.50412 (14)	0.4193 (3)	0.59605 (9)	0.0581 (4)
H14	0.5466	0.2782	0.5902	0.070*
H2'	0.3950 (16)	0.782 (4)	0.5836 (10)	0.096 (7)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0707 (8)	0.0746 (8)	0.0390 (6)	0.0179 (6)	0.0081 (5)	0.0004 (5)
O2	0.1141 (12)	0.0833 (9)	0.0435 (7)	0.0295 (8)	0.0038 (7)	0.0089 (6)
N1	0.0613 (9)	0.0802 (10)	0.0388 (7)	-0.0018 (8)	0.0048 (6)	-0.0081 (7)
C1	0.0840 (14)	0.0642 (11)	0.0508 (10)	-0.0055 (10)	-0.0001 (9)	-0.0043 (8)
C2	0.0821 (14)	0.0747 (13)	0.0530 (10)	-0.0032 (10)	0.0090 (9)	0.0074 (9)
C3	0.0769 (13)	0.0786 (13)	0.0441 (9)	0.0174 (11)	0.0023 (9)	-0.0037 (9)
C4	0.0873 (15)	0.0703 (12)	0.0649 (12)	0.0022 (11)	-0.0031 (10)	-0.0198 (10)
C5	0.0802 (14)	0.0650 (12)	0.0670 (12)	-0.0016 (10)	0.0140 (10)	-0.0020 (9)
C6	0.0666 (11)	0.0569 (10)	0.0425 (9)	0.0132 (9)	0.0062 (8)	-0.0006 (7)
C7	0.0836 (14)	0.0724 (12)	0.0466 (10)	0.0215 (10)	0.0098 (9)	0.0025 (8)
C8	0.0510 (9)	0.0604 (10)	0.0403 (8)	-0.0010 (8)	0.0059 (7)	-0.0005 (7)
C9	0.0653 (11)	0.0584 (10)	0.0460 (9)	0.0109 (9)	0.0050 (8)	-0.0003 (8)
C10	0.0617 (11)	0.0589 (10)	0.0409 (8)	-0.0026 (8)	-0.0007 (7)	0.0034 (7)
C11	0.0521 (10)	0.0609 (10)	0.0406 (8)	-0.0033 (8)	0.0040 (7)	-0.0020 (7)
C12	0.0656 (12)	0.0687 (12)	0.0491 (10)	0.0157 (9)	0.0072 (8)	0.0002 (8)
C13	0.0661 (11)	0.0682 (11)	0.0439 (9)	0.0128 (9)	0.0053 (8)	0.0059 (8)
C14	0.0588 (11)	0.0715 (11)	0.0443 (9)	-0.0005 (9)	0.0037 (8)	-0.0057 (8)

*Geometric parameters (Å, °)*

O1—C8	1.3607 (17)	C5—H5	0.9300
O1—C7	1.431 (2)	C6—C7	1.496 (2)
O2—C10	1.3505 (19)	C7—H7A	0.9700
O2—H2'	0.874 (15)	C7—H7B	0.9700
N1—C14	1.288 (2)	C8—C9	1.376 (2)
N1—N1 <sup>i</sup>	1.396 (2)	C8—C13	1.385 (2)
C1—C6	1.370 (2)	C9—C10	1.387 (2)
C1—C2	1.374 (2)	C9—H9	0.9300
C1—H1	0.9300	C10—C11	1.397 (2)
C2—C3	1.359 (3)	C11—C12	1.394 (2)

C2—H2	0.9300	C11—C14	1.434 (2)
C3—C4	1.360 (3)	C12—C13	1.364 (2)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.384 (2)	C13—H13	0.9300
C4—H4	0.9300	C14—H14	0.9300
C5—C6	1.374 (3)		
C8—O1—C7	117.41 (12)	O1—C7—H7B	110.1
C10—O2—H2'	107.8 (14)	C6—C7—H7B	110.1
C14—N1—N1 <sup>i</sup>	113.47 (19)	H7A—C7—H7B	108.4
C6—C1—C2	121.17 (17)	O1—C8—C9	124.69 (15)
C6—C1—H1	119.4	O1—C8—C13	114.82 (14)
C2—C1—H1	119.4	C9—C8—C13	120.49 (14)
C3—C2—C1	120.14 (18)	C8—C9—C10	119.72 (16)
C3—C2—H2	119.9	C8—C9—H9	120.1
C1—C2—H2	119.9	C10—C9—H9	120.1
C2—C3—C4	119.79 (17)	O2—C10—C9	117.49 (15)
C2—C3—H3	120.1	O2—C10—C11	121.55 (14)
C4—C3—H3	120.1	C9—C10—C11	120.95 (15)
C3—C4—C5	120.15 (18)	C12—C11—C10	117.17 (14)
C3—C4—H4	119.9	C12—C11—C14	120.39 (16)
C5—C4—H4	119.9	C10—C11—C14	122.44 (15)
C6—C5—C4	120.57 (18)	C13—C12—C11	122.50 (16)
C6—C5—H5	119.7	C13—C12—H12	118.8
C4—C5—H5	119.7	C11—C12—H12	118.8
C1—C6—C5	118.16 (16)	C12—C13—C8	119.15 (16)
C1—C6—C7	120.25 (16)	C12—C13—H13	120.4
C5—C6—C7	121.58 (16)	C8—C13—H13	120.4
O1—C7—C6	107.98 (13)	N1—C14—C11	122.21 (17)
O1—C7—H7A	110.1	N1—C14—H14	118.9
C6—C7—H7A	110.1	C11—C14—H14	118.9
C6—C1—C2—C3	-0.3 (3)	C8—C9—C10—O2	-178.25 (16)
C1—C2—C3—C4	-0.7 (3)	C8—C9—C10—C11	1.5 (3)
C2—C3—C4—C5	0.7 (3)	O2—C10—C11—C12	179.36 (16)
C3—C4—C5—C6	0.1 (3)	C9—C10—C11—C12	-0.4 (2)
C2—C1—C6—C5	1.1 (3)	O2—C10—C11—C14	0.2 (3)
C2—C1—C6—C7	-177.71 (17)	C9—C10—C11—C14	-179.61 (16)
C4—C5—C6—C1	-1.0 (3)	C10—C11—C12—C13	-0.9 (3)
C4—C5—C6—C7	177.77 (17)	C14—C11—C12—C13	178.29 (17)
C8—O1—C7—C6	179.40 (14)	C11—C12—C13—C8	1.1 (3)
C1—C6—C7—O1	-74.4 (2)	O1—C8—C13—C12	-179.31 (16)
C5—C6—C7—O1	106.85 (19)	C9—C8—C13—C12	0.1 (3)
C7—O1—C8—C9	4.0 (2)	N1 <sup>i</sup> —N1—C14—C11	178.83 (17)
C7—O1—C8—C13	-176.67 (16)	C12—C11—C14—N1	-177.39 (17)

O1—C8—C9—C10	177.95 (16)	C10—C11—C14—N1	1.8 (3)
C13—C8—C9—C10	-1.4 (3)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2'...N1	0.87 (2)	1.84 (2)	2.625 (2)	148 (2)