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2,2'-Diethoxy-4,4'-[(*E,E*)-hydrazinediylidene]bis(methanylylidene)diphenol

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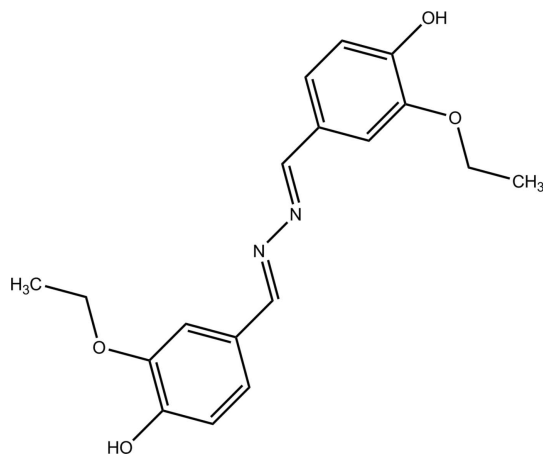
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.098; data-to-parameter ratio = 16.5.

The complete molecule of the title compound, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$, is generated by inversion symmetry. The conformation around the $\text{C}=\text{N}$ bond is *E*. With the exception of the ethoxy substituent, the molecule is essentially planar with an r.m.s. deviation of 0.0455 Å. In the crystal, molecules are linked by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds into a two-dimensional supramolecular network parallel to the *bc* plane.

Related literature

For the structure of 4,4'-(1*E*,1'*E*)-1,2-diylidenebis(methan-1-yl-1-ylidene) bis(2-methoxyphenol), see: Qu *et al.* (2005). For applications of azines and their derivatives, see: Dudis *et al.* (1993); Facchetti *et al.* (2002); Kim *et al.* (2010); Pandeya *et al.* (1999); Wadher *et al.* (2009).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_4$
 $M_r = 328.36$
 Monoclinic, $P2_1/n$
 $a = 5.2176$ (1) Å
 $b = 10.3422$ (1) Å
 $c = 14.9135$ (2) Å
 $\beta = 97.206$ (1)°

$V = 798.40$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 100$ K
 $0.16 \times 0.08 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.650$, $T_{\max} = 0.746$

7447 measured reflections
 1831 independent reflections
 1654 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.098$
 $S = 1.05$
 1831 reflections

111 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O2}-\text{H2}\cdots\text{N1}^i$	0.84	1.99	2.7787 (12)	156

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2092).

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supporting information

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2,2'-Diethoxy-4,4'-[(*E,E*)-hydrazinediylidenebis(methanylylidene)]diphenol

Wisam Naji Atiyah Al-Mehana, Rosiyah Yahya, Faridah Sonsudin, Ihsan Naji Atiyah Al-Mehana and Kong Mun Lo

S1. Comment

Aromatic carbonyl compounds react easily with hydrazine forming hydrazones, which could condense with a second molecule of the carbonyl compound to yield an azine. Due to the fascinating physical and chemical properties, azines and their derivatives have been extensively applied in such area as dyes [Kim *et al.*], non-linear fluorophores [Facchetti *et al.*], biological and pharmaceutical applications [Wadher *et al.*, Pandeya *et al.*]. Furthermore, there are many reports on polyazines as highly conjugated polymers in electronic, optoelectronic and photonic applications [Dudis *et al.*]. In our work on a new class of monomers based upon the hydrazone moieties, we report here a new bis imine monomer. The title compound, C₁₈H₂₀N₂O₄, is centrosymmetric around the central azine bond [N1—N1ⁱ = 1.416 (2) Å; symmetry operation i: -x + 2, -y + 1, -z + 1], with the *E* configuration around the N1=C1 bond [1.284 (1) Å]. In the crystal structure of the title compound in Fig 2, the molecules are linked together by O—H⋯N hydrogen bonds [O2—H2⋯N1ⁱⁱ = 2.7782 (12) Å; symmetry operation ii: 3/2 - x, 1/2 + y, 1/2 + z] resulting in the formation of a two-dimensional supramolecular network which propagated parallel to the *bc* plane. C—H⋯π interaction is also present; C8—H8b⋯CgIⁱⁱⁱ = 2.71 Å where CgI is the centroid of the ring C2 - C7, [symmetry code: (iii) -1 + x, y, z]. In contrast to the title compound, the methoxy substituted analogue [Qu, *et al.*] consists of two asymmetric units with the presence of additional intermolecular O—H⋯O hydrogen bonds with the adjacent asymmetric unit.

S2. Experimental

A mixture of 3-ethoxy-4-hydroxybenzaldehyde (3 g, 18 mmol), hydrazine sulfate (1.17 g, 9 mmol) and 1.7 ml of concentrated ammonia solution in 20 ml of 95% ethanol was stirred for 3 h. The solvent was removed under reduced pressure and the yellow residue was recrystallized from tetrahydrofuran to yield yellow crystals, m.p. 471 - 472 K.

S3. Refinement

Hydrogen atoms were placed at calculated positions (C—H 0.95 to 0.99 Å and O—H 0.84 Å) and were treated as riding on their parent carbon atoms, with $U(\text{H})$ set to 1.2–1.5 times $U_{\text{eq}}(\text{C})$.

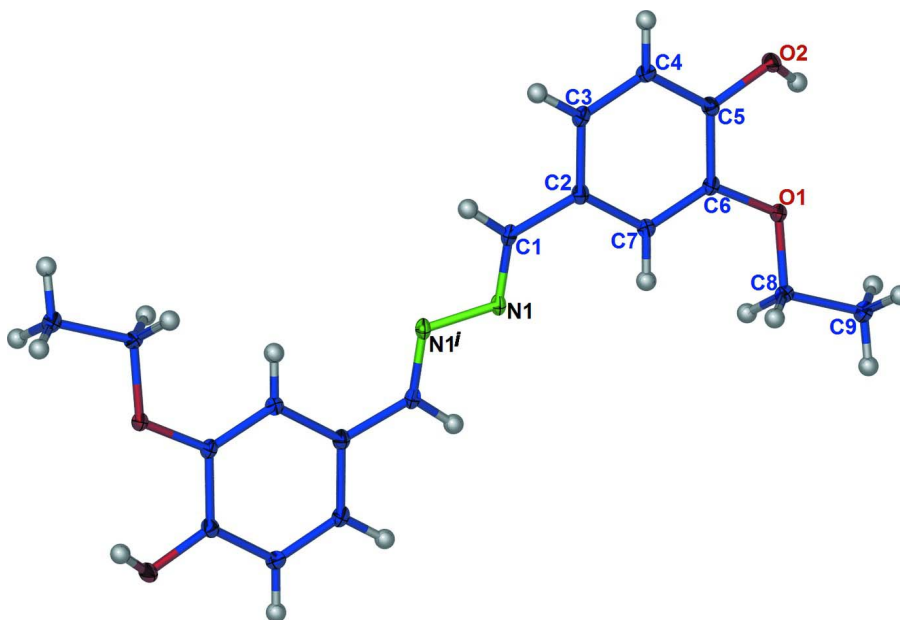


Figure 1

The molecular structure of 4,4'-(1*E*,1'*E*)-1,2-diylidenebis(methan-1-yl-1-ylidene) bis(2-ethoxyphenol) showing 50% probability displacement ellipsoids. Hydrogen atoms are drawn as spheres of arbitrary radius. Symmetry operation *i*: $-x + 2, -y + 1, -z + 1$.

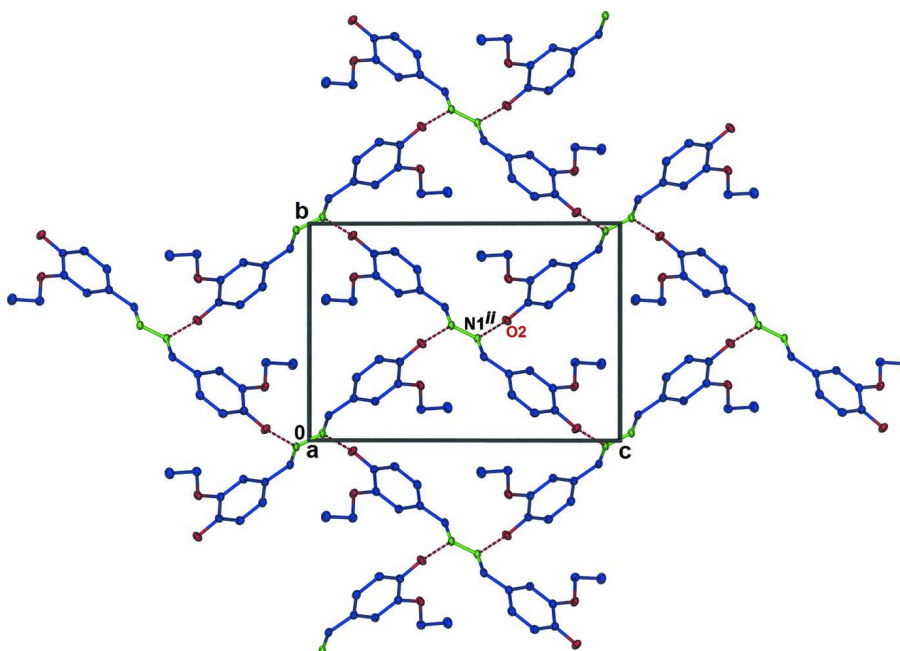


Figure 2

A view of the two-dimensional supramolecular network in the title compound showing the O—H...N hydrogen bonds (in red dotted lines).

2,2'-Diethoxy-4,4'-[(E,E)-hydrazinediylidenebis(methanylylidene)]diphenol

Crystal data

C₁₈H₂₀N₂O₄ $M_r = 328.36$ Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

 $a = 5.2176$ (1) Å $b = 10.3422$ (1) Å $c = 14.9135$ (2) Å $\beta = 97.206$ (1)° $V = 798.40$ (2) Å³ $Z = 2$ $F(000) = 348$ $D_x = 1.366$ Mg m⁻³

Melting point = 471–472 K

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

Cell parameters from 4187 reflections

 $\theta = 2.4$ – 28.4 ° $\mu = 0.10$ mm⁻¹ $T = 100$ K

Block, yellow

 $0.16 \times 0.08 \times 0.08$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 ω scansAbsorption correction: multi-scan
(SADABS; Sheldrick, 1996) $T_{\min} = 0.650$, $T_{\max} = 0.746$

7447 measured reflections

1831 independent reflections

1654 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.020$ $\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.4$ ° $h = -6$ → 6 $k = -13$ → 13 $l = -19$ → 18

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.098$ $S = 1.05$

1831 reflections

111 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.3158P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.33$ e Å⁻³ $\Delta\rho_{\min} = -0.23$ 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 (Å²)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.1226 (2)	0.61425 (10)	0.43730 (7)	0.0140 (2)
H1	1.2770	0.6254	0.4776	0.017*
C2	1.0867 (2)	0.69416 (10)	0.35602 (7)	0.0138 (2)
C3	1.2699 (2)	0.79013 (10)	0.34702 (7)	0.0150 (2)

H3	1.4163	0.7982	0.3914	0.018*
C4	1.2397 (2)	0.87397 (10)	0.27353 (7)	0.0149 (2)
H4	1.3647	0.9394	0.2683	0.018*
C5	1.0277 (2)	0.86239 (10)	0.20780 (7)	0.0137 (2)
C6	0.84916 (19)	0.76106 (10)	0.21383 (7)	0.0133 (2)
C7	0.87615 (19)	0.67949 (10)	0.28809 (7)	0.0140 (2)
H7	0.7521	0.6135	0.2931	0.017*
C8	0.4920 (2)	0.64171 (10)	0.14038 (7)	0.0163 (2)
H8B	0.3966	0.6416	0.1937	0.020*
H8A	0.5954	0.5614	0.1412	0.020*
C9	0.3053 (2)	0.64918 (12)	0.05452 (8)	0.0217 (3)
H9A	0.2111	0.7313	0.0529	0.033*
H9B	0.1825	0.5772	0.0528	0.033*
H9C	0.4011	0.6439	0.0022	0.033*
N1	0.95919 (17)	0.52993 (9)	0.45792 (6)	0.0138 (2)
O1	0.65817 (14)	0.75311 (7)	0.14250 (5)	0.0160 (2)
O2	1.00276 (14)	0.94690 (7)	0.13780 (5)	0.01629 (19)
H2	0.8462	0.9532	0.1167	0.024*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0148 (5)	0.0157 (5)	0.0109 (5)	0.0022 (4)	-0.0010 (3)	-0.0018 (4)
C2	0.0150 (5)	0.0141 (5)	0.0119 (5)	0.0026 (4)	0.0011 (4)	-0.0007 (4)
C3	0.0139 (5)	0.0169 (5)	0.0136 (5)	0.0009 (4)	-0.0013 (4)	-0.0016 (4)
C4	0.0143 (5)	0.0141 (5)	0.0162 (5)	-0.0011 (4)	0.0012 (4)	-0.0007 (4)
C5	0.0155 (5)	0.0131 (5)	0.0127 (5)	0.0020 (4)	0.0025 (4)	0.0007 (4)
C6	0.0125 (5)	0.0146 (5)	0.0123 (5)	0.0010 (4)	-0.0004 (4)	-0.0009 (4)
C7	0.0147 (5)	0.0139 (5)	0.0134 (5)	-0.0002 (4)	0.0012 (4)	0.0004 (4)
C8	0.0168 (5)	0.0154 (5)	0.0156 (5)	-0.0036 (4)	-0.0017 (4)	0.0009 (4)
C9	0.0225 (6)	0.0236 (6)	0.0172 (5)	-0.0062 (4)	-0.0043 (4)	0.0018 (4)
N1	0.0162 (4)	0.0148 (4)	0.0098 (4)	0.0031 (3)	-0.0008 (3)	0.0004 (3)
O1	0.0162 (4)	0.0167 (4)	0.0135 (4)	-0.0036 (3)	-0.0039 (3)	0.0033 (3)
O2	0.0144 (4)	0.0169 (4)	0.0167 (4)	-0.0009 (3)	-0.0014 (3)	0.0052 (3)

Geometric parameters (Å, °)

C1—N1	1.2835 (14)	C6—C7	1.3853 (14)
C1—C2	1.4596 (14)	C7—H7	0.9500
C1—H1	0.9500	C8—O1	1.4399 (12)
C2—C3	1.3959 (15)	C8—C9	1.5106 (14)
C2—C7	1.4062 (14)	C8—H8B	0.9900
C3—C4	1.3910 (15)	C8—H8A	0.9900
C3—H3	0.9500	C9—H9A	0.9800
C4—C5	1.3880 (14)	C9—H9B	0.9800
C4—H4	0.9500	C9—H9C	0.9800
C5—O2	1.3551 (12)	N1—N1 ⁱ	1.4163 (16)
C5—C6	1.4126 (14)	O2—H2	0.8400

C6—O1	1.3658 (12)		
N1—C1—C2	124.33 (9)	C6—C7—C2	120.14 (9)
N1—C1—H1	117.8	C6—C7—H7	119.9
C2—C1—H1	117.8	C2—C7—H7	119.9
C3—C2—C7	119.34 (9)	O1—C8—C9	107.47 (8)
C3—C2—C1	117.68 (9)	O1—C8—H8B	110.2
C7—C2—C1	122.98 (9)	C9—C8—H8B	110.2
C4—C3—C2	120.52 (9)	O1—C8—H8A	110.2
C4—C3—H3	119.7	C9—C8—H8A	110.2
C2—C3—H3	119.7	H8B—C8—H8A	108.5
C5—C4—C3	120.27 (10)	C8—C9—H9A	109.5
C5—C4—H4	119.9	C8—C9—H9B	109.5
C3—C4—H4	119.9	H9A—C9—H9B	109.5
O2—C5—C4	118.65 (9)	C8—C9—H9C	109.5
O2—C5—C6	121.81 (9)	H9A—C9—H9C	109.5
C4—C5—C6	119.51 (9)	H9B—C9—H9C	109.5
O1—C6—C7	125.25 (9)	C1—N1—N1 ⁱ	111.99 (10)
O1—C6—C5	114.69 (9)	C6—O1—C8	116.35 (8)
C7—C6—C5	120.07 (9)	C5—O2—H2	109.5
N1—C1—C2—C3	174.08 (10)	C4—C5—C6—C7	4.43 (15)
N1—C1—C2—C7	-5.05 (16)	O1—C6—C7—C2	177.64 (9)
C7—C2—C3—C4	2.56 (15)	C5—C6—C7—C2	-2.41 (15)
C1—C2—C3—C4	-176.60 (9)	C3—C2—C7—C6	-1.07 (15)
C2—C3—C4—C5	-0.53 (16)	C1—C2—C7—C6	178.05 (9)
C3—C4—C5—O2	179.09 (9)	C2—C1—N1—N1 ⁱ	-178.00 (10)
C3—C4—C5—C6	-2.96 (15)	C7—C6—O1—C8	-7.68 (15)
O2—C5—C6—O1	2.27 (14)	C5—C6—O1—C8	172.36 (9)
C4—C5—C6—O1	-175.61 (9)	C9—C8—O1—C6	-177.35 (9)
O2—C5—C6—C7	-177.68 (9)		

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

<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 ⁱⁱ	0.84	1.99	2.7787 (12)	156

Symmetry code: (ii) $-x+3/2, y+1/2, -z+1/2$.