



(*E*)-4-Bromo-2-[(phenylimino)methyl]phenol: a new polymorph and thermochromism

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A new polymorph of (*E*)-4-bromo-2-[(phenylimino)methyl]phenol, C₁₃H₁₀BrNO, is reported, together with a low-temperature structure determination of the previously published polymorph. Both polymorphs were found to have an intramolecular O—H...N hydrogen bond between the phenol OH group and the imine N atom, forming an *S*(6) ring. The crystals were observed to have different colours at room temperature, with the previously published polymorph being more orange and the new polymorph more yellow. The planarity of the molecule in the two polymorphs was found to be significantly different, with dihedral angles (Φ) between the two aromatic rings for the previously published 'orange' polymorph of $\Phi = 1.8(2)^\circ$ at 120 K, while the new 'yellow' polymorph had $\Phi = 45.6(1)^\circ$ at 150 K. It was also observed that both polymorphs displayed some degree of thermochromism and upon cooling the 'orange' polymorph became more yellow, while the 'yellow' polymorph became paler upon cooling.

1. Introduction

A wide range of *N*-salicylideneanilines, Schiff bases of salicylaldehyde derivatives with aniline derivatives, have been synthesized (Özek *et al.*, 2007; Johmoto *et al.*, 2012). The *N*-salicylideneaniline derivatives are interesting as they have generally been found to display thermochromism, with some also showing photochromism in the solid state (Cohen & Schmidt, 1962; Cohen *et al.*, 1964; Fujiwara *et al.*, 2004). The mechanism for the chromic colour change is believed to be due to a keto–enol tautomerism (Hadjoudis & Mavridis, 2004; Robert *et al.*, 2009). The keto form is coloured, while the enol form is colourless and the switch can be induced either by changes in temperature or by irradiation. A link has been proposed between the thermochromic behaviour of a compound and the dihedral angle (Φ) between the two aromatic rings, with those having $\Phi < 25^\circ$ being more likely to be strongly thermochromic (Hadjoudis & Mavridis, 2004; Robert *et al.*, 2009). A larger *interplanar* angle allows increased orbital overlap and greater delocalization into the π -system, which reduces the basicity of the N atom and thus the thermochromism. The effect of substituents on the OH bond strength, nitrogen-accepting ability and crystal packing have also been postulated as important in the chromic behaviour of the *N*-salicylideneanilines (Hadjoudis & Mavridis, 2004; Robert *et al.*, 2009). It has also been observed that, in general, the *N*-salicylideneanilines that are more strongly coloured, typically red/orange, at room temperature, tend to be more strongly thermochromic than those that are paler, typically yellow, at room temperature (Ogawa *et al.*, 2001; Fujiwara *et al.*, 2009).

The structures of (*E*)-4-halogeno-2-[(phenylimino)methyl]phenol have been reported for fluoro (Swetha *et al.*, 2017),

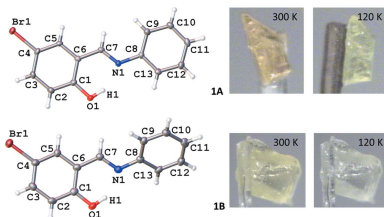


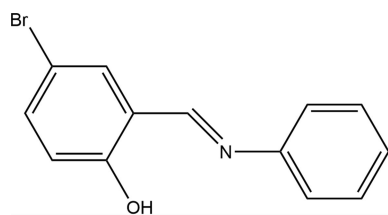
Table 1
Experimental details.

For both structures: $C_{13}H_{10}BrNO$, $M_r = 276.13$, $Z = 4$. Experiments were carried out with Mo $K\alpha$ radiation using an Oxford Diffraction Xcalibur (Sapphire3, Gemini ultra) diffractometer. An analytical absorption correction [*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)] was used. Refinement was with 2 restraints. H atoms were treated by a mixture of independent and constrained refinement.

	Polymorph 1A	Polymorph 1B
Crystal data		
Crystal system, space group	Orthorhombic, $Pca2_1$	Monoclinic, Cc
Temperature (K)	120	150
a, b, c (Å)	12.2768 (3), 4.4829 (1), 19.6694 (4)	25.8944 (13), 6.9439 (4), 6.1499 (4)
α, β, γ (°)	90, 90, 90	90, 91.381 (5), 90
V (Å ³)	1082.52 (4)	1105.48 (11)
μ (mm ⁻¹)	3.77	3.69
Crystal size (mm)	0.46 × 0.20 × 0.05	0.58 × 0.49 × 0.22
Data collection		
T_{min}, T_{max}	0.383, 0.847	0.190, 0.585
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13133, 2215, 2133	7049, 2254, 2142
R_{int}	0.043	0.051
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.625	0.625
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.053, 1.05	0.039, 0.100, 1.05
No. of reflections	2215	2254
No. of parameters	149	148
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.39, -0.23	0.95, -0.34
Absolute structure	Flack x determined using 993 quotients [[I^+ - (I^-)]/[I^+ + (I^-)] (Parsons <i>et al.</i> , 2013)	Flack x determined using 1007 quotients [[I^+ - (I^-)]/[I^+ + (I^-)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.006 (8)	-0.010 (19)

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2010), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015) and *OLEX* (Dolomanov *et al.*, 2009).

chloro (Bregman *et al.*, 1964; Ogawa *et al.*, 1998), bromo (Yan *et al.*, 2014) and iodo (Swetha *et al.*, 2019). Herein a new polymorph of (*E*)-4-bromo-2-[(phenylimino)methyl]phenol, denoted **1B**, is reported together with a new low-temperature determination of the previously reported polymorph, **1A** (Yan *et al.*, 2014). Both polymorphs were found to be thermochromic to some extent.



Polymorph **1A/1B**

2. Experimental

2.1. Synthesis and crystallization

(*E*)-4-Bromo-2-[(phenylimino)methyl]phenol was synthesized by direct condensation of 5-bromosalicylaldehyde and aniline in ethanol. The two materials (0.005 mol of each, 1.000 g of 5-bromosalicylaldehyde and 0.466 g of aniline) were dissolved separately in ethanol (25 ml). The resultant solutions were combined and refluxed with stirring for 4 h. After removal of any precipitate, the solution was rotary evaporated until further precipitate formed, the solid filtered off, rinsed with ethanol and left to dry, giving a yield of 94% (1.304 g, 0.0047 mol). Yellow single crystals (of **1B**) crashed out of the

crude reaction mixture and orange single crystals (of **1A**) were produced by recrystallization from ethanol.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms, apart from the OH hydrogen involved in the intramolecular hydrogen bonding with the imine N atom, were positioned geometrically and refined using a riding model. The H atoms involved in the intramolecular hydrogen bond were located in the Fourier difference map wherever feasible. In **1A**, the O—H distance was restrained to 0.86 (1) Å.

3. Results and discussion

The structures of polymorphs **1A** and **1B** are shown in Fig. 1. The structure of **1A** at 120 K was consistent with the previously published structure at room temperature (Yan *et al.*, 2014). The structure of **1A** was obtained in the orthorhombic space group $Pca2_1$, while **1B** was obtained in the monoclinic space group Cc . The compound consists of a hydroxy-substituted phenyl ring linked *via* an imine group to a second unsubstituted phenyl group. In both polymorphs, the structures were found to exist in the enol form, with C7=N1 bond lengths of 1.282 (4) Å for **1A** and 1.284 (10) Å for **1B**, indicating a double bond, and C1—O1 bond lengths of 1.350 (5) Å for **1A** and 1.351 (9) Å for **1B**, indicating a single bond. The structures showed quite different dihedral angles, with **1A** having $\Phi = 1.8$ (2)° at 120 K and **1B** having $\Phi =$

Table 2
Hydrogen-bond geometry (Å, °) for polymorph **1A**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots N1	0.86 (1)	1.82 (3)	2.593 (4)	150 (5)

Table 3
Hydrogen-bond geometry (Å, °) for polymorph **1B**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots N1	0.86 (11)	1.82 (11)	2.590 (10)	148 (10)

45.6 (1)° at 150 K. Upon cooling, the structures were both found to display some degree of thermochromism with **1A** changing from orange at room temperature to yellow at 120 K and **1B**, which was yellow at room temperature, becoming slightly paler at 150 K (Fig. 2). The differences in the thermochromic behaviour of the two polymorphs are consistent with literature suggestions that a larger dihedral angle increases the overlap of the π -system reducing the nitrogen basicity, disfavours the keto form and thus also reducing the thermochromism of the compound.

An intramolecular O1–H1 \cdots N1 hydrogen bond, involving the phenol OH group and imine N atom, was identified in the structures of both polymorphs and creates an $S(6)$ ring. The hydrogen-bonding parameters were almost identical in the two structures, with a donor–acceptor distance of ~ 2.59 Å and a hydrogen-bond angle of $\sim 150^\circ$ (Tables 2 and 3.). The packing of the two polymorphs was unsurprisingly significantly different given the large difference in the dihedral angles. In polymorph **1A**, the molecules are essentially planar

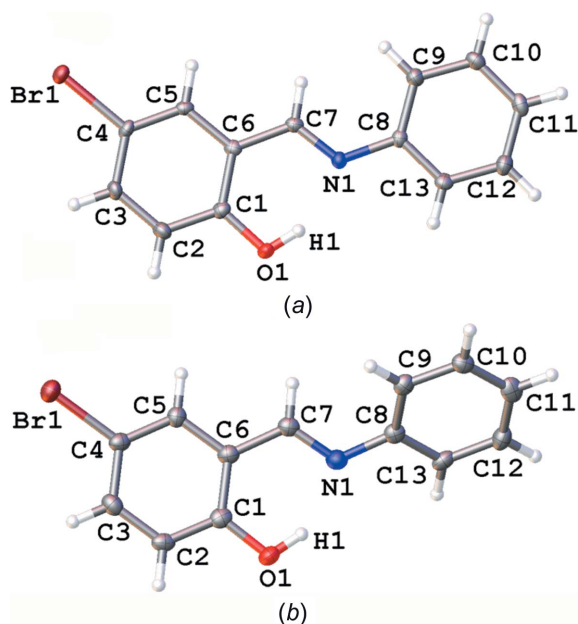


Figure 1
Illustration of the structures of (a) **1A** and (b) **1B** at 120 (2) and 150 (2) K, respectively, with the atomic numbering schemes depicted. Anisotropic displacement parameters are shown at the 50% probability level.

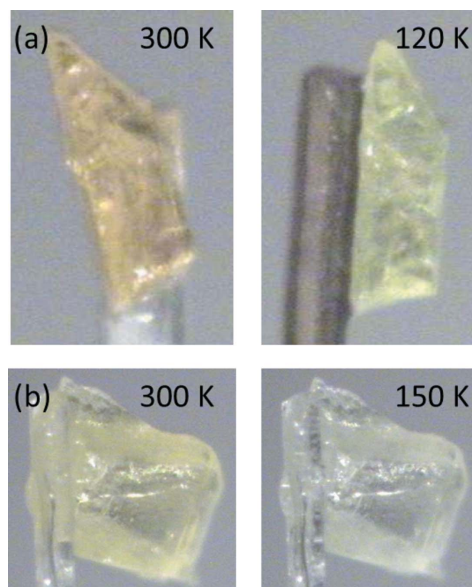


Figure 2
Illustration of the colour change observed upon cooling (a) **1A** and (b) **1B**.

and orientated diagonally such that the plane of the molecule is perpendicular to the bc plane and, as a result of the 2_1 screw axis, the diagonal slant of alternate molecules along the a -axis direction essentially align in opposite directions (Fig. 3a). It was also noted that there were short π -type contacts between the C=N group and the phenol ring in the $0\bar{1}1$ direction, with a centroid-to-centroid (C=N) distance of 3.326 (1) Å. These can be seen on the Hirshfeld surface of **1A** as red dots (Fig. 4a). In polymorph **1B**, although the molecules themselves are

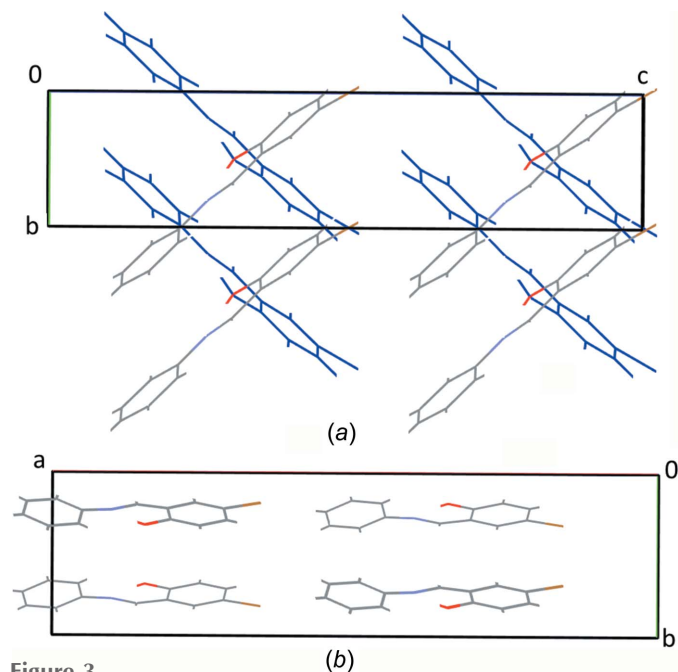


Figure 3
(a) Illustration of the packing for **1A**, looking down the a axis; molecules in blue are in-plane behind those in element colours. (b) View of polymorph **1B**, looking down the c axis.

twisted, the molecules are orientated relative to each other such that they create planes parallel to the *ac* plane direction (see Fig. 3*b*).

Examining the Hirshfeld fingerprint plots (Turner *et al.*, 2017) for the two structures highlights the differences in the two structures, not least in the shapes of the two plots (Fig. 4). For **1A**, the O···H and Br···H contacts are quite obvious, while in **1B** the H···H and C···H contacts are significantly more pronounced, slightly masking the O···H and Br···H contacts. These differences are very apparent on the Hirshfeld surface for both compounds with a greater number of red spots on the surface of **1A** that are more noticeable than for **1B**, showing that **1A** has more short contacts.

The two polymorphs of (*E*)-4-bromo-2-[(phenylimino)-methyl]phenol reported herein are particularly interesting as part of a study into *N*-salicylideneanilines because they show significantly different molecular conformations and colours at room temperature. In line with the literature, the extent of the thermochromism was found to be linked to the dihedral angle, with **1A** [$\Phi = 1.8 (2)^\circ$] showing a greater colour change upon cooling than observed for **1B** [$\Phi = 45.6 (1)^\circ$].

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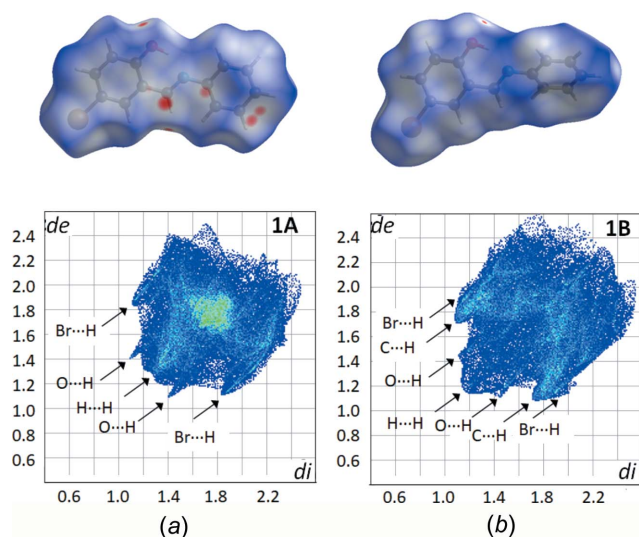


Figure 4
The Hirshfeld surface plot (top) and fingerprint plot (bottom) for (a) **1A** and (b) **1B**.

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Computing details

For both structures, data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2010); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *OLEX* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX* (Dolomanov *et al.*, 2009).

(*E*)-4-Bromo-2-[(phenylimino)methyl]phenol (1A)

Crystal data

$C_{13}H_{10}BrNO$

$M_r = 276.13$

Orthorhombic, *Pca*2₁

$a = 12.2768$ (3) Å

$b = 4.4829$ (1) Å

$c = 19.6694$ (4) Å

$V = 1082.52$ (4) Å³

$Z = 4$

$F(000) = 552$

$D_x = 1.694$ Mg m⁻³

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

Cell parameters from 5409 reflections

$\theta = 2.7$ – 30.6°

$\mu = 3.77$ mm⁻¹

$T = 120$ K

Block, orange

$0.46 \times 0.20 \times 0.05$ mm

Data collection

Xcalibur, Sapphire3, Gemini ultra diffractometer

Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator

Detector resolution: 16.1511 pixels mm⁻¹

ω scans

Absorption correction: analytical

[*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.383$, $T_{\max} = 0.847$

13133 measured reflections

2215 independent reflections

2133 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 3.3^\circ$

$h = -15 \rightarrow 15$

$k = -5 \rightarrow 5$

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.053$

$S = 1.05$

2215 reflections

149 parameters

2 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.2498P]$

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

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

$\Delta\rho_{\max} = 0.39$ e Å⁻³

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
993 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: -0.006 (8)

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.

Refinement. Single-crystal X-ray diffraction measurements for **1A** were collected at 120 (2) K and **1B** were collected at 150 (2) K on an Oxford Diffraction diffractometer. Both datasets were collected using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and recorded on a CCD detector. The structures were solved using direct methods in ShelXS (Sheldrick, 2008). All structures were refined by full matrix least squares on F^2 using SHELXL (Sheldrick, 2008; Sheldrick, 2015) in Olex2 (Dolomanov *et al.*, 2009).

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.42487 (2)	1.04053 (7)	0.52257 (3)	0.01818 (11)
C4	0.3325 (3)	0.8715 (8)	0.45495 (18)	0.0151 (7)
C5	0.3746 (3)	0.6746 (8)	0.40824 (17)	0.0136 (7)
H5	0.449969	0.627095	0.409090	0.016*
C3	0.2233 (3)	0.9502 (8)	0.45376 (19)	0.0174 (8)
H3	0.195360	1.087904	0.486075	0.021*
C6	0.3066 (3)	0.5436 (8)	0.35936 (19)	0.0139 (7)
C2	0.1551 (3)	0.8270 (9)	0.40524 (19)	0.0188 (8)
H2	0.080442	0.882022	0.403983	0.023*
C1	0.1956 (3)	0.6224 (9)	0.35818 (18)	0.0161 (8)
O1	0.1258 (3)	0.5046 (6)	0.31239 (14)	0.0199 (6)
C7	0.3514 (3)	0.3292 (8)	0.31122 (18)	0.0145 (7)
H7	0.427300	0.288024	0.311612	0.017*
N1	0.2898 (2)	0.1953 (6)	0.26834 (14)	0.0138 (6)
C8	0.3316 (3)	-0.0169 (7)	0.2211 (2)	0.0139 (8)
C13	0.2578 (3)	-0.1317 (8)	0.17480 (18)	0.0171 (7)
H13	0.184046	-0.068148	0.175947	0.021*
C11	0.3978 (4)	-0.4362 (8)	0.1251 (2)	0.0193 (8)
H11	0.420342	-0.577964	0.092026	0.023*
C9	0.4398 (3)	-0.1160 (9)	0.2201 (2)	0.0176 (8)
H9	0.490778	-0.040319	0.252150	0.021*
C10	0.4724 (3)	-0.3257 (8)	0.17207 (19)	0.0187 (8)
H10	0.545717	-0.393545	0.171327	0.022*
C12	0.2912 (3)	-0.3398 (9)	0.12650 (19)	0.0200 (8)
H12	0.240293	-0.415470	0.094460	0.024*
H1	0.161 (3)	0.369 (8)	0.291 (2)	0.036 (14)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01826 (17)	0.02317 (18)	0.01312 (16)	-0.00238 (12)	-0.0012 (2)	-0.0025 (3)

C4	0.0181 (19)	0.0169 (17)	0.0104 (17)	-0.0043 (15)	-0.0021 (13)	0.0006 (15)
C5	0.0115 (17)	0.0143 (17)	0.0149 (17)	-0.0001 (14)	-0.0009 (14)	0.0041 (14)
C3	0.019 (2)	0.0194 (18)	0.0138 (18)	0.0009 (15)	0.0035 (16)	-0.0029 (15)
C6	0.0147 (18)	0.0149 (17)	0.0122 (18)	0.0005 (14)	0.0009 (14)	0.0048 (14)
C2	0.0167 (19)	0.0221 (19)	0.0175 (19)	0.0039 (16)	0.0023 (15)	0.0003 (16)
C1	0.0161 (18)	0.0187 (18)	0.0135 (18)	-0.0012 (15)	-0.0011 (15)	0.0029 (15)
O1	0.0129 (14)	0.0282 (15)	0.0186 (14)	0.0013 (11)	-0.0026 (11)	-0.0074 (12)
C7	0.0129 (17)	0.0149 (17)	0.0156 (17)	0.0004 (15)	0.0007 (14)	0.0036 (15)
N1	0.0157 (15)	0.0138 (15)	0.0120 (13)	0.0003 (11)	0.0005 (13)	0.0007 (12)
C8	0.017 (2)	0.0127 (17)	0.0115 (18)	-0.0014 (14)	0.0011 (13)	0.0018 (14)
C13	0.0175 (19)	0.0157 (16)	0.0181 (18)	0.0025 (15)	-0.0012 (15)	0.0031 (15)
C11	0.028 (2)	0.0154 (19)	0.0144 (19)	0.0009 (16)	0.0066 (16)	0.0014 (15)
C9	0.0182 (19)	0.0170 (18)	0.0176 (19)	0.0005 (15)	0.0007 (14)	-0.0001 (15)
C10	0.0173 (19)	0.0197 (19)	0.0190 (19)	0.0019 (15)	0.0048 (15)	0.0026 (16)
C12	0.025 (2)	0.0184 (19)	0.0170 (18)	-0.0016 (16)	-0.0010 (16)	-0.0016 (16)

Geometric parameters (Å, °)

Br1—C4	1.905 (4)	C7—N1	1.282 (4)
C4—C5	1.375 (5)	N1—C8	1.425 (5)
C4—C3	1.387 (5)	C8—C13	1.384 (5)
C5—H5	0.9500	C8—C9	1.401 (5)
C5—C6	1.402 (5)	C13—H13	0.9500
C3—H3	0.9500	C13—C12	1.393 (5)
C3—C2	1.384 (6)	C11—H11	0.9500
C6—C1	1.408 (5)	C11—C10	1.393 (6)
C6—C7	1.457 (5)	C11—C12	1.379 (6)
C2—H2	0.9500	C9—H9	0.9500
C2—C1	1.394 (5)	C9—C10	1.392 (5)
C1—O1	1.350 (5)	C10—H10	0.9500
O1—H1	0.857 (14)	C12—H12	0.9500
C7—H7	0.9500		
C5—C4—Br1	119.9 (3)	N1—C7—H7	119.5
C5—C4—C3	121.0 (3)	C7—N1—C8	121.9 (3)
C3—C4—Br1	119.1 (3)	C13—C8—N1	116.2 (3)
C4—C5—H5	119.9	C13—C8—C9	119.6 (4)
C4—C5—C6	120.2 (3)	C9—C8—N1	124.2 (3)
C6—C5—H5	119.9	C8—C13—H13	119.8
C4—C3—H3	120.2	C8—C13—C12	120.4 (4)
C2—C3—C4	119.6 (3)	C12—C13—H13	119.8
C2—C3—H3	120.2	C10—C11—H11	120.0
C5—C6—C1	118.8 (3)	C12—C11—H11	120.0
C5—C6—C7	119.8 (3)	C12—C11—C10	119.9 (4)
C1—C6—C7	121.3 (3)	C8—C9—H9	120.1
C3—C2—H2	119.8	C10—C9—C8	119.7 (4)
C3—C2—C1	120.3 (4)	C10—C9—H9	120.1
C1—C2—H2	119.8	C11—C10—H10	119.9

C2—C1—C6	119.9 (3)	C9—C10—C11	120.1 (4)
O1—C1—C6	121.8 (3)	C9—C10—H10	119.9
O1—C1—C2	118.3 (3)	C13—C12—H12	119.9
C1—O1—H1	107 (3)	C11—C12—C13	120.2 (4)
C6—C7—H7	119.5	C11—C12—H12	119.9
N1—C7—C6	120.9 (3)		
Br1—C4—C5—C6	178.4 (3)	C1—C6—C7—N1	-3.3 (5)
Br1—C4—C3—C2	-179.5 (3)	C7—C6—C1—C2	179.6 (3)
C4—C5—C6—C1	1.4 (5)	C7—C6—C1—O1	-0.3 (6)
C4—C5—C6—C7	-178.4 (3)	C7—N1—C8—C13	-176.1 (3)
C4—C3—C2—C1	0.7 (6)	C7—N1—C8—C9	5.1 (5)
C5—C4—C3—C2	0.6 (6)	N1—C8—C13—C12	179.8 (3)
C5—C6—C1—C2	-0.1 (5)	N1—C8—C9—C10	179.6 (3)
C5—C6—C1—O1	179.9 (3)	C8—C13—C12—C11	0.9 (6)
C5—C6—C7—N1	176.4 (3)	C8—C9—C10—C11	0.1 (6)
C3—C4—C5—C6	-1.6 (5)	C13—C8—C9—C10	0.8 (6)
C3—C2—C1—C6	-0.9 (6)	C9—C8—C13—C12	-1.3 (6)
C3—C2—C1—O1	179.0 (3)	C10—C11—C12—C13	0.1 (5)
C6—C7—N1—C8	-179.5 (3)	C12—C11—C10—C9	-0.6 (5)

Hydrogen-bond geometry (Å, °)

<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>
O1—H1...N1	0.86 (1)	1.82 (3)	2.593 (4)	150 (5)

(*E*)-4-Bromo-2-((phenylimino)methyl)phenol (1B)

Crystal data

C₁₃H₁₀BrNO

M_r = 276.13

Monoclinic, *Cc*

a = 25.8944 (13) Å

b = 6.9439 (4) Å

c = 6.1499 (4) Å

β = 91.381 (5)°

V = 1105.48 (11) Å³

Z = 4

F(000) = 552

D_x = 1.659 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3202 reflections

θ = 3.0–30.7°

μ = 3.69 mm⁻¹

T = 150 K

Block, yellow

0.58 × 0.49 × 0.22 mm

Data collection

Xcalibur, Sapphire3, Gemini ultra
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 16.1511 pixels mm⁻¹

ω scans

Absorption correction: analytical

[CrysAlis PRO (Oxford Diffraction, 2010),
based on expressions derived by Clark & Reid
(1995)]

T_{min} = 0.190, *T_{max}* = 0.585

7049 measured reflections

2254 independent reflections

2142 reflections with *I* > 2σ(*I*)

R_{int} = 0.051

θ_{max} = 26.4°, θ_{min} = 3.0°

h = -32→32

k = -8→8

l = -7→7

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.100$

$S = 1.05$

2254 reflections

148 parameters

2 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.067P)^2]$

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

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

$\Delta\rho_{\max} = 0.95 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$

Absolute structure: Flack x determined using
1007 quotients $[(I+)-(I-)]/[(I+)+(I-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.010 (19)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.15729 (2)	0.68317 (7)	0.23237 (2)	0.0279 (2)
C5	0.2655 (3)	0.6834 (8)	0.3219 (12)	0.0199 (13)
H5	0.268030	0.635213	0.177996	0.024*
C2	0.2577 (3)	0.8229 (8)	0.7462 (12)	0.0211 (15)
H2	0.254820	0.870832	0.890033	0.025*
C4	0.2176 (3)	0.7189 (9)	0.4073 (11)	0.0209 (13)
C3	0.2131 (3)	0.7895 (8)	0.6189 (12)	0.0227 (13)
H3	0.179986	0.814594	0.675762	0.027*
C6	0.3105 (3)	0.7189 (9)	0.4487 (11)	0.0205 (13)
O1	0.3481 (2)	0.8190 (6)	0.7919 (9)	0.0261 (11)
H1	0.375 (4)	0.789 (12)	0.720 (18)	0.031*
N1	0.4028 (3)	0.7276 (11)	0.4603 (12)	0.0217 (14)
C7	0.3609 (3)	0.6969 (8)	0.3496 (12)	0.0206 (13)
H7	0.362760	0.659495	0.201366	0.025*
C1	0.3059 (3)	0.7863 (8)	0.6634 (12)	0.0214 (13)
C8	0.4511 (3)	0.7333 (9)	0.3593 (11)	0.0201 (12)
C10	0.5062 (3)	0.8319 (8)	0.0687 (12)	0.0225 (14)
H10	0.510473	0.889386	-0.069899	0.027*
C9	0.4569 (3)	0.8171 (8)	0.1546 (12)	0.0217 (14)
H9	0.427585	0.863641	0.074706	0.026*
C12	0.5427 (3)	0.6791 (9)	0.3880 (13)	0.0248 (15)
H12	0.571957	0.630545	0.466579	0.030*
C13	0.4940 (3)	0.6661 (8)	0.4764 (12)	0.0221 (14)
H13	0.490036	0.611519	0.616581	0.027*
C11	0.5489 (3)	0.7631 (11)	0.1843 (13)	0.0257 (15)
H11	0.582359	0.773163	0.124973	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0212 (3)	0.0346 (3)	0.0276 (3)	0.0000 (4)	-0.0036 (2)	-0.0023 (4)
C5	0.020 (3)	0.017 (3)	0.023 (4)	0.000 (2)	0.000 (3)	0.002 (2)
C2	0.030 (4)	0.016 (3)	0.017 (4)	-0.004 (3)	0.001 (3)	0.000 (2)
C4	0.025 (3)	0.020 (3)	0.018 (3)	-0.003 (2)	0.000 (2)	0.000 (2)
C3	0.025 (3)	0.020 (3)	0.024 (3)	0.004 (2)	0.005 (3)	0.002 (2)
C6	0.025 (3)	0.017 (3)	0.020 (3)	0.001 (2)	-0.001 (2)	0.000 (2)
O1	0.023 (3)	0.035 (3)	0.021 (3)	0.0002 (19)	-0.004 (2)	-0.0046 (19)
N1	0.025 (3)	0.020 (3)	0.020 (3)	0.003 (2)	0.000 (2)	0.001 (2)
C7	0.025 (4)	0.017 (3)	0.020 (3)	0.000 (2)	0.001 (3)	0.000 (2)
C1	0.027 (4)	0.017 (3)	0.021 (3)	-0.001 (2)	-0.001 (3)	0.004 (2)
C8	0.024 (3)	0.014 (3)	0.022 (3)	0.000 (2)	0.000 (2)	-0.001 (2)
C10	0.027 (4)	0.019 (3)	0.022 (3)	-0.002 (2)	0.003 (3)	0.000 (2)
C9	0.023 (3)	0.017 (3)	0.025 (4)	-0.001 (2)	-0.002 (3)	-0.001 (2)
C12	0.020 (4)	0.023 (3)	0.031 (4)	0.001 (2)	-0.004 (3)	-0.001 (2)
C13	0.026 (4)	0.018 (3)	0.021 (4)	-0.001 (2)	-0.007 (3)	-0.001 (2)
C11	0.026 (4)	0.016 (4)	0.036 (4)	-0.005 (3)	0.004 (3)	-0.001 (3)

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

Br1—C4	1.891 (7)	N1—C8	1.410 (10)
C5—H5	0.9500	C7—H7	0.9500
C5—C4	1.380 (10)	C8—C9	1.398 (10)
C5—C6	1.409 (10)	C8—C13	1.391 (10)
C2—H2	0.9500	C10—H10	0.9500
C2—C3	1.398 (11)	C10—C9	1.398 (10)
C2—C1	1.383 (11)	C10—C11	1.385 (11)
C4—C3	1.398 (9)	C9—H9	0.9500
C3—H3	0.9500	C12—H12	0.9500
C6—C7	1.463 (9)	C12—C13	1.388 (11)
C6—C1	1.409 (10)	C12—C11	1.395 (11)
O1—H1	0.86 (11)	C13—H13	0.9500
O1—C1	1.351 (9)	C11—H11	0.9500
N1—C7	1.284 (10)		
C4—C5—H5	120.1	O1—C1—C2	118.5 (7)
C4—C5—C6	119.8 (6)	O1—C1—C6	121.2 (6)
C6—C5—H5	120.1	C9—C8—N1	121.6 (7)
C3—C2—H2	119.9	C13—C8—N1	118.0 (7)
C1—C2—H2	119.9	C13—C8—C9	120.2 (6)
C1—C2—C3	120.3 (7)	C9—C10—H10	119.8
C5—C4—Br1	119.8 (5)	C11—C10—H10	119.8
C5—C4—C3	120.9 (6)	C11—C10—C9	120.4 (7)
C3—C4—Br1	119.3 (5)	C8—C9—H9	120.3
C2—C3—H3	120.2	C10—C9—C8	119.3 (7)
C4—C3—C2	119.5 (6)	C10—C9—H9	120.3

C4—C3—H3	120.2	C13—C12—H12	119.9
C5—C6—C7	119.1 (6)	C13—C12—C11	120.3 (7)
C5—C6—C1	119.3 (6)	C11—C12—H12	119.9
C1—C6—C7	121.4 (6)	C8—C13—H13	120.0
C1—O1—H1	108 (7)	C12—C13—C8	119.9 (7)
C7—N1—C8	121.1 (7)	C12—C13—H13	120.0
C6—C7—H7	119.6	C10—C11—C12	119.8 (7)
N1—C7—C6	120.8 (7)	C10—C11—H11	120.1
N1—C7—H7	119.6	C12—C11—H11	120.1
C2—C1—C6	120.2 (7)		
Br1—C4—C3—C2	-177.7 (5)	C7—C6—C1—C2	173.9 (5)
C5—C4—C3—C2	-0.6 (9)	C7—C6—C1—O1	-5.2 (9)
C5—C6—C7—N1	-179.8 (6)	C7—N1—C8—C9	38.4 (11)
C5—C6—C1—C2	-2.0 (9)	C7—N1—C8—C13	-146.6 (7)
C5—C6—C1—O1	178.8 (5)	C1—C2—C3—C4	0.0 (9)
C4—C5—C6—C7	-174.6 (6)	C1—C6—C7—N1	4.2 (10)
C4—C5—C6—C1	1.4 (9)	C8—N1—C7—C6	-171.0 (6)
C3—C2—C1—C6	1.3 (9)	C9—C8—C13—C12	-1.2 (9)
C3—C2—C1—O1	-179.5 (5)	C9—C10—C11—C12	-0.2 (10)
C6—C5—C4—Br1	176.9 (4)	C13—C8—C9—C10	0.3 (9)
C6—C5—C4—C3	-0.1 (9)	C13—C12—C11—C10	-0.7 (10)
N1—C8—C9—C10	175.2 (6)	C11—C10—C9—C8	0.4 (9)
N1—C8—C13—C12	-176.3 (6)	C11—C12—C13—C8	1.5 (10)

Hydrogen-bond geometry (Å, °)

<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>
O1—H1...N1	0.86 (11)	1.82 (11)	2.590 (10)	148 (10)