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# (*E*)-2-[[*(2*-Aminophenyl)imino]methyl]-5-(benzyloxy)phenol and (*Z*)-3-benzyloxy-6-[[*(5*-chloro-2-hydroxyphenyl)amino]methylidene}cyclohexa-2,4-dien-1-one

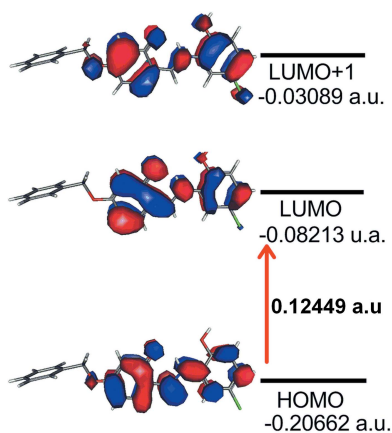
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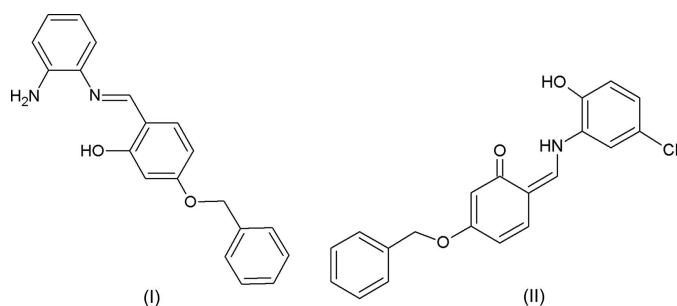
The title Schiff base compounds, C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> (I) and C<sub>20</sub>H<sub>16</sub>ClNO<sub>3</sub> (II), were synthesized from 4-benzyloxy-2-hydroxybenzaldehyde by reaction with 1,2-diaminobenzene for (I), and condensation with 2-amino-4-chlorophenol for (II). Compound (I) adopts the enol–imine tautomeric form with an *E* configuration about the C=N imine bond. In contrast, the *o*-hydroxy Schiff base (II), is in the keto–imine tautomeric form with a *Z* configuration about the CH–NH bond. Neither molecule is planar. In (I), the central benzene ring makes dihedral angles of 46.80 (10) and 78.19 (10)° with the outer phenylamine and phenyl rings, respectively, while for (II), the corresponding angles are 5.11 (9) and 58.42 (11)°, respectively. The molecular structures of both compounds are affected by the formation of intramolecular contacts, an O–H···N hydrogen bond for (I) and an N–H···O hydrogen bond for (II); each contact generates an *S*(6) ring motif. In the crystal of (I), strong N–H···O hydrogen bonds form zigzag chains of molecules along the *b*-axis direction. Molecules are further linked by C–H···π interactions and offset π–π contacts and these combine to form a three-dimensional network. The density functional theory (DFT) optimized structure of compound (II), at the B3LYP/6–311+G(*d*) level, confirmed that the keto tautomeric form of the compound, as found in the structure determination, is the lowest energy form. The antioxidant capacities of both compounds were determined by the cupric reducing antioxidant capacity (CUPRAC) process.

## 1. Chemical context

Schiff base compounds have been used as fine chemicals and medicinal substrates (Fun *et al.*, 2011). Studies of the tautomerism of Schiff bases (Alpaslan *et al.*, 2011; Blagus *et al.*, 2010; Ünver *et al.*, 2002) have demonstrated that the stabilization of the keto–amino tautomer in the crystal depends mostly on the parent *o*-hydroxyl aldehyde, the type of the N-substituent, the electron withdrawing or donating of the N-substituent, its position and stereochemistry (Blagus *et al.*, 2010). Schiff base compounds exhibit a broad range of biological activities, including antifungal and antibacterial (da Silva *et al.*, 2011). They are used as anion sensors (Dalapati *et al.*, 2011; Khalil *et al.*, 2009), non-linear optical compounds (Sun *et al.*, 2012), and as versatile ligands in coordination chemistry (Khanmohammadi *et al.*, 2009; Keypour *et al.*, 2010). In view of the interest in such materials we have synthesized the title compounds, (I) and (II), and report their crystal

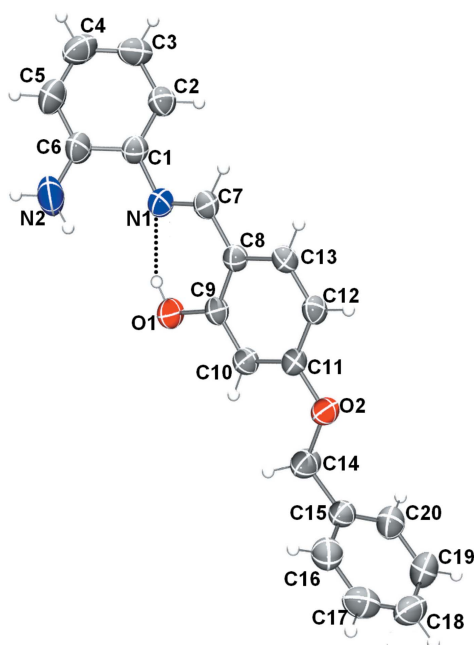


structures here. The common structural feature of these compounds is the presence of a benzyloxy substituent on the central ring, although each molecule adopts a different tautomeric form. Density functional theory (DFT) calculations on (II), carried out at the B3LYP/6-311+G(d) level, are compared with the experimentally determined molecular structure and confirm that the keto tautomeric form of this compound, similar to that found in the structure determination, is the lowest energy form. The antioxidant capacity of both compounds was determined by the cupric reducing antioxidant capacity (CUPRAC) process.



## 2. Structural commentary

The molecular structures of compounds (I) and (II), illustrated in Figs. 1 and 2, respectively, are influenced by intramolecular hydrogen bonds: the O—H···N hydrogen bond in (I) and the N—H···O contact in (II) (Tables 1 and 2) both form *S*(6) ring motifs. In compound (II), the N atom is protonated and the C9—O1 bond length, 1.277 (2) Å confirms



**Figure 1**  
The molecular structure of compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular O—H···N hydrogen bond is shown as a dashed line.

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

*Cg*1 and *Cg*3 are the centroids of the C1–C6 and C15–C20 rings respectively.

<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	0.82	1.90	2.629 (2)	147
N2—H2A···O2 <sup>i</sup>	0.86	2.43	3.211 (3)	151
C14—H14B··· <i>Cg</i> 1 <sup>ii</sup>	0.97	2.74	3.704 (3)	171
C16—H16··· <i>Cg</i> 1 <sup>iii</sup>	0.93	2.96	3.792 (3)	150
C18—H18··· <i>Cg</i> 3 <sup>iv</sup>	0.93	2.94	3.620 (2)	131

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

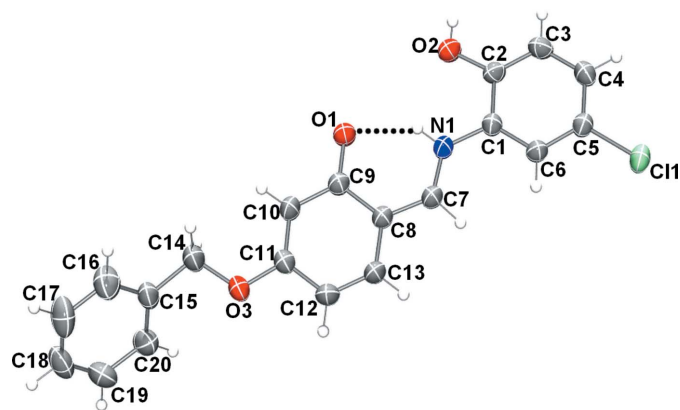
**Table 2**  
Hydrogen-bond geometry (Å, °) for (II).

*Cg*3 is the centroid of the C15–C20 ring.

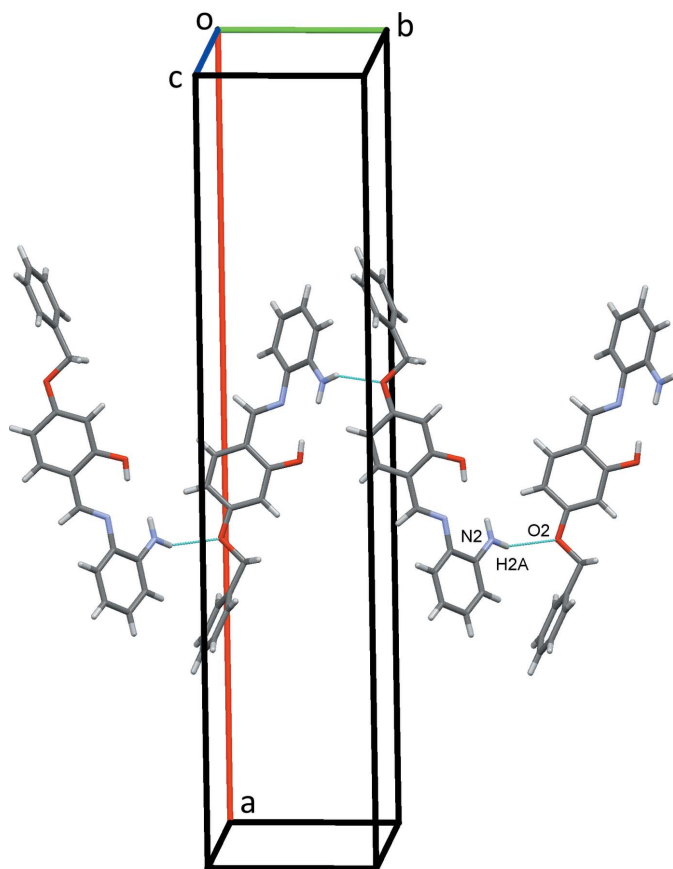
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1···O1	0.86 (2)	1.93 (2)	2.637 (2)	139 (2)
N1—H1···O2	0.86 (2)	2.27 (2)	2.620 (2)	104.5 (18)
O2—H2···O1 <sup>i</sup>	0.80 (3)	1.84 (3)	2.619 (2)	165 (3)
C7—H7···Cl1 <sup>ii</sup>	0.98 (2)	2.84 (2)	3.7971 (18)	164.5 (17)
C14—H14A··· <i>Cg</i> 3 <sup>iii</sup>	0.97	2.71	3.569 (3)	148

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

this to be double bond. In compound (I), however, the C9=O1 bond length of 1.3498 (19) Å indicates a single bond. Bond C7=C8 [1.395 (3) Å] is a double bond in compound (II), whereas the corresponding bond in (I) [1.435 (3) Å] is a single bond. Compound (I) adopts the enol-imine tautomeric form and the configuration of the C7=N1 imine bond is *E* with a length of 1.288 (3) Å. In contrast the *o*-hydroxy Schiff base of (II), has a *Z* configuration about the C7=C8 double bond and the molecule adopts the keto-imine tautomeric form, with the N1—C7 bond length being 1.309 (2) Å. Neither molecule is planar: in (I), the central ring (C8–C13) is inclined to the two outer rings (C1–C6 and C15–C20) by 46.80 (10) and 78.19 (10)°, respectively, while for (II), the dihedral angles between these rings are 5.11 (9) and 58.42 (11)°, respectively. In compound (II), the C1—N1—C7 angle is 127.15 (17)°.



**Figure 2**  
The molecular structure of compound (II), with the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular N—H···O hydrogen bond is shown as a dashed line.

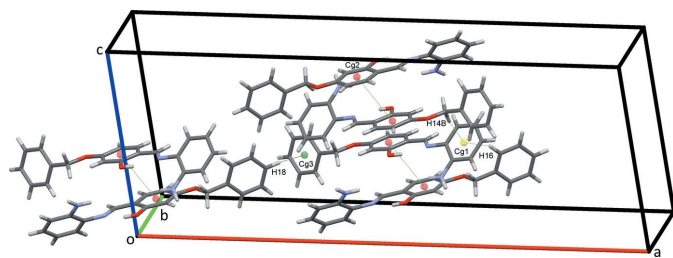


**Figure 3**  
Zigzag chains of molecules of (I) along the  $b$ -axis direction. Hydrogen bonds are drawn as blue dashed lines.

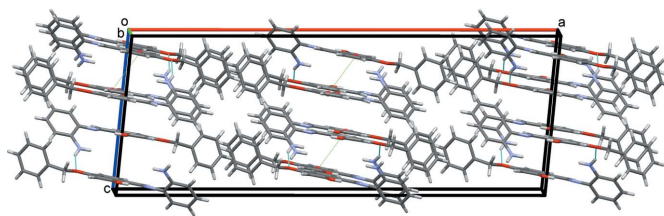
### 3. Supramolecular features

In the crystal of (I), strong  $N2-H2A \cdots O2^i$  hydrogen bonds, Table 1, form zigzag chains of molecules along the  $b$ -axis direction, Fig. 3. Weaker  $C-H \cdots \pi$  and offset  $\pi-\pi$  stacking interactions also contribute to the packing (Fig. 4) [ $Cg2 \cdots Cg2(-x, y, -z + \frac{1}{2}) = 3.8151(11) \text{ \AA}$ ;  $Cg2$  is the centroid of the central ring]. The overall crystal packing for this structure is shown in Fig. 5.

For (II), strong  $O2-H2 \cdots O1^i$  hydrogen bonds Table 2, form inversion dimers that enclose  $R_2^2(18)$  rings. These combine with weaker  $C7-H7 \cdots Cl1$  hydrogen bonds, which



**Figure 4**  
 $C-H \cdots \pi$  and  $\pi-\pi$  contacts (dotted green lines) in the crystal structure of (I).

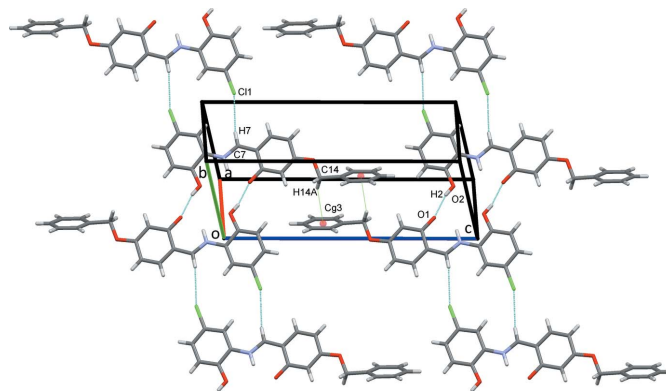


**Figure 5**  
Overall packing for (I) viewed along the  $b$ -axis direction.

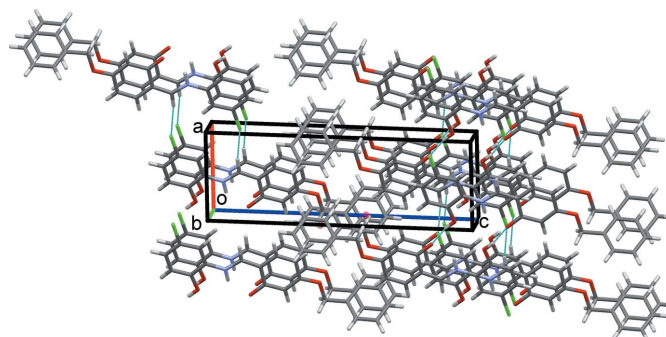
also generate inversion dimers but with  $R_2^2(14)$  motifs. Inversion-related  $C14-H14A \cdots Cg3^{ii}$  contacts lead to the formation of sheets of molecules parallel to  $(\bar{1}20)$ , Fig. 6, which are stacked approximately along the  $b$ -axis direction. The overall packing for this structure is shown in Fig. 7.

### 4. Database survey

A search of the Cambridge Database (Version 5.39, updated February 2018; Groom *et al.* 2016) for structures similar to (I) gave two hits, *viz.* ( $Z$ )-6-{2-[( $E$ )-2,4-dihydroxybenzylidene-amino]phenylaminomethylene}-3-hydroxycyclohexa-2,4-dienone (Fun *et al.*, 2008) and ( $E$ )-5-(benzyloxy)-2-[(4-nitrophenyl)carboimidoyl]phenol reported by us in 2015 (Ghichi *et al.*, 2015). More recently, we have described the very similar structure of ( $E$ )-5-benzyloxy-2-[[4-(chlorophenyl)imino]methyl]phenol (Ghichi *et al.*, 2018). A search for analogues of (II) produced three related phenylethylamino)methyl-



**Figure 6**  
Sheets of molecules of (II) parallel to  $(\bar{1}20)$ .



**Figure 7**  
Overall packing for (II) viewed along the  $b$ -axis direction.

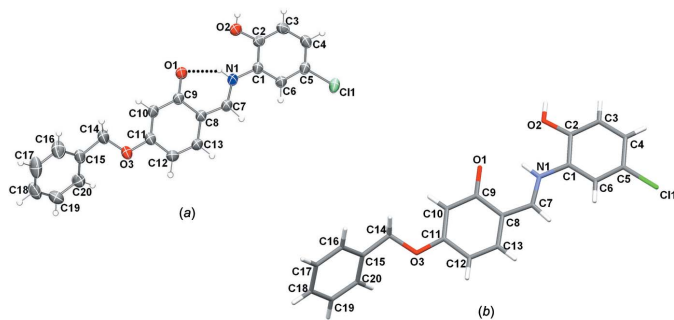
**Table 3**  
Experimental and calculated bond lengths (Å) for compound (II).

Bond	X-ray	B3LYP/6–311+G( <i>d</i> )
N1–C1	1.406 (2)	1.399
N1–C7	1.309 (2)	1.340
O1–C9	1.277 (2)	1.254
O2–C2	1.351 (2)	1.364
O3–C11	1.363 (2)	1.355
O3–C14	1.432 (3)	1.439
C1–C2	1.403 (2)	1.410
C1–C6	1.389 (2)	1.398
C2–C3	1.384 (3)	1.389
C3–C4	1.381 (3)	1.394
C5–C11	1.742 (2)	1.759
C7–C8	1.395 (3)	1.385
C9–C10	1.418 (3)	1.411
C10–C11	1.373 (3)	1.373
C12–C13	1.350 (3)	1.358
C14–C15	1.504 (3)	1.504
C16–C17	1.392 (4)	1.393
C19–C20	1.387 (3)	1.393

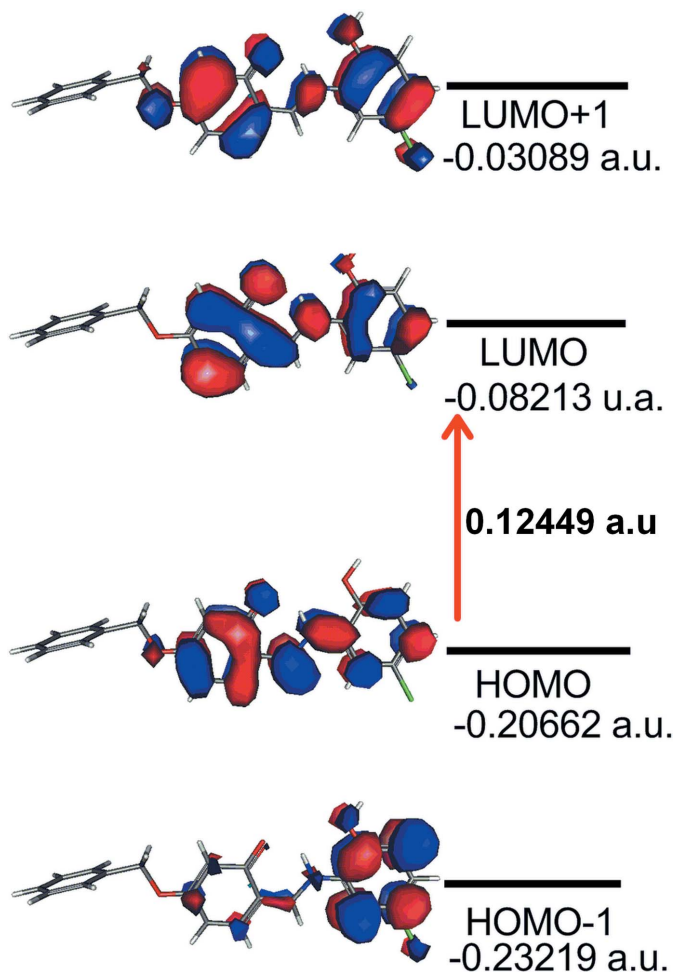
ene)cyclohexa-2,4-dien-1-ones (Chatziefthimiou *et al.*, 2006) and our recent contribution also reported (*E*)-5-benzyloxy-2-([2-(1*H*-indol-3-yl)ethyl]iminiumyl)methyl)phenolate, which is closely similar to (II). The structures of Schiff bases derived from hydroxyaryl aldehydes have been the subject of a general survey, in which a number of structural errors, often involving misplaced H atoms, were pointed out (Blagus *et al.*, 2010).

## 5. DFT-optimized calculations

DFT quantum chemical calculations were performed on molecule (II) using the hybrid functional B3LYP (Becke *et al.*, 1993; Lee *et al.*, 1988), and base 6–311+G (*d*). The DFT structure optimization of (II) was performed starting from the X-ray geometry. The DFT and X-ray structures are compared in Fig. 8. The calculated values of bond lengths (Table 3) compare well with experimental values with the largest bond-length deviation being less than 0.031 Å from those found in the crystal structure. The adoption of the keto–imine tautomeric form is also predicted by these calculations. The study also shows that the HOMO and LUMO are localized in the plane extending from the chlorohydroxybenzene ring to the



**Figure 8**  
Comparison of the structures of (II) obtained from (a) the X-ray determination and (b) the DFT calculations.



**Figure 9**  
Electron distribution in the HOMO-1, HOMO, LUMO and LUMO-1 energy levels for (II).

central phenol ring. The electron distribution of the HOMO-1, HOMO, LUMO and LUMO+1 energy levels is shown in Fig. 9. The occupied orbitals are predominantly of  $\sigma$ -character as is the LUMO, while LUMO+1 is mainly of  $\pi$ -character. The HOMO–LUMO gap is 0.12449 a.u., with frontier molecular orbital energies,  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of  $-5.622$  and  $-2.234$  eV, respectively.

## 6. Antioxidant activity

The antioxidant activity profiles of (I) and (II) were determined using the copper(II)–neocuprine [ $\text{Cu}^{\text{II}}\text{-Nc}$ ] (CUPRAC) process (Apak *et al.*, 2004). The CUPRAC method (cupric ion reducing antioxidant capacity) follows the variation in the absorbance of the neocuproine (2,9-dimethyl-1,10-phenanthroline, Nc), copper<sup>+2</sup> complex  $\text{Nc}_2\text{-Cu}^{+2}$ . In the presence of an antioxidant, the copper–neocuproine complex is reduced and this reaction is followed and quantified spectrophotometrically at a wavelength of 450 nm. The results indicate that the percentage (%) inhibition ( $\text{IC}_{50}$ ) in the CUPRAC assay is small for both compounds in comparison to that for



**Table 4**  
Cupric ion reducing antioxidant capacity of compounds (I) and (II).

	Percentage (%) Inhibition							
	3.125 µg	6.25 µg	12.5 µg	25 µg	50 µg	100 µg	200 µg	A0.50 (µg/ml)
Compound (I)	0.28±0.01	0.46±0.00	0.76±0.03	1.55±0.04	2.60±0.14	3.81±0.15	4.33±0.04	7.4±0.21
Compound (II)	0.30±0.00	0.46±0.01	0.78±0.01	1.12±0.07	1.84±0.19	2.34±0.12	4.39±0.04	6.10±0.26
BHT	0.19±0.01	0.33±0.04	0.66±0.07	1.03±0.07	1.48±0.09	2.04±0.14	2.32±0.28	9.62±0.87

butylated hydroxytoluene (BHT) that was used as a positive control. In Table 4 the values shown are the means of three separate measurements.

## 7. Synthesis and crystallization

### Compound (I)

1,2-Diaminobenzene (1 equiv.) and 4-benzyloxy-2-hydroxybenzaldehyde (1 equiv.) in ethanol (15–20 ml) were refluxed for 1 h, the solvent was evaporated in *vacuo*. The residue was recrystallized from ethanol, yielding yellow block-like crystals on slow evaporation of the solvent. The purity of the compound was determined from its NMR spectrum (250 MHz, CDCl<sub>3</sub>). The azomethine proton appears in the 8.5–8.6 p.p.m. range, while the imine bond is characterized in the <sup>13</sup>C NMR spectrum with the imine C and the C atom bound to the OH group appearing in the 161.58–163.20 p.p.m. range. <sup>1</sup>H NMR: δ = 6.6–7.6 (*m*, 12H; *H-ar*), δ = 13.5 (*s*, 1H; *OH*), δ = 4 (*s*, 1H; *NH<sub>2</sub>*), δ = 5.1 (*s*, 1H; *CH<sub>2</sub>-O*). <sup>13</sup>C NMR: 70.22, 127.66, 127.73, 128.32, 128.8, 140.66, 161.58, 163.02, 163.2.

### Compound (II)

2-Amino-4-chlorophenol (1 equiv.) and 4-benzyloxy-2-hydroxybenzaldehyde (1 equiv.) in ethanol (20 ml) were refluxed for 30–60 min, the solvent was evaporated in *vacuo*. The residue was recrystallized from ethanol, yielding orange block-like crystals on slow evaporation of the solvent. The purity of the compound was determined by its NMR spectrum (250 MHz, CDCl<sub>3</sub>). <sup>1</sup>H NMR: δ = 6.5–7.7 (*m*, 11H; *H-ar*), δ = 8.5–8.6 (*s*, 1H; *OH*), δ = 5.1 (*s*, 1H; *CH<sub>2</sub>-O*). <sup>13</sup>C NMR: 55.6, 128.2, 128.7, 133.3, 136.4, 141.4, 159.69, 162.82, 163.77.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. In compound (I), the hydroxyl H atom was located in a difference-Fourier map and initially freely refined. In the final cycles of refinements it was positioned geometrically (O–H = 0.82 Å) and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . In compound (II), the H atoms on N1, C7 and O2 were located in a difference-Fourier and refined freely. For both compounds, the other C-bound H atoms were posi-

**Table 5**  
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>20</sub> H <sub>16</sub> ClNO <sub>3</sub>
<i>M<sub>r</sub></i>	318.36	353.79
Crystal system, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P1̄</i>
Temperature (K)	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	35.1343 (12), 7.2564 (2), 13.1450 (5)	5.9590 (2), 7.8710 (3), 17.9743 (6)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 95.553 (2), 90	98.381 (2), 93.817 (2), 90.294 (2)
<i>V</i> (Å <sup>3</sup> )	3335.57 (19)	832.11 (5)
<i>Z</i>	8	2
Radiation type	Mo <i>Kα</i>	Mo <i>Kα</i>
<i>μ</i> (mm <sup>-1</sup> )	0.08	0.25
Crystal size (mm)	0.03 × 0.02 × 0.01	0.03 × 0.02 × 0.01
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	18218, 3811, 1915	13513, 3052, 2490
<i>R</i> <sub>int</sub>	0.072	0.025
( <i>sin θ</i> /λ) <sub>max</sub> (Å <sup>-1</sup> )	0.650	0.606
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>	0.049, 0.134, 1.00	0.042, 0.133, 1.10
No. of reflections	3811	3052
No. of parameters	221	238
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.17, -0.15	0.21, -0.21

Computer programs: APEX2 and SAINT (Bruker, 2012), SHELXS97 and SHELXTL (Sheldrick, 2008) and SHELXL2017 (Sheldrick, 2015).

tioned geometrically ( $C-H = 0.97-0.97 \text{ \AA}$ ) and refined as riding with  $U_{iso}(H) = 1.2U_{eq}(C)$ .

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## supporting information

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**(*E*)-2-[[2-(Aminophenyl)imino]methyl]-5-(benzyloxy)phenol and (*Z*)-3-benzyloxy-6-[[5-chloro-2-hydroxyphenyl)amino]methylidene)cyclohexa-2,4-dien-1-one**

**Nadir Ghichi, Ali Benboudiaf, Chawki Bensouici, Yacine Djebli and Hocine Merazig**

**Computing details**

For both structures, data collection: *APEX2* (Bruker, 2012); cell refinement: *S SAINT* (Bruker, 2012); data reduction: *S SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

**(*E*)-2-[[2-(Aminophenyl)imino]methyl]-5-(benzyloxy)phenol (I)**

*Crystal data*

$C_{20}H_{18}N_2O_2$

$M_r = 318.36$

Monoclinic, *C2/c*

$a = 35.1343$  (12) Å

$b = 7.2564$  (2) Å

$c = 13.1450$  (5) Å

$\beta = 95.553$  (2)°

$V = 3335.57$  (19) Å<sup>3</sup>

$Z = 8$

$F(000) = 1344$

$D_x = 1.268$  Mg m<sup>-3</sup>

Mo *K*α radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1907 reflections

$\theta = 2.9$ – $21.9$ °

$\mu = 0.08$  mm<sup>-1</sup>

$T = 293$  K

Block, yellow

$0.03 \times 0.02 \times 0.01$  mm

*Data collection*

Bruker APEXII CCD  
diffractometer

Detector resolution: 18.4 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

18218 measured reflections

3811 independent reflections

1915 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.072$

$\theta_{max} = 27.5$ °,  $\theta_{min} = 3.4$ °

$h = -45$ → $45$

$k = -9$ → $9$

$l = -16$ → $17$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.134$

$S = 1.00$

3811 reflections

221 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.5669P]$

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

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

$\Delta\rho_{max} = 0.17$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.15$  e Å<sup>-3</sup>

*Special details*

**Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

*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	0.00836 (4)	-0.03108 (16)	0.12180 (11)	0.0578 (5)
O2	0.10314 (4)	0.43746 (16)	0.17382 (10)	0.0513 (5)
N1	-0.06331 (5)	0.0754 (2)	0.08936 (12)	0.0477 (6)
N2	-0.09669 (6)	-0.1879 (3)	0.19901 (17)	0.0913 (9)
C1	-0.10273 (6)	0.0392 (2)	0.06599 (15)	0.0458 (7)
C2	-0.12530 (6)	0.1274 (3)	-0.01145 (17)	0.0529 (8)
C3	-0.16347 (7)	0.0816 (3)	-0.03355 (19)	0.0653 (9)
C4	-0.17934 (7)	-0.0518 (3)	0.0237 (2)	0.0708 (10)
C5	-0.15720 (7)	-0.1400 (3)	0.1008 (2)	0.0683 (10)
C6	-0.11880 (6)	-0.1003 (3)	0.12233 (17)	0.0553 (8)
C7	-0.05090 (6)	0.2425 (3)	0.09311 (14)	0.0436 (7)
C8	-0.01110 (5)	0.2870 (2)	0.11319 (14)	0.0396 (6)
C9	0.01726 (6)	0.1499 (2)	0.12587 (14)	0.0411 (7)
C10	0.05547 (6)	0.1960 (2)	0.14368 (15)	0.0452 (7)
C11	0.06603 (5)	0.3795 (2)	0.15199 (14)	0.0410 (6)
C12	0.03863 (6)	0.5185 (2)	0.13959 (14)	0.0431 (7)
C13	0.00105 (6)	0.4708 (2)	0.12065 (14)	0.0421 (7)
C14	0.13205 (6)	0.2969 (3)	0.18376 (19)	0.0617 (9)
C15	0.16990 (6)	0.3854 (2)	0.21507 (18)	0.0490 (7)
C16	0.18486 (7)	0.3842 (3)	0.3151 (2)	0.0623 (9)
C17	0.22001 (7)	0.4634 (3)	0.3441 (2)	0.0693 (10)
C18	0.24053 (7)	0.5423 (3)	0.2725 (2)	0.0698 (10)
C19	0.22599 (7)	0.5434 (3)	0.1723 (2)	0.0715 (10)
C20	0.19090 (6)	0.4654 (3)	0.14359 (19)	0.0617 (9)
H1	-0.01490	-0.04310	0.11149	0.0870*
H2	-0.11464	0.21904	-0.04924	0.0640*
H2A	-0.10663	-0.27019	0.23540	0.1100*
H2B	-0.07285	-0.16065	0.21082	0.1100*
H3	-0.17822	0.14023	-0.08652	0.0780*
H4	-0.20504	-0.08226	0.01022	0.0850*
H5	-0.16836	-0.22861	0.13952	0.0820*
H7	-0.0691 (5)	0.349 (3)	0.0810 (13)	0.045 (5)*
H10	0.07401	0.10419	0.15006	0.0540*
H12	0.04583	0.64178	0.14416	0.0520*
H13	-0.01720	0.56385	0.11238	0.0510*
H14A	0.12613	0.20744	0.23476	0.0740*
H14B	0.13296	0.23331	0.11913	0.0740*
H16	0.17121	0.32937	0.36425	0.0750*
H17	0.22971	0.46292	0.41244	0.0830*
H18	0.26425	0.59506	0.29182	0.0840*



H19	0.23986	0.59698	0.12325	0.0860*
H20	0.18125	0.46665	0.07518	0.0740*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0526 (9)	0.0348 (7)	0.0852 (11)	-0.0032 (6)	0.0022 (8)	0.0001 (6)
O2	0.0397 (9)	0.0389 (7)	0.0745 (10)	0.0008 (6)	0.0021 (7)	-0.0048 (6)
N1	0.0457 (11)	0.0460 (10)	0.0507 (11)	-0.0054 (7)	0.0018 (8)	0.0016 (7)
N2	0.0912 (17)	0.0807 (15)	0.0962 (17)	-0.0325 (12)	-0.0211 (13)	0.0422 (12)
C1	0.0440 (13)	0.0420 (11)	0.0509 (13)	-0.0023 (9)	0.0028 (10)	-0.0036 (9)
C2	0.0527 (15)	0.0473 (11)	0.0581 (14)	0.0000 (9)	0.0020 (11)	0.0007 (10)
C3	0.0532 (16)	0.0590 (14)	0.0801 (18)	0.0082 (11)	-0.0113 (13)	-0.0071 (12)
C4	0.0454 (15)	0.0639 (15)	0.102 (2)	-0.0072 (11)	0.0012 (14)	-0.0144 (14)
C5	0.0598 (17)	0.0602 (14)	0.0848 (19)	-0.0201 (11)	0.0058 (14)	0.0032 (12)
C6	0.0544 (15)	0.0470 (12)	0.0633 (15)	-0.0100 (10)	-0.0002 (12)	0.0042 (10)
C7	0.0474 (13)	0.0430 (11)	0.0403 (12)	0.0003 (9)	0.0041 (9)	0.0017 (8)
C8	0.0417 (12)	0.0403 (10)	0.0365 (11)	-0.0009 (8)	0.0027 (9)	0.0003 (8)
C9	0.0476 (13)	0.0347 (10)	0.0411 (12)	-0.0006 (8)	0.0056 (10)	-0.0004 (8)
C10	0.0434 (13)	0.0369 (10)	0.0553 (13)	0.0036 (8)	0.0043 (10)	-0.0015 (9)
C11	0.0401 (12)	0.0418 (10)	0.0415 (11)	-0.0024 (8)	0.0056 (9)	-0.0018 (8)
C12	0.0471 (13)	0.0344 (10)	0.0472 (12)	-0.0014 (8)	0.0021 (10)	-0.0014 (8)
C13	0.0457 (13)	0.0380 (10)	0.0422 (12)	0.0044 (8)	0.0021 (9)	0.0006 (8)
C14	0.0454 (14)	0.0441 (12)	0.0954 (19)	0.0041 (9)	0.0055 (12)	-0.0047 (11)
C15	0.0398 (13)	0.0381 (10)	0.0683 (15)	0.0037 (8)	0.0017 (11)	0.0001 (9)
C16	0.0557 (16)	0.0601 (14)	0.0720 (18)	0.0053 (11)	0.0111 (13)	0.0067 (11)
C17	0.0664 (18)	0.0707 (15)	0.0673 (17)	0.0101 (13)	-0.0113 (14)	-0.0064 (12)
C18	0.0473 (15)	0.0571 (14)	0.102 (2)	-0.0037 (11)	-0.0074 (15)	-0.0060 (13)
C19	0.0623 (17)	0.0643 (15)	0.088 (2)	-0.0158 (12)	0.0079 (15)	0.0094 (13)
C20	0.0618 (16)	0.0554 (13)	0.0668 (16)	-0.0088 (11)	0.0014 (13)	0.0057 (11)

*Geometric parameters (Å, °)*

O1—C9	1.3498 (19)	C14—C15	1.498 (3)
O2—C11	1.374 (2)	C15—C20	1.378 (3)
O2—C14	1.437 (3)	C15—C16	1.368 (3)
N1—C1	1.414 (3)	C16—C17	1.382 (3)
N1—C7	1.288 (3)	C17—C18	1.366 (4)
O1—H1	0.8200	C18—C19	1.366 (4)
N2—C6	1.368 (3)	C19—C20	1.376 (3)
C1—C2	1.385 (3)	C2—H2	0.9300
C1—C6	1.405 (3)	C3—H3	0.9300
N2—H2A	0.8600	C4—H4	0.9300
N2—H2B	0.8600	C5—H5	0.9300
C2—C3	1.385 (3)	C7—H7	1.01 (2)
C3—C4	1.377 (3)	C10—H10	0.9300
C4—C5	1.375 (4)	C12—H12	0.9300
C5—C6	1.382 (3)	C13—H13	0.9300

C7—C8	1.435 (3)	C14—H14A	0.9700
C8—C9	1.407 (2)	C14—H14B	0.9700
C8—C13	1.401 (2)	C16—H16	0.9300
C9—C10	1.381 (3)	C17—H17	0.9300
C10—C11	1.384 (2)	C18—H18	0.9300
C11—C12	1.393 (2)	C19—H19	0.9300
C12—C13	1.364 (3)	C20—H20	0.9300
C11—O2—C14	116.75 (13)	C17—C18—C19	119.6 (2)
C1—N1—C7	120.27 (16)	C18—C19—C20	120.3 (2)
C9—O1—H1	109.00	C15—C20—C19	120.7 (2)
N1—C1—C2	123.57 (17)	C1—C2—H2	119.00
C2—C1—C6	119.33 (19)	C3—C2—H2	119.00
N1—C1—C6	117.04 (17)	C2—C3—H3	120.00
H2A—N2—H2B	120.00	C4—C3—H3	120.00
C6—N2—H2B	120.00	C3—C4—H4	120.00
C1—C2—C3	121.1 (2)	C5—C4—H4	120.00
C6—N2—H2A	120.00	C4—C5—H5	119.00
C2—C3—C4	119.3 (2)	C6—C5—H5	119.00
C3—C4—C5	120.0 (2)	N1—C7—H7	120.6 (11)
C4—C5—C6	121.7 (2)	C8—C7—H7	116.7 (11)
N2—C6—C5	121.8 (2)	C9—C10—H10	120.00
C1—C6—C5	118.5 (2)	C11—C10—H10	120.00
N2—C6—C1	119.7 (2)	C11—C12—H12	121.00
N1—C7—C8	122.64 (19)	C13—C12—H12	121.00
C7—C8—C9	121.96 (15)	C8—C13—H13	119.00
C7—C8—C13	120.81 (17)	C12—C13—H13	119.00
C9—C8—C13	117.23 (17)	O2—C14—H14A	110.00
O1—C9—C10	117.38 (16)	O2—C14—H14B	110.00
C8—C9—C10	120.97 (14)	C15—C14—H14A	110.00
O1—C9—C8	121.65 (17)	C15—C14—H14B	110.00
C9—C10—C11	119.68 (16)	H14A—C14—H14B	108.00
C10—C11—C12	120.70 (17)	C15—C16—H16	120.00
O2—C11—C10	123.57 (15)	C17—C16—H16	120.00
O2—C11—C12	115.72 (14)	C16—C17—H17	120.00
C11—C12—C13	118.90 (14)	C18—C17—H17	120.00
C8—C13—C12	122.50 (16)	C17—C18—H18	120.00
O2—C14—C15	108.77 (16)	C19—C18—H18	120.00
C14—C15—C16	120.6 (2)	C18—C19—H19	120.00
C14—C15—C20	120.9 (2)	C20—C19—H19	120.00
C16—C15—C20	118.5 (2)	C15—C20—H20	120.00
C15—C16—C17	120.8 (2)	C19—C20—H20	120.00
C16—C17—C18	120.1 (2)		
C14—O2—C11—C10	2.8 (3)	C13—C8—C9—O1	178.84 (17)
C14—O2—C11—C12	-178.09 (17)	C13—C8—C9—C10	-0.8 (3)
C11—O2—C14—C15	-175.82 (17)	C7—C8—C13—C12	-179.96 (18)
C7—N1—C1—C2	44.0 (3)	C9—C8—C13—C12	-0.1 (3)

C7—N1—C1—C6	-139.06 (19)	O1—C9—C10—C11	-177.83 (17)
C1—N1—C7—C8	-177.94 (17)	C8—C9—C10—C11	1.8 (3)
N1—C1—C2—C3	177.54 (19)	C9—C10—C11—O2	177.20 (17)
C6—C1—C2—C3	0.6 (3)	C9—C10—C11—C12	-1.9 (3)
N1—C1—C6—N2	3.0 (3)	O2—C11—C12—C13	-178.16 (16)
N1—C1—C6—C5	-179.52 (19)	C10—C11—C12—C13	1.0 (3)
C2—C1—C6—N2	-179.9 (2)	C11—C12—C13—C8	0.0 (3)
C2—C1—C6—C5	-2.4 (3)	O2—C14—C15—C16	99.2 (2)
C1—C2—C3—C4	1.1 (3)	O2—C14—C15—C20	-82.5 (2)
C2—C3—C4—C5	-1.0 (4)	C14—C15—C16—C17	179.1 (2)
C3—C4—C5—C6	-0.8 (4)	C20—C15—C16—C17	0.8 (3)
C4—C5—C6—N2	-180.0 (2)	C14—C15—C20—C19	-178.73 (19)
C4—C5—C6—C1	2.5 (3)	C16—C15—C20—C19	-0.4 (3)
N1—C7—C8—C9	2.8 (3)	C15—C16—C17—C18	-0.8 (3)
N1—C7—C8—C13	-177.43 (18)	C16—C17—C18—C19	0.4 (3)
C7—C8—C9—O1	-1.4 (3)	C17—C18—C19—C20	-0.1 (3)
C7—C8—C9—C10	179.05 (18)	C18—C19—C20—C15	0.1 (3)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1 and Cg3 are the centroids of the C1–C6 and C15–C20 rings respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ N1	0.82	1.90	2.629 (2)	147
N2—H2A $\cdots$ O2 <sup>i</sup>	0.86	2.43	3.211 (3)	151
C14—H14B $\cdots$ Cg1 <sup>ii</sup>	0.97	2.74	3.704 (3)	171
C16—H16 $\cdots$ Cg1 <sup>iii</sup>	0.93	2.96	3.792 (3)	150
C18—H18 $\cdots$ Cg3 <sup>iv</sup>	0.93	2.94	3.620 (2)	131

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

### (Z)-3-Benzyloxy-6-[[[(5-chloro-2-hydroxyphenyl)amino]methylidene]cyclohexa-2,4-dien-1-one (II)

#### Crystal data

$C_{20}H_{16}ClNO_3$

$M_r = 353.79$

Triclinic,  $P\bar{1}$

$a = 5.9590$  (2)  $\text{\AA}$

$b = 7.8710$  (3)  $\text{\AA}$

$c = 17.9743$  (6)  $\text{\AA}$

$\alpha = 98.381$  (2) $^\circ$

$\beta = 93.817$  (2) $^\circ$

$\gamma = 90.294$  (2) $^\circ$

$V = 832.11$  (5)  $\text{\AA}^3$

$Z = 2$

$F(000) = 368$

$D_x = 1.412$   $\text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$   $\text{\AA}$

Cell parameters from 5281 reflections

$\theta = 2.7\text{--}30.7^\circ$

$\mu = 0.25$   $\text{mm}^{-1}$

$T = 293$  K

Block, orange

$0.03 \times 0.02 \times 0.01$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Detector resolution: 18.4 pixels  $\text{mm}^{-1}$

$\varphi$  and  $\omega$  scans

13513 measured reflections

3052 independent reflections

2490 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 25.5^\circ$ ,  $\theta_{\text{min}} = 2.6^\circ$

$h = -6 \rightarrow 7$

$k = -9 \rightarrow 9$

$l = -21 \rightarrow 21$

*Refinement*Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.042$  $wR(F^2) = 0.133$  $S = 1.10$ 

3052 reflections

238 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methodsSecondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0727P)^2 + 0.2078P]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} < 0.001$  $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$ *Special details***Geometry.** Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.93492 (8)	0.93423 (7)	-0.13197 (3)	0.0533 (2)
O1	0.1309 (2)	0.6289 (2)	0.14736 (7)	0.0518 (5)
O2	0.1581 (3)	0.5583 (2)	-0.05318 (9)	0.0546 (5)
O3	0.3158 (2)	0.7742 (2)	0.41212 (7)	0.0520 (5)
N1	0.4214 (3)	0.7241 (2)	0.05641 (8)	0.0382 (5)
C1	0.4780 (3)	0.7305 (2)	-0.01782 (10)	0.0348 (5)
C2	0.3343 (3)	0.6417 (2)	-0.07572 (10)	0.0381 (6)
C3	0.3805 (3)	0.6429 (3)	-0.15011 (10)	0.0444 (6)
C4	0.5643 (3)	0.7329 (3)	-0.16776 (10)	0.0433 (6)
C5	0.7028 (3)	0.8202 (2)	-0.11011 (10)	0.0374 (6)
C6	0.6635 (3)	0.8205 (2)	-0.03551 (10)	0.0371 (5)
C7	0.5388 (3)	0.7860 (2)	0.11873 (10)	0.0394 (6)
C8	0.4718 (3)	0.7766 (2)	0.19092 (10)	0.0380 (5)
C9	0.2627 (3)	0.6945 (2)	0.20317 (10)	0.0380 (5)
C10	0.2119 (3)	0.6906 (3)	0.27886 (10)	0.0426 (6)
C11	0.3535 (3)	0.7669 (3)	0.33778 (10)	0.0409 (6)
C12	0.5562 (3)	0.8502 (3)	0.32557 (11)	0.0481 (7)
C13	0.6123 (3)	0.8526 (3)	0.25418 (11)	0.0465 (6)
C14	0.1117 (4)	0.6974 (3)	0.43003 (11)	0.0572 (8)
C15	0.1044 (4)	0.7217 (3)	0.51439 (10)	0.0474 (7)
C16	-0.0740 (4)	0.8010 (3)	0.54911 (14)	0.0632 (8)
C17	-0.0843 (5)	0.8143 (3)	0.62686 (15)	0.0719 (9)
C18	0.0817 (5)	0.7470 (3)	0.66975 (12)	0.0631 (8)
C19	0.2599 (5)	0.6690 (4)	0.63599 (13)	0.0677 (9)
C20	0.2723 (4)	0.6576 (3)	0.55862 (12)	0.0621 (8)
H1	0.299 (4)	0.674 (3)	0.0639 (13)	0.057 (7)*
H2	0.080 (5)	0.509 (4)	-0.0877 (18)	0.086 (10)*
H3	0.28678	0.58262	-0.18855	0.0530*
H4	0.59415	0.73465	-0.21778	0.0520*

H6	0.75959	0.88004	0.00245	0.0450*
H7	0.686 (4)	0.840 (3)	0.1147 (11)	0.043 (5)*
H10	0.08097	0.63559	0.28872	0.0510*
H12	0.64933	0.90248	0.36612	0.0580*
H13	0.74667	0.90542	0.24615	0.0560*
H14A	0.10695	0.57595	0.41018	0.0690*
H14B	-0.01698	0.75127	0.40768	0.0690*
H16	-0.18852	0.84600	0.52046	0.0760*
H17	-0.20480	0.86928	0.64988	0.0860*
H18	0.07282	0.75461	0.72159	0.0760*
H19	0.37329	0.62325	0.66483	0.0810*
H20	0.39585	0.60591	0.53619	0.0740*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0448 (3)	0.0693 (4)	0.0476 (3)	-0.0148 (2)	0.0136 (2)	0.0105 (2)
O1	0.0473 (8)	0.0697 (10)	0.0352 (7)	-0.0287 (7)	-0.0005 (6)	-0.0002 (6)
O2	0.0469 (8)	0.0723 (11)	0.0437 (8)	-0.0303 (8)	-0.0049 (7)	0.0105 (7)
O3	0.0513 (8)	0.0735 (10)	0.0313 (7)	-0.0160 (7)	0.0047 (6)	0.0075 (6)
N1	0.0356 (8)	0.0456 (9)	0.0330 (8)	-0.0118 (7)	0.0042 (6)	0.0039 (6)
C1	0.0346 (9)	0.0376 (9)	0.0323 (9)	-0.0039 (7)	0.0041 (7)	0.0046 (7)
C2	0.0340 (9)	0.0399 (10)	0.0397 (10)	-0.0075 (8)	-0.0029 (8)	0.0066 (7)
C3	0.0469 (11)	0.0494 (11)	0.0349 (10)	-0.0082 (9)	-0.0067 (8)	0.0037 (8)
C4	0.0487 (11)	0.0505 (11)	0.0310 (9)	-0.0036 (9)	0.0038 (8)	0.0068 (8)
C5	0.0340 (9)	0.0404 (10)	0.0385 (10)	-0.0029 (8)	0.0062 (7)	0.0066 (7)
C6	0.0343 (9)	0.0421 (10)	0.0335 (9)	-0.0077 (8)	0.0011 (7)	0.0017 (7)
C7	0.0352 (10)	0.0454 (11)	0.0373 (10)	-0.0108 (8)	0.0025 (8)	0.0052 (8)
C8	0.0353 (9)	0.0440 (10)	0.0345 (9)	-0.0087 (8)	0.0025 (7)	0.0051 (7)
C9	0.0370 (9)	0.0407 (10)	0.0352 (9)	-0.0089 (8)	0.0021 (7)	0.0028 (7)
C10	0.0388 (10)	0.0513 (11)	0.0379 (10)	-0.0134 (8)	0.0057 (8)	0.0063 (8)
C11	0.0426 (10)	0.0484 (11)	0.0321 (9)	-0.0043 (8)	0.0034 (8)	0.0068 (8)
C12	0.0414 (11)	0.0641 (13)	0.0370 (10)	-0.0152 (9)	-0.0041 (8)	0.0047 (9)
C13	0.0376 (10)	0.0631 (13)	0.0380 (10)	-0.0178 (9)	0.0004 (8)	0.0066 (9)
C14	0.0551 (13)	0.0804 (16)	0.0358 (10)	-0.0195 (11)	0.0051 (9)	0.0072 (10)
C15	0.0520 (12)	0.0559 (12)	0.0340 (10)	-0.0134 (9)	0.0084 (9)	0.0035 (8)
C16	0.0670 (15)	0.0686 (15)	0.0584 (14)	0.0097 (12)	0.0141 (12)	0.0195 (11)
C17	0.0911 (19)	0.0635 (15)	0.0647 (15)	0.0071 (14)	0.0405 (15)	0.0050 (12)
C18	0.0877 (18)	0.0656 (15)	0.0342 (10)	-0.0144 (13)	0.0125 (11)	-0.0020 (10)
C19	0.0683 (16)	0.0918 (19)	0.0397 (12)	-0.0086 (14)	-0.0080 (11)	0.0046 (11)
C20	0.0496 (13)	0.0896 (18)	0.0434 (12)	0.0007 (12)	0.0051 (10)	-0.0033 (11)

*Geometric parameters (Å, °)*

C11—C5	1.7423 (18)	C14—C15	1.504 (3)
O1—C9	1.277 (2)	C15—C20	1.380 (3)
O2—C2	1.351 (2)	C15—C16	1.375 (3)
O3—C11	1.363 (2)	C16—C17	1.392 (4)



O3—C14	1.432 (3)	C17—C18	1.370 (4)
N1—C1	1.406 (2)	C18—C19	1.363 (4)
N1—C7	1.309 (2)	C19—C20	1.387 (3)
O2—H2	0.80 (3)	C3—H3	0.9300
C1—C2	1.403 (2)	C4—H4	0.9300
C1—C6	1.389 (2)	C6—H6	0.9300
N1—H1	0.86 (2)	C7—H7	0.98 (2)
C2—C3	1.384 (3)	C10—H10	0.9300
C3—C4	1.381 (3)	C12—H12	0.9300
C4—C5	1.378 (3)	C13—H13	0.9300
C5—C6	1.376 (3)	C14—H14A	0.9700
C7—C8	1.395 (3)	C14—H14B	0.9700
C8—C13	1.422 (3)	C16—H16	0.9300
C8—C9	1.445 (2)	C17—H17	0.9300
C9—C10	1.418 (3)	C18—H18	0.9300
C10—C11	1.373 (3)	C19—H19	0.9300
C11—C12	1.416 (3)	C20—H20	0.9300
C12—C13	1.350 (3)		
C11—O3—C14	117.35 (14)	C15—C16—C17	120.4 (2)
C1—N1—C7	127.15 (17)	C16—C17—C18	120.5 (2)
C2—O2—H2	113 (2)	C17—C18—C19	119.6 (2)
N1—C1—C6	123.47 (16)	C18—C19—C20	120.1 (2)
C2—C1—C6	119.86 (16)	C15—C20—C19	121.1 (2)
N1—C1—C2	116.67 (16)	C2—C3—H3	120.00
C1—N1—H1	119.4 (15)	C4—C3—H3	120.00
C7—N1—H1	113.4 (15)	C3—C4—H4	121.00
C1—C2—C3	119.57 (16)	C5—C4—H4	121.00
O2—C2—C3	124.73 (17)	C1—C6—H6	121.00
O2—C2—C1	115.70 (16)	C5—C6—H6	121.00
C2—C3—C4	120.61 (17)	N1—C7—H7	118.2 (12)
C3—C4—C5	118.97 (17)	C8—C7—H7	117.5 (12)
C11—C5—C4	119.22 (14)	C9—C10—H10	120.00
C11—C5—C6	118.73 (13)	C11—C10—H10	120.00
C4—C5—C6	122.05 (17)	C11—C12—H12	121.00
C1—C6—C5	118.93 (16)	C13—C12—H12	120.00
N1—C7—C8	124.28 (17)	C8—C13—H13	119.00
C9—C8—C13	119.22 (16)	C12—C13—H13	119.00
C7—C8—C9	121.97 (16)	O3—C14—H14A	110.00
C7—C8—C13	118.80 (16)	O3—C14—H14B	110.00
O1—C9—C8	120.48 (16)	C15—C14—H14A	110.00
O1—C9—C10	122.15 (16)	C15—C14—H14B	110.00
C8—C9—C10	117.36 (16)	H14A—C14—H14B	108.00
C9—C10—C11	120.87 (17)	C15—C16—H16	120.00
C10—C11—C12	121.61 (17)	C17—C16—H16	120.00
O3—C11—C12	113.29 (16)	C16—C17—H17	120.00
O3—C11—C10	125.09 (17)	C18—C17—H17	120.00
C11—C12—C13	119.03 (18)	C17—C18—H18	120.00

C8—C13—C12	121.89 (18)	C19—C18—H18	120.00
O3—C14—C15	108.26 (17)	C18—C19—H19	120.00
C14—C15—C16	121.1 (2)	C20—C19—H19	120.00
C14—C15—C20	120.6 (2)	C15—C20—H20	119.00
C16—C15—C20	118.32 (19)	C19—C20—H20	119.00
C14—O3—C11—C10	-0.5 (3)	C7—C8—C9—C10	179.38 (17)
C14—O3—C11—C12	178.36 (19)	C13—C8—C9—O1	178.32 (17)
C11—O3—C14—C15	-179.52 (18)	C13—C8—C9—C10	-1.6 (3)
C7—N1—C1—C2	174.54 (17)	C7—C8—C13—C12	179.1 (2)
C7—N1—C1—C6	-6.3 (3)	C9—C8—C13—C12	0.1 (3)
C1—N1—C7—C8	179.41 (17)	O1—C9—C10—C11	-177.95 (19)
N1—C1—C2—O2	-0.6 (2)	C8—C9—C10—C11	2.0 (3)
N1—C1—C2—C3	180.00 (18)	C9—C10—C11—O3	177.97 (19)
C6—C1—C2—O2	-179.83 (16)	C9—C10—C11—C12	-0.8 (3)
C6—C1—C2—C3	0.8 (3)	O3—C11—C12—C13	-179.7 (2)
N1—C1—C6—C5	-179.28 (16)	C10—C11—C12—C13	-0.8 (3)
C2—C1—C6—C5	-0.2 (2)	C11—C12—C13—C8	1.2 (3)
O2—C2—C3—C4	179.61 (19)	O3—C14—C15—C16	124.1 (2)
C1—C2—C3—C4	-1.1 (3)	O3—C14—C15—C20	-58.9 (3)
C2—C3—C4—C5	0.7 (3)	C14—C15—C16—C17	176.5 (2)
C3—C4—C5—C11	-179.94 (17)	C20—C15—C16—C17	-0.5 (4)
C3—C4—C5—C6	0.0 (3)	C14—C15—C20—C19	-175.6 (2)
C11—C5—C6—C1	179.67 (13)	C16—C15—C20—C19	1.4 (4)
C4—C5—C6—C1	-0.2 (3)	C15—C16—C17—C18	-0.7 (4)
N1—C7—C8—C9	0.5 (3)	C16—C17—C18—C19	1.1 (4)
N1—C7—C8—C13	-178.51 (18)	C17—C18—C19—C20	-0.2 (4)
C7—C8—C9—O1	-0.7 (3)	C18—C19—C20—C15	-1.1 (4)

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg3 is the centroid of the C15–C20 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O1	0.86 (2)	1.93 (2)	2.637 (2)	139 (2)
N1—H1 $\cdots$ O2	0.86 (2)	2.27 (2)	2.620 (2)	104.5 (18)
O2—H2 $\cdots$ O1 <sup>i</sup>	0.80 (3)	1.84 (3)	2.619 (2)	165 (3)
C7—H7 $\cdots$ C11 <sup>ii</sup>	0.98 (2)	2.84 (2)	3.7971 (18)	164.5 (17)
C14—H14A $\cdots$ Cg3 <sup>iii</sup>	0.97	2.71	3.569 (3)	148

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