



# Zwitterionic 1-[(1*E*)-[(4-hydroxyphenyl)iminio]-methyl]naphthalen-2-olate: crystal structure and Hirshfeld surface analysis

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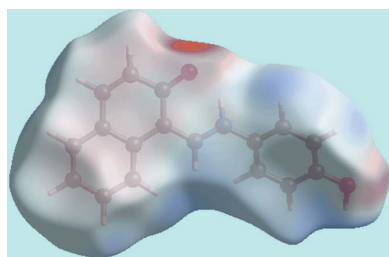
The title zwitterion, C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub> (systematic name: 1-[(1*E*)-[(4-hydroxyphenyl)iminium]methyl]naphthalen-2-olate), features an intramolecular charge-assisted N<sup>+</sup>—H···O<sup>−</sup> hydrogen bond. A twist in the molecule is evident around the N—C(hydroxybenzene) bond [C—N—C—C torsion angle = 39.42 (8)°] and is reflected in the dihedral angle of 39.42 (8)° formed between the aromatic regions of the molecule. In the crystal, zigzag supramolecular chains along the *a* axis are formed by charge-assisted hydroxy-O—H···O(phenoxide) hydrogen bonding. These are connected into a layer in the *ab* plane by charge-assisted hydroxybenzene-C—H···O(phenoxide) interactions and  $\pi$ — $\pi$  contacts [intercentroid distance between naphthyl-C<sub>6</sub> rings = 3.4905 (12) Å]. Layers stack along the *c* axis with no specific interactions between them. The Hirshfeld surface analysis points to the significance C···H contacts between layers.

## 1. Chemical context

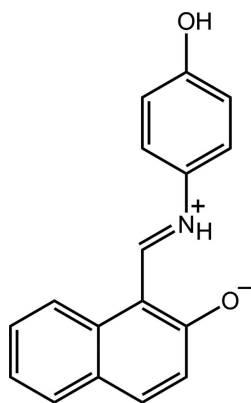
Schiff bases derived from *o*-hydroxynaphthaldehyde have attracted significant attention owing to their biological properties, such as anti-tumour activity (Richardson & Bernhardt, 1999; Gou *et al.*, 2015), and their photophysical properties, such as thermo- and photochromism (Matiječić-Sosa *et al.*, 2006). Furthermore, the physical properties of these molecules led to their application in various areas of materials science, such as in the control and measurement of radiation intensity, display systems and optical memory devices (Dürr, 1989; Hadjoudis & Mavridis, 2004). These Schiff bases have also been used as tools for assessing the nature of hydrogen bonding (Richardson & Bernhardt, 1999), as well as keto-amine and phenol-imine tautomerism (Ünver *et al.*, 2000) in related molecules. In view of these various applications, our recent investigations have focused on the structure determination of Schiff bases of this type, *e.g.* of (*E*)-*N*-[(2-methoxynaphthalen-1-yl)methylidene]-3-nitroaniline (Bhai *et al.*, 2015). As a continuation of these studies, the crystal and molecular structures of the title compound, (I), are described herein along with an analysis of the Hirshfeld surface, performed in order to gain more information on the nature of the molecular packing.

## 2. Structural commentary

The molecular structure of (I) is shown in Fig. 1. Crystallography established the molecule to exist in a zwitterionic

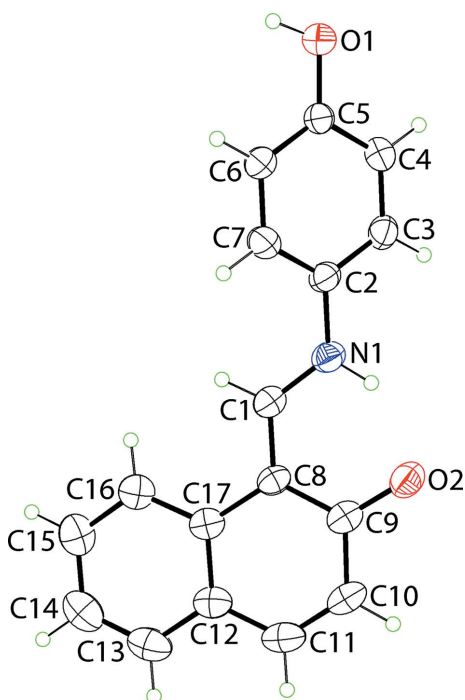


form with the putative H atom of the naphthyl-hydroxy group being located on the imine-N atom. This assignment is supported by the short C9—O2 bond length of 1.283 (2) Å. The molecule features two planar regions connected by an imine (iminiumyl) bridge; the configuration about the imine bond [C1=N = 1.308 (2) Å] is *E*. The twist in the molecule occurs around the N1—C2 bond, is seen in the value of the C1—N1—C2—C7 torsion angle of 31.1 (3)°. The dihedral angle between the two aromatic regions is 39.42 (8)°. The coplanar relationship between the imine and naphthyl residues is stabilized by an intramolecular charge-assisted N<sup>+</sup>—H···O<sup>−</sup> hydrogen bond, Table 1.



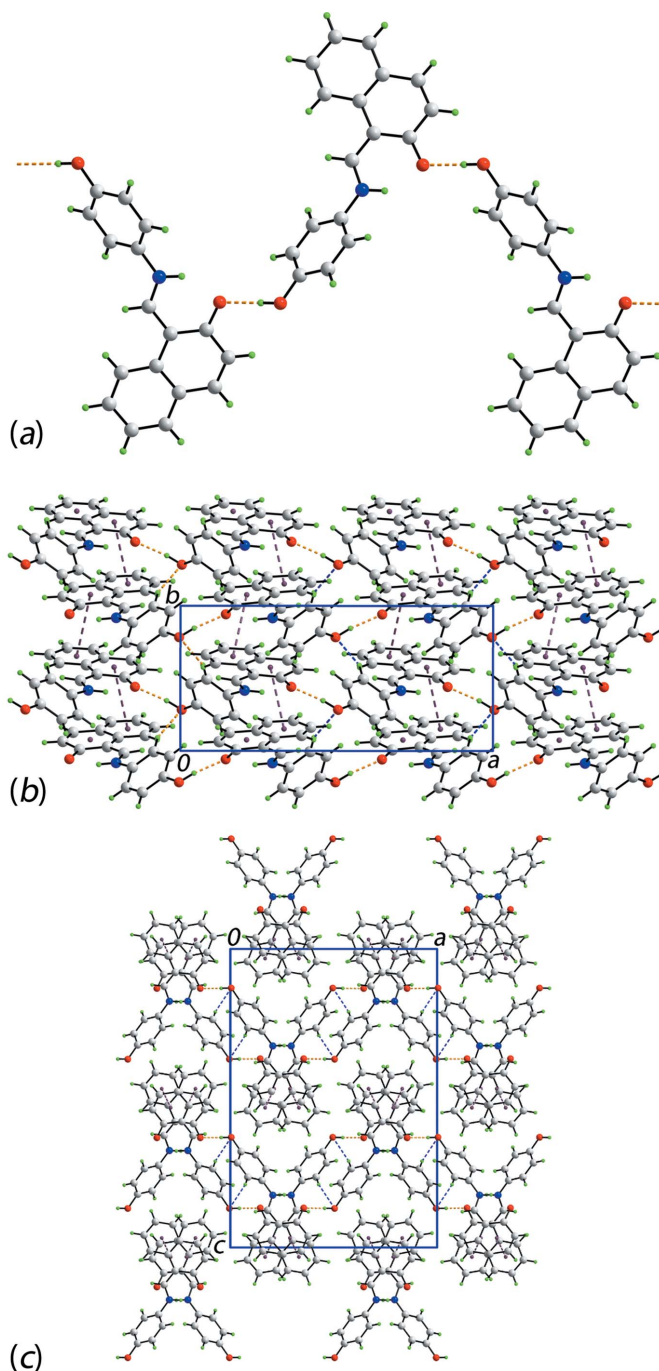
### 3. Supramolecular features

The most prominent feature of the molecular packing is the formation of a zigzag (glide symmetry) supramolecular chain



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 35% probability level.

along the *a* axis mediated by hydroxy-O—H···O(phenoxide) charge-assisted hydrogen bonding, Fig. 2*a* and Table 1. Chains are connected into a supramolecular layer in the *ab* plane by charge-assisted hydroxybenzene-C—H···O(phenoxide) inter-



**Figure 2**  
The molecular packing for (I): (a) a view of the zigzag supramolecular chain along the *a* axis mediated by charge-assisted hydroxy-O—H···O(phenoxide) hydrogen bonding, (b) a view of the supramolecular layer in the *ab* plane stabilized by charge-assisted hydroxybenzene-C—H···O(phenoxide) interactions and  $\pi$ – $\pi$  contacts and (c) a view of the unit-cell contents shown in projection down the *b* axis, highlighting the stacking of layers along the *c* axis. The O—H···O, C—H···O and  $\pi$ – $\pi$  interactions are shown as orange, blue and purple dashed lines, respectively.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots O2$	0.88 (1)	1.81 (2)	2.553 (2)	141 (2)
$O1-H1O\cdots O2^i$	0.89 (1)	1.74 (1)	2.622 (2)	173 (1)
$C7-H7\cdots O1^{ii}$	0.93	2.60	3.487 (3)	160

Symmetry codes: (i)  $-x - \frac{3}{2}, y - \frac{1}{2}, z$ ; (ii)  $-x + \frac{3}{2}, -y - 1, z + \frac{1}{2}$ .

**Table 2**  
Summary of short interatomic contacts (Å) in (I).

Contact	Distance	Symmetry operation
$C4\cdots H13$	2.69	$\frac{3}{2} - x, -y, \frac{1}{2} + z$
$C5\cdots H7$	2.69	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
$C9\cdots H10$	2.638 (16)	$\frac{1}{2} + x, y, \frac{1}{2} - z$
$C9\cdots C17$	3.367 (2)	$-x, -\frac{1}{2} + y, z$
$H15\cdots H16$	2.38	$1 - x, -y, -z$

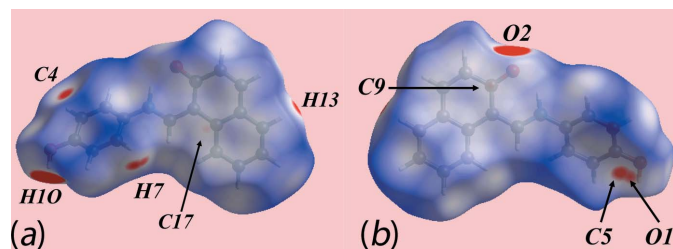
**Table 3**  
Percentage contributions of interatomic contacts to the Hirshfeld surface for (I).

Contact	Percentage contribution
H···H	46.5
C···H/H···C	24.9
O···H/H···O	14.9
C···C	10.5
C···O/O···C	1.0
N···H/H···N	1.0
N···O/O···N	0.6
C···N/N···C	0.6

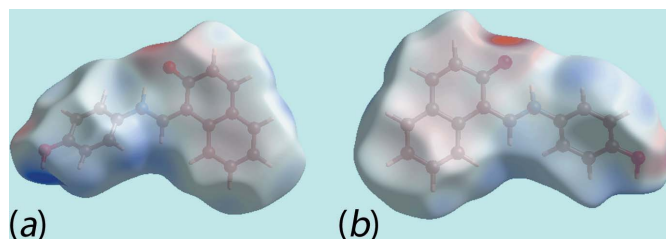
actions, Table 1, as well as  $\pi$ - $\pi$  contacts between the two rings of the naphthyl residue; the inter-centroid separation for  $(C8-C12, C17)\cdots(C12-C17)^i = 3.4905$  (12) Å and angle of inclination = 2.68 (8)° [symmetry code (i)  $\frac{3}{2} - x, \frac{1}{2} + y, z$ ], Fig. 2b. Layers stack along the  $c$  axis with no directional interactions between them, Fig. 2c.

#### 4. Analysis of the Hirshfeld surface

The Hirshfeld surface was calculated for (I) according to earlier work on organic molecules (Tan *et al.*, 2017) and provides more detailed information on the intermolecular interactions influential in the crystal. In addition to the bright-

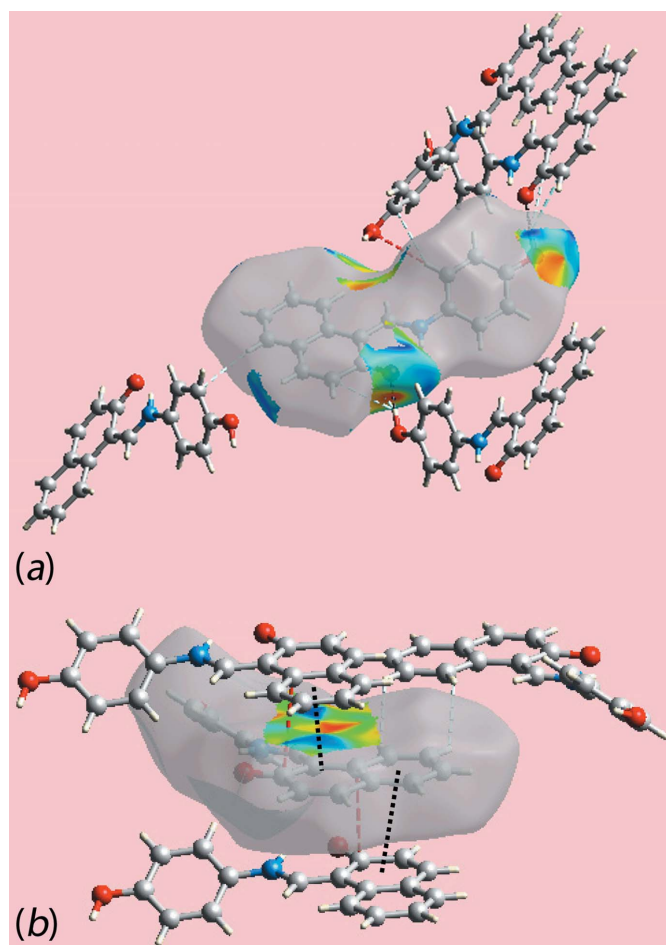


**Figure 3**  
Views of the Hirshfeld surface for (I) mapped over  $d_{\text{norm}}$  in the range  $-0.150$  to  $+1.460$  a.u.



**Figure 4**  
Views of the Hirshfeld surface for (I) mapped over the electrostatic potential in the range  $\pm 0.116$  a.u.

red spots near those atoms participating in charge-assisted  $O1-H10\cdots O2$  and  $C7-H7\cdots O1$  interactions on the Hirshfeld surface mapped over  $d_{\text{norm}}$ , Fig. 3, the bright-red spots appearing near the benzene-C4, -C5 and -H7, and naphthyl-H13 atoms are indicative of short interatomic  $C\cdots H/H\cdots C$  contacts significant in the crystal, Table 2. The  $C4\cdots H13$  contact occurs in the inter-layer region. Further, the



**Figure 5**  
Views of the Hirshfeld surfaces about a reference molecule mapped over the shape-index property highlighting (a) intermolecular  $O-H\cdots O$  and  $C-H\cdots O$  interactions, and short interatomic  $C\cdots H/H\cdots C$  contacts by black, red and sky-blue dashed lines, respectively, and (b) short interatomic  $C\cdots C$  and  $H\cdots H$  contacts, and  $\pi$ - $\pi$  stacking interactions by red, sky-blue and black dashed lines, respectively.

short interatomic C··C contacts between the naphthyl-C9 and -C17 atoms, Table 2, assigned to  $\pi$ - $\pi$  stacking interactions, appear as faint-red spots in Fig. 3. The donors and acceptors of the aforementioned interactions appear as blue and red regions, respectively, around the atoms on the Hirshfeld surface mapped over electrostatic potential in the views shown in Fig. 4. The short interatomic contacts together with the charge-assisted O—H··O and C—H··O interactions formed with the atoms of a reference molecule within shape-index mapped Hirshfeld surface are highlighted in the views of Fig. 5.

The overall two-dimensional fingerprint plot, Fig. 6a, and those delineated into H··H, C··H/H··C, O··H/H··O and C··C contacts (McKinnon *et al.*, 2007) are illustrated in Figs. 6b–e, respectively; the relative contributions from different interatomic contacts to the Hirshfeld surfaces are summarized in Table 3. The presence of a small peak in the centre at  $d_e + d_i \sim 2.3$  Å in the fingerprint plot delineated into H··H contacts, Fig. 6b, results from the short interatomic H··H contact between symmetry related naphthyl-H15 and -H16 atoms, Table 2. In the fingerprint plot delineated into C··H/H··C contacts, Fig. 6c, the short interatomic contacts summarized in Table 2 appear as the points distributed as the pair of thick spikes with tips at  $d_e + d_i \sim 2.6$  Å. The presence of charge-assisted O—H··O hydrogen bonds in the structure are characterized by the distinctive spikes with tips at  $d_e + d_i \sim 1.7$  Å, Fig. 6d, whereas the points belong to intermolecular C—H··O hydrogen bond are merged within the plot. The fingerprint plot delineated into C··C contacts, Fig. 6e, indicate the presence of the  $\pi$ - $\pi$  stacking interactions between symmetry related naphthyl-(C8–C12/C17) and -(C12–C17) rings through the arrow-shaped distribution with the green points spread about  $d_e = d_i = 1.8$  Å. The small contributions from other interatomic contacts summarized in Table 3 have negligible effect on the molecular packing.

## 5. Database survey

The most closely related structure to (I) in the crystallographic literature (Groom *et al.*, 2016) is that of the ethanol hemisolvate of (I), *i.e.* (I)·0.5EtOH (Safia *et al.*, 2015). Here, there are two molecules in the asymmetric unit and each exists in the zwitterionic form with C—O<sup>−</sup> = 1.288 (4) and 1.2943 (19) Å. By contrast to (I), the zwitterions in (I)·0.5EtOH are more

planar than in (I), with the dihedral angles between the aromatic residues being 7.59 (4)° in one of the independent zwitterions and 8.01 (4)° in the other. The other structure deserving of comment is that of 2-[[4-(hydroxyphenyl)imino]methyl]phenol, where the 2-oxidonaphthyl group of (I) has been replaced by a 2-oxidobenzene residue. This has been crystallized in two forms, *viz.* a  $P2_1/c$  form with  $Z' = 2$  (Ersanlı *et al.*, 2004) and a  $C2/c$  form with  $Z' = 1$  (Wang *et al.*, 2011). The common feature of the three molecules is the formation of hydroxyl/imine tautomer, as opposed to zwitterionic (I) and (I)·0.5EtOH (Safia *et al.*, 2015). The three molecules have smaller deviations from planarity than (I), as seen in the dihedral angles between the aromatic rings of 10.43 (6) and 15.70 (6)° for the  $P2_1/c$  form, and 14.91 (9)° for the  $C2/c$  form. Finally, a deprotonated form of (I), with the 4-hydroxy group intact, forms a six-membered {Pd—O—C··C—C=N} chelate ring in its bis-complex with palladium(II) (Tardiff *et al.*, 2007).

## 6. Synthesis and crystallization

4-Hydroxyaniline (0.00916 mol, 1.00 g) was added to a solution of 2-hydroxy-1-naphthaldehyde (0.00916 mol, 1.58 g) in ethanol (25 ml). The resulting mixture was refluxed at 333 K and stirred for 2.5 h. The reaction mixture was cooled to room temperature and the resulting orange precipitate was filtered off and washed with cold ethanol to obtain the pure product in 65% yield. Crystals of (I) were grown from a mixture of chloroform and methanol (1:1 *v/v*) by slow evaporation.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The carbon-bound H atoms were placed in calculated positions (C—H = 0.95 Å) and were included in the refinement in the riding-model approximation, with  $U_{iso}(\text{H})$  values set at  $1.2U_{eq}(\text{C})$ . The O- and N-bound H atoms were located in a difference Fourier map, but were refined with distance restraints of O—H =  $0.82 \pm 0.01$  Å and N—H =  $0.86 \pm 0.01$  Å, and with  $U_{iso}(\text{H})$  values set at  $1.5U_{eq}(\text{O})$  and  $1.2U_{eq}(\text{N})$ , respectively. To confirm the positions of the acidic-H atoms, a separate refinement was conducted whereby no distance restraints were applied resulting in O—H and N—H bond lengths of 0.93 (2) and 1.00 (3) Å, respectively.

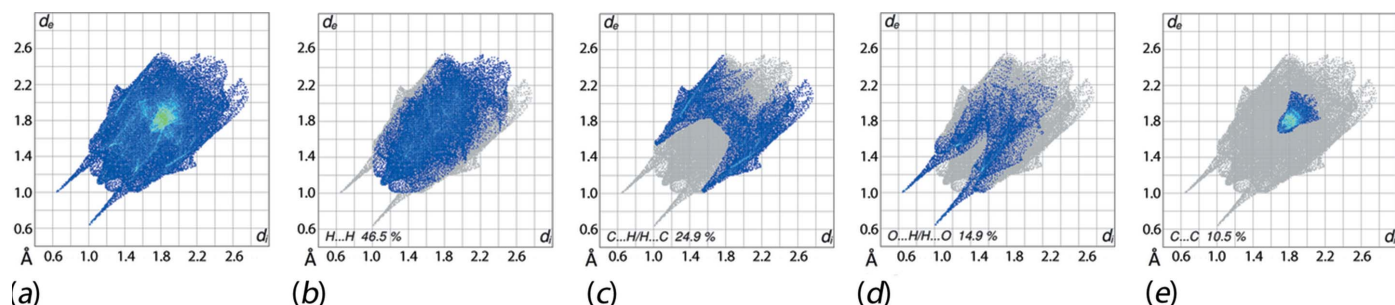


Figure 6

(a) The full two-dimensional fingerprint plots for (I), and those delineated into (b) H··H, (c) C··H/H··C, (d) O··H/H··O and (e) C··C contacts.

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>17</sub> H <sub>13</sub> NO <sub>2</sub>
<i>M<sub>r</sub></i>	263.28
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.7473 (14), 7.3042 (5), 22.7257 (19)
<i>V</i> (Å <sup>3</sup> )	2613.9 (4)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	0.09
Crystal size (mm)	0.35 × 0.25 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2016)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.941, 0.982
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	17744, 2253, 1518
<i>R<sub>int</sub></i>	0.043
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.591
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.041, 0.115, 1.04
No. of reflections	2253
No. of parameters	189
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.15, -0.16

Computer programs: *APEX3* and *SAINTE* (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

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## supporting information

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## Zwitterionic 1-[(1*E*)-[(4-hydroxyphenyl)iminio]methyl]naphthalen-2-olate: crystal structure and Hirshfeld surface analysis

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### Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### 1-[(1*E*)-[(4-Hydroxyphenyl)iminio]methyl]naphthalen-2-olate

#### Crystal data

$C_{17}H_{13}NO_2$	$D_x = 1.338 \text{ Mg m}^{-3}$
$M_r = 263.28$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, <i>Pbca</i>	Cell parameters from 3652 reflections
$a = 15.7473 (14) \text{ \AA}$	$\theta = 2.5\text{--}22.5^\circ$
$b = 7.3042 (5) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$c = 22.7257 (19) \text{ \AA}$	$T = 293 \text{ K}$
$V = 2613.9 (4) \text{ \AA}^3$	Block, colourless
$Z = 8$	$0.35 \times 0.25 \times 0.10 \text{ mm}$
$F(000) = 1104$	

#### Data collection

Bruker AXS Kappa APEXII CCD diffractometer	2253 independent reflections
$\omega$ and $\varphi$ scans	1518 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$R_{\text{int}} = 0.043$
$T_{\text{min}} = 0.941$ , $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 24.8^\circ$ , $\theta_{\text{min}} = 2.2^\circ$
17744 measured reflections	$h = -17 \rightarrow 18$
	$k = -8 \rightarrow 5$
	$l = -26 \rightarrow 26$

#### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.3444P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
2253 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
189 parameters	Extinction correction: SHELXL2014 (Sheldrick, 2015),
2 restraints	$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Hydrogen site location: mixed	Extinction coefficient: 0.0094 (11)

*Special details*

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

*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	0.50441 (9)	0.2166 (2)	0.36926 (6)	0.0610 (4)
O2	0.85495 (9)	0.0585 (2)	0.13238 (6)	0.0619 (4)
N1	0.70553 (11)	0.0841 (2)	0.17521 (7)	0.0508 (4)
C1	0.68015 (13)	0.0167 (2)	0.12484 (8)	0.0478 (5)
H1	0.6223	-0.0034	0.1199	0.057*
C2	0.65339 (12)	0.1142 (3)	0.22458 (8)	0.0466 (5)
C3	0.67240 (12)	0.2537 (3)	0.26274 (8)	0.0510 (5)
H3	0.7199	0.3265	0.2562	0.061*
C4	0.62150 (13)	0.2861 (3)	0.31052 (8)	0.0522 (5)
H4	0.6342	0.3821	0.3359	0.063*
C5	0.55214 (12)	0.1784 (3)	0.32124 (7)	0.0471 (5)
C6	0.53407 (13)	0.0373 (3)	0.28381 (8)	0.0606 (6)
H62	0.4873	-0.0373	0.2908	0.073*
C7	0.58493 (14)	0.0058 (3)	0.23593 (9)	0.0617 (6)
H7	0.5725	-0.0910	0.2108	0.074*
C8	0.73349 (12)	-0.0267 (2)	0.07838 (7)	0.0436 (5)
C9	0.82215 (13)	-0.0075 (2)	0.08526 (9)	0.0492 (5)
C10	0.87583 (14)	-0.0632 (3)	0.03806 (10)	0.0588 (6)
H10	0.9345	-0.0557	0.0423	0.071*
C11	0.84314 (15)	-0.1261 (3)	-0.01218 (10)	0.0643 (6)
H11	0.8801	-0.1621	-0.0419	0.077*
C12	0.75490 (14)	-0.1402 (3)	-0.02208 (8)	0.0533 (5)
C13	0.72247 (18)	-0.1984 (3)	-0.07628 (10)	0.0704 (7)
H13	0.7599	-0.2305	-0.1062	0.084*
C14	0.63811 (19)	-0.2091 (3)	-0.08611 (10)	0.0742 (7)
H14	0.6176	-0.2476	-0.1224	0.089*
C15	0.58281 (16)	-0.1625 (3)	-0.04171 (10)	0.0679 (6)
H15	0.5246	-0.1697	-0.0482	0.082*
C16	0.61235 (14)	-0.1058 (3)	0.01170 (9)	0.0571 (5)
H16	0.5737	-0.0761	0.0411	0.069*
C17	0.69907 (13)	-0.0913 (2)	0.02326 (8)	0.0460 (5)
H1O	0.4563 (9)	0.154 (2)	0.3685 (9)	0.069*
H1N	0.7609 (7)	0.095 (3)	0.1766 (9)	0.082 (8)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0498 (9)	0.0847 (11)	0.0486 (8)	-0.0037 (7)	0.0043 (7)	-0.0102 (7)
O2	0.0443 (9)	0.0836 (10)	0.0577 (9)	0.0018 (7)	0.0002 (7)	0.0086 (7)

N1	0.0434 (11)	0.0608 (11)	0.0482 (10)	-0.0001 (8)	0.0060 (8)	0.0034 (7)
C1	0.0427 (12)	0.0513 (11)	0.0493 (12)	0.0016 (9)	0.0034 (9)	0.0052 (9)
C2	0.0397 (11)	0.0558 (11)	0.0444 (11)	-0.0003 (9)	0.0040 (9)	0.0028 (9)
C3	0.0431 (12)	0.0576 (12)	0.0524 (12)	-0.0095 (9)	-0.0018 (9)	0.0015 (9)
C4	0.0519 (13)	0.0567 (12)	0.0480 (11)	-0.0030 (10)	-0.0056 (9)	-0.0067 (9)
C5	0.0394 (12)	0.0626 (12)	0.0392 (10)	0.0029 (9)	-0.0030 (9)	-0.0021 (8)
C6	0.0510 (13)	0.0763 (14)	0.0546 (12)	-0.0212 (11)	0.0115 (10)	-0.0124 (11)
C7	0.0611 (15)	0.0691 (14)	0.0550 (13)	-0.0174 (11)	0.0104 (10)	-0.0177 (10)
C8	0.0409 (12)	0.0443 (10)	0.0455 (10)	0.0046 (8)	0.0055 (9)	0.0082 (8)
C9	0.0467 (12)	0.0484 (11)	0.0527 (12)	0.0055 (9)	0.0060 (10)	0.0132 (9)
C10	0.0441 (13)	0.0581 (13)	0.0743 (15)	0.0068 (10)	0.0167 (11)	0.0091 (11)
C11	0.0722 (17)	0.0536 (13)	0.0671 (15)	0.0053 (11)	0.0281 (13)	0.0009 (11)
C12	0.0642 (15)	0.0428 (11)	0.0530 (12)	0.0023 (10)	0.0136 (11)	0.0065 (9)
C13	0.098 (2)	0.0580 (13)	0.0553 (14)	0.0023 (12)	0.0181 (13)	-0.0011 (10)
C14	0.104 (2)	0.0611 (14)	0.0575 (14)	-0.0012 (13)	-0.0080 (15)	-0.0014 (11)
C15	0.0748 (17)	0.0584 (14)	0.0706 (15)	0.0020 (11)	-0.0147 (13)	0.0028 (11)
C16	0.0608 (15)	0.0538 (12)	0.0568 (13)	0.0057 (10)	-0.0004 (11)	0.0038 (10)
C17	0.0520 (13)	0.0366 (10)	0.0495 (11)	0.0049 (8)	0.0053 (9)	0.0085 (8)

*Geometric parameters (Å, °)*

O1—C5	1.354 (2)	C8—C9	1.412 (3)
O1—H10	0.886 (10)	C8—C17	1.444 (3)
O2—C9	1.283 (2)	C9—C10	1.425 (3)
N1—C1	1.308 (2)	C10—C11	1.334 (3)
N1—C2	1.408 (2)	C10—H10	0.9300
N1—H1N	0.877 (10)	C11—C12	1.411 (3)
C1—C8	1.386 (2)	C11—H11	0.9300
C1—H1	0.9300	C12—C13	1.400 (3)
C2—C7	1.362 (3)	C12—C17	1.401 (3)
C2—C3	1.371 (2)	C13—C14	1.349 (3)
C3—C4	1.370 (3)	C13—H13	0.9300
C3—H3	0.9300	C14—C15	1.376 (3)
C4—C5	1.368 (3)	C14—H14	0.9300
C4—H4	0.9300	C15—C16	1.364 (3)
C5—C6	1.366 (2)	C15—H15	0.9300
C6—C7	1.371 (3)	C16—C17	1.395 (3)
C6—H62	0.9300	C16—H16	0.9300
C7—H7	0.9300		
C5—O1—H10	110.6 (13)	O2—C9—C8	121.87 (17)
C1—N1—C2	125.31 (18)	O2—C9—C10	119.78 (19)
C1—N1—H1N	111.7 (15)	C8—C9—C10	118.35 (19)
C2—N1—H1N	122.5 (15)	C11—C10—C9	120.9 (2)
N1—C1—C8	124.56 (19)	C11—C10—H10	119.5
N1—C1—H1	117.7	C9—C10—H10	119.5
C8—C1—H1	117.7	C10—C11—C12	122.8 (2)
C7—C2—C3	119.01 (17)	C10—C11—H11	118.6



C7—C2—N1	121.44 (17)	C12—C11—H11	118.6
C3—C2—N1	119.55 (17)	C13—C12—C17	119.7 (2)
C4—C3—C2	120.11 (18)	C13—C12—C11	121.5 (2)
C4—C3—H3	119.9	C17—C12—C11	118.81 (19)
C2—C3—H3	119.9	C14—C13—C12	121.5 (2)
C5—C4—C3	120.62 (18)	C14—C13—H13	119.3
C5—C4—H4	119.7	C12—C13—H13	119.3
C3—C4—H4	119.7	C13—C14—C15	119.2 (2)
O1—C5—C6	122.77 (18)	C13—C14—H14	120.4
O1—C5—C4	117.95 (17)	C15—C14—H14	120.4
C6—C5—C4	119.28 (17)	C16—C15—C14	120.8 (2)
C5—C6—C7	119.95 (19)	C16—C15—H15	119.6
C5—C6—H62	120.0	C14—C15—H15	119.6
C7—C6—H62	120.0	C15—C16—C17	121.6 (2)
C2—C7—C6	121.01 (18)	C15—C16—H16	119.2
C2—C7—H7	119.5	C17—C16—H16	119.2
C6—C7—H7	119.5	C16—C17—C12	117.17 (19)
C1—C8—C9	119.49 (18)	C16—C17—C8	123.76 (17)
C1—C8—C17	120.53 (18)	C12—C17—C8	119.06 (19)
C9—C8—C17	119.98 (17)		
C2—N1—C1—C8	-174.22 (17)	C8—C9—C10—C11	2.3 (3)
C1—N1—C2—C7	31.1 (3)	C9—C10—C11—C12	0.5 (3)
C1—N1—C2—C3	-149.93 (18)	C10—C11—C12—C13	176.90 (19)
C7—C2—C3—C4	-1.9 (3)	C10—C11—C12—C17	-1.9 (3)
N1—C2—C3—C4	179.13 (17)	C17—C12—C13—C14	-0.1 (3)
C2—C3—C4—C5	1.0 (3)	C11—C12—C13—C14	-178.9 (2)
C3—C4—C5—O1	179.76 (17)	C12—C13—C14—C15	-0.3 (3)
C3—C4—C5—C6	0.2 (3)	C13—C14—C15—C16	0.1 (3)
O1—C5—C6—C7	-179.99 (19)	C14—C15—C16—C17	0.6 (3)
C4—C5—C6—C7	-0.5 (3)	C15—C16—C17—C12	-0.9 (3)
C3—C2—C7—C6	1.7 (3)	C15—C16—C17—C8	178.00 (18)
N1—C2—C7—C6	-179.39 (19)	C13—C12—C17—C16	0.7 (3)
C5—C6—C7—C2	-0.5 (3)	C11—C12—C17—C16	179.54 (17)
N1—C1—C8—C9	3.4 (3)	C13—C12—C17—C8	-178.30 (16)
N1—C1—C8—C17	-176.69 (16)	C11—C12—C17—C8	0.6 (3)
C1—C8—C9—O2	-3.8 (3)	C1—C8—C17—C16	3.3 (3)
C17—C8—C9—O2	176.27 (16)	C9—C8—C17—C16	-176.73 (17)
C1—C8—C9—C10	176.36 (16)	C1—C8—C17—C12	-177.76 (16)
C17—C8—C9—C10	-3.6 (2)	C9—C8—C17—C12	2.2 (2)
O2—C9—C10—C11	-177.56 (18)		

*Hydrogen-bond geometry* (Å, °)

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...O2	0.88 (1)	1.81 (2)	2.553 (2)	141 (2)

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O1—H1O···O2 <sup>i</sup>	0.89 (1)	1.74 (1)	2.622 (2)	173 (1)
C7—H7···O1 <sup>ii</sup>	0.93	2.60	3.487 (3)	160

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