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An X-ray crystallographic and density functional theory study of (3*Z*)-4-(5-ethylsulfonyl-2-hydroxyanilino)pent-3-en-2-one and (3*Z*)-4-(5-*tert*-butyl-2-hydroxyanilino)pent-3-en-2-one

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The Schiff base enaminones (3*Z*)-4-(5-ethylsulfonyl-2-hydroxyanilino)pent-3-en-2-one, $C_{13}H_{17}NO_4S$, (I), and (3*Z*)-4-(5-*tert*-butyl-2-hydroxyanilino)pent-3-en-2-one, $C_{15}H_{21}NO_2$, (II), were studied by X-ray crystallography and density functional theory (DFT). Although the keto tautomer of these compounds is dominant, the O=C—C=C—N bond lengths are consistent with some electron delocalization and partial enol character. Both (I) and (II) are nonplanar, with the amino–phenol group canted relative to the rest of the molecule; the twist about the N(enamine)—C(aryl) bond leads to dihedral angles of 40.5 (2) and −116.7 (1)° for (I) and (II), respectively. Compound (I) has a bifurcated intramolecular hydrogen bond between the N—H group and the flanking carbonyl and hydroxy O atoms, as well as an intermolecular hydrogen bond, leading to an infinite one-dimensional hydrogen-bonded chain. Compound (II) has one intramolecular hydrogen bond and one intermolecular C=O···H—O hydrogen bond, and consequently also forms a one-dimensional hydrogen-bonded chain. The DFT-calculated structures [*in vacuo*, B3LYP/6-311G(d,p) level] for the keto tautomers compare favourably with the X-ray crystal structures of (I) and (II), confirming the dominance of the keto tautomer. The simulations indicate that the keto tautomers are 20.55 and 18.86 kJ mol^{-1} lower in energy than the enol tautomers for (I) and (II), respectively.

Comment

Schiff base enaminones have been widely studied, due to their diverse chemistry and various applications in coordination chemistry (Kim *et al.*, 2001; Doherty *et al.*, 1999; Xiu *et al.*, 1997; Zhang & Zhu, 2008). Studies of the free ligands have shown that the O=C—C=C—N bond lengths reflect electron delocalization and the presence of keto and enol tautomeric forms (Shi *et al.*, 2004; Gilli *et al.*, 2000).

The structure of 4-amino-*N*-(2-hydroxyphenyl)pent-3-en-2-one, consisting of phenol and aminopent-3-en-2-one groups, has been studied previously by X-ray crystallography and AM1 calculations (Kabak *et al.*, 1998). Both keto and enol tautomeric forms of this compound can exist, but the keto form is dominant in the enthalpically favoured nonplanar structure (in which the ketone bridge is canted relative to the aminophenol group). Nonplanarity in this system is brought about by nonbonded H···H repulsions, consistent with previous observations for *N*-benzylideneaniline and related compounds (Burgi & Dunitz, 1971). Interestingly, the latter study suggested that delocalization of the N-atom lone-pair electrons onto the aniline ring when the compound is in a nonplanar conformation possibly contributes to the stability of the observed molecular geometry. Studies of tridentate Schiff base compounds similar to those reported here, *e.g.* 2-hydroxy-*N*-(2-hydroxy-5-methylphenyl)benzaldehydeimine (Kabak *et al.*, 1999), 3-(2-hydroxyphenylimino)-1-phenylbutan-1-one (Dey *et al.*, 2009) and 4-chloro-2-(4-oxopent-2-en-2-ylamino)phenol (Arıcı *et al.*, 1999), have likewise highlighted the occurrence of nonplanar conformations with a dominant keto tautomer. Planarity in 3-methoxyphenylsalicylaldimine, which contains a *meta*-substituted methoxy group rather than the hydroxy group on the ring, has been attributed to a lack of nonbonded intramolecular repulsions (Elmali *et al.*, 1999). From a more general perspective, the conformation of a Schiff base compound may dictate aspects of its physical behaviour and thus some of its potential applications. Thus, some planar Schiff base compounds are reportedly thermochromic in the solid state (the mechanism involves proton transfer), while those with a nonplanar geometry may exhibit photochromism (Hadjoudis *et al.*, 1987; Moustakali-Mavridis *et al.*, 1978).

Although interesting in its own right, the Schiff base 4-amino-*N*-(2-hydroxyphenyl)pent-3-en-2-one is a synthetically tractable tridentate ligand for metal ions and has been chelated to both Ni^{II} (Zhang & Zhu, 2008) and Si^{IV} (Seiler *et al.*, 2005). The ligand coordinates the metal ions *via* its hydroxyphenol *O*- and *N*-donor atoms and its enolate *O*-donor atom, thereby forming adjacent five- and six-membered chelate rings with the metal ion. In such complexes, the N=C, C—O and C—C bond lengths of the bridge are consistent with the enolic form of the compound. The ligand itself is nonplanar due to the out-of-plane tilt of the phenyl group relative to the remainder of the molecule. Interestingly, although square-planar complexes are formed with such ligands and Ni^{II}, distorted trigonal–bipyramidal complexes are favoured with Si^{IV}, in which the N atom of the ligand occupies an axial position while the O atoms bind in equatorial positions. Similar results are obtained for other tridentate derivatives chelated to Cu^{II}, Ni^{II}, Co^{II} and Fe^{III}, where the metal–ligand ratios vary from 1:1 to 1:2 (Sallam *et al.*, 2002).

In this paper, we report the X-ray structures of the two tridentate Schiff base enaminones, (3*Z*)-4-(5-ethylsulfonyl-2-hydroxyanilino)pent-3-en-2-one, (I), and (3*Z*)-4-(5-*tert*-butyl-

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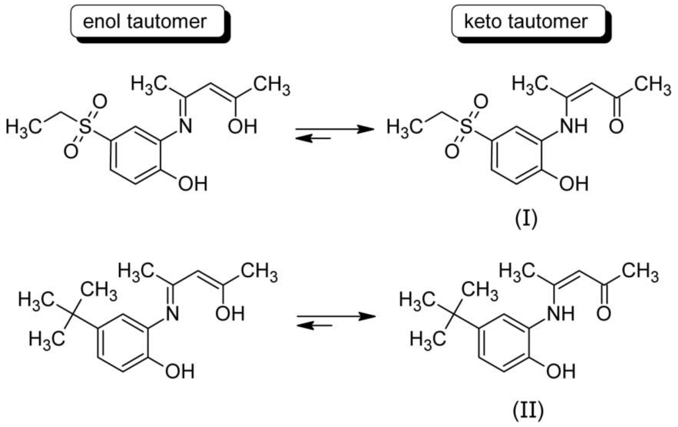
2-hydroxyanilino)pent-3-en-2-one, (II) consisting of a pent-3-en-2-one group (referred to as part *A*), comprising atoms C1–C5 and O1, and an aminophenol group (referred to as part *B*), comprising atoms C6–C11, N1 and O2. Compound (I) has an ethylsulfonyl group in the *para* position relative to the hydroxy group on the phenol ring, while (II) has a *tert*-butyl group in the *para* position.



Both (I) and (II) are nonplanar, but parts *A* and *B* of both compounds approach planarity. The maximum deviations from planarity in (I) are 0.013 (1) (for atom C4 of part *A*) and 0.031 (1) Å (for atom C6 of part *B*). The deviations from planarity exhibited by (II) are 0.036 (1) (for atom C3 of part *A*) and 0.045 (1) Å (for atom N1 of part *B*). In (I), the mean planes through parts *A* and *B* subtend an angle of 31.7 (5)°; this angle is reflected predominantly in a twist around the N1—C6 bond, with a C11—C6—N1—C4 torsion angle of 40.5 (2)°. Even with this out-of-plane twist, atoms O2, N1 and O1 all face each other, a geometry similar to that observed for the parent compound, 4-amino-*N*-(2-hydroxyphenyl)pent-3-en-2-one, for which the equivalent angle is 32.8 (1)° (Kabak *et al.*, 1998). In (II), the mean planes through parts *A* and *B* are at a much wider angle of 67.5 (1)° to each other. The twist around the N1—N6 bond means that parts *A* and *B* of (II) are nearly perpendicular, with a C11—C6—N1—C4 torsion angle of −116.7 (1)°. The result of this angle is that, in contrast with (I) and the parent compound, atoms N1 and O1 face each other while atom O2 faces in the opposite direction. The three-atom mean plane through the ethylsulfonyl group of (I) is at an angle of 78.7 (4)° to the mean plane of part *B*, with a C9—C10—S1—C12 torsion angle of 100.1 (1)°.

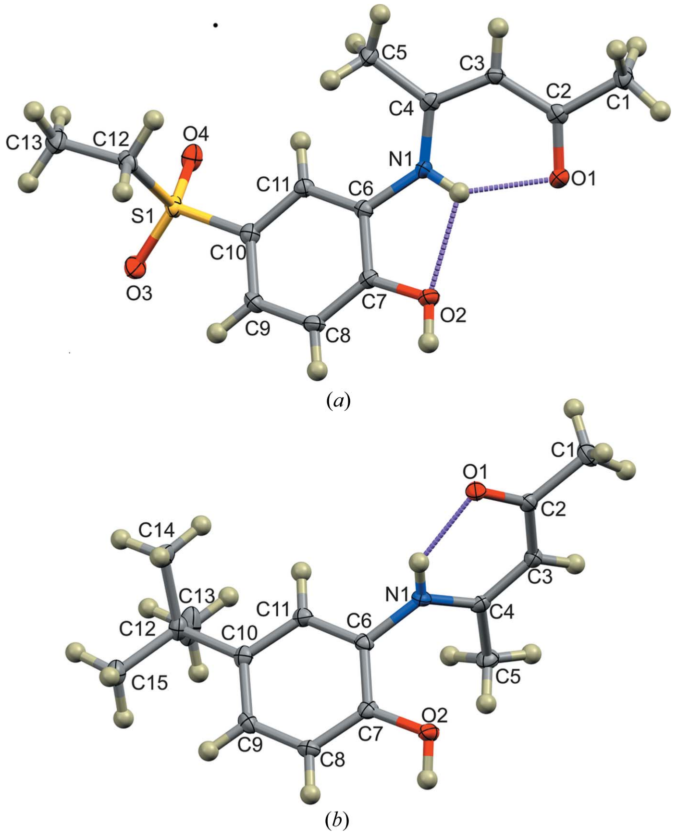


Figure 1
Displacement ellipsoid plots (50% probability surfaces) of (*a*) (I) and (*b*) (II). Intramolecular hydrogen bonds are shown as dashed lines.

The C2—O1 bond lengths for (I) and (II) (Tables 1 and 4) suggest that they have a bond order of 1.5, based on the standard values of single and double C—O bonds (Allen *et al.*, 1987). This, coupled with short C3—C4 bonds for (I) and (II), indicates the presence of a significant contribution from the keto tautomer (as reported for the parent compound; Kabak *et al.*, 1998). The C2—C3 bond lengths of (I) and (II) are intermediate between typical C—C single bonds and C═C double bonds (Allen *et al.*, 1987). Compounds (I) and (II) have C7—O2 bond lengths typical of a phenolic C—O bond. Compound (I) has an average C—S bond length of 1.771 (1) Å and an average S═O bond length of 1.444 (2) Å. Compounds (I) and (II) have average O1—C—C angles of 120.9 (2) and 120.3 (1)°, respectively. These average angles highlight the sp^2 hybridization of the C atom and are consistent with the values reported for the parent compound. The average O—S—C angle and C12—S1—C10 angles of (I) are 108.6 (7) and 103.8 (6)°, respectively (Tables 2 and 5).

As might be anticipated for phenolic compounds bearing additional groups with N and O heteroatoms, (I) and (II) exhibit interesting intra- and intermolecular hydrogen-bonding patterns (Fig. 2). In (I), a bifurcated intramolecular N1—H100···O1/O2 hydrogen bond is observed. The N1—H100···O1 hydrogen bond results in a six-membered ring, while the N1—H100···O2 hydrogen bond results in a five-membered ring. There is also one intermolecular O2—H200···$O1^{i}$ hydrogen bond (Table 3). This hydrogen bond links the molecules into extended one-dimensional columns collinear with the *b* axis. There are two additional C—H···O interactions (C12—H12*B*···$O4^{iii}$ and C1—H1*B*···$O2^{ii}$; Table 3) which link the one-dimensional chains into a three-dimensional network. The three-dimensional network exhibits a herringbone pattern when viewed down the *b* axis.

In contrast with (I), the N—H group of (II) is not involved in a bifurcated hydrogen bond; rather, there is a conventional intramolecular N1—H100···O1 hydrogen bond (Table 6). The intramolecular hydrogen bonds of (I) and (II) are both

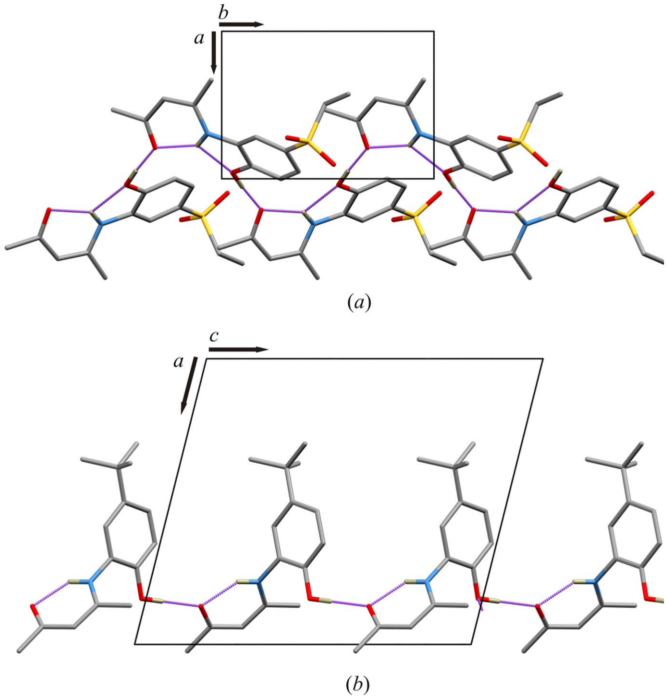
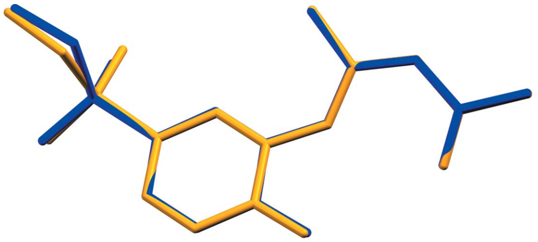
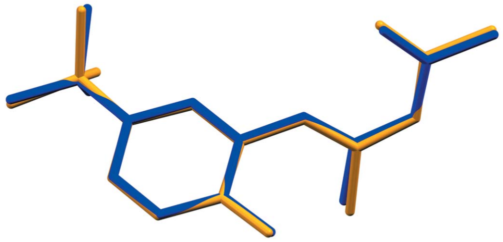


Figure 2
(*a*) The extended one-dimensional hydrogen-bonded chain formed in (I), viewed down the *c* axis. (*b*) The extended one-dimensional hydrogen-bonded chain formed in (II), viewed down the *b* axis. Hydrogen bonds are shown as thin lines (purple in the electronic version of the paper). H atoms not involved in hydrogen bonding have been omitted for clarity.



(*a*) r.m.s. deviation = 0.192 Å



(*b*) r.m.s. deviation = 0.190 Å

Figure 3
An overlay of the DFT-calculated (yellow in the electronic version of the paper) and experimental (blue) structures of the keto tautomer for (*a*) (I) and (*b*) (II).

considerably shorter than the sum of the van der Waals radii, although this gives little indication of bond strength as the lengths of the interactions are governed by the geometry of the molecule and not bond strength. In addition to the intramolecular hydrogen bond, atom O1 also acts as a hydrogen-bond acceptor for an intermolecular hydrogen bond from the O2—H200 group ($O2—H200\cdots O1^{i}$; Table 6). This interaction results in a one-dimensional hydrogen-bonded chain collinear with the *c* axis. The intermolecular hydrogen bond is characterized by a short nonbonded contact distance and an interaction angle that approaches an ideal value, suggesting that the interaction is likely to be moderate to strong. The rotation about the N1—C6 bond of (II) compared with (I) allows for an intramolecular C5—H5*B*···O2 interaction involving the methyl group of the bridge.

Density functional theory (DFT) calculations were performed *in vacuo* using *GAUSSIAN09W* (Frisch *et al.*, 2009) at the B3LYP (Becke, 1993; Lee *et al.*, 1988; Vosko *et al.*, 1980; Stephens *et al.*, 1994) /6-311G(d,p) (McLean & Chandler, 1980; Raghavachari *et al.*, 1980) level of theory to explore further the energy differences between the keto and enol tautomeric forms. The geometry-optimized structures and the energies of the two tautomeric forms were calculated for both (I) and (II) using the X-ray coordinates of the non-H atoms for the input structures. As portrayed in Fig. 3, the high degree of similarity for the least-squares fits (*Mercury*; Macrae *et al.*, 2008) of the X-ray structures to the keto forms of the DFT-calculated structures confirms the appropriateness of the level of theory used for the calculations [the r.m.s. differences are 0.192 Å for (I) and 0.190 Å for (II)]. Moreover, the DFT-calculated structures clearly show that the molecules are nonplanar, with the C11—C6—N1—C4 torsion angle in (I) measuring 29.81° for the keto tautomer and 29.58° for the enol tautomer; the corresponding dihedral angles for (II) are −120.97 and −123.29°. In both cases, the calculated conformations are in good agreement with those determined experimentally.

Finally, the DFT-calculated structures allow one to delineate cleanly between the keto and enol tautomers of the compound and to assign confidently the tautomer present in the X-ray structure. Thus, the DFT-calculated keto tautomer of (I) has a C2—O1 bond length of 1.237 Å, while the enol tautomer has a bond length of 1.323 Å; the former matches that observed for the X-ray structure [C2—O1 = 1.2630 (18) Å; see above]. The keto form may be similarly assigned from the C3—C4 bond distances for the keto and enol tautomers, which are 1.376 and 1.441 Å, respectively, in the DFT-calculated structures. As noted above, the X-ray structure of (I) has a C3—C4 bond length of 1.3937 (19) Å and is clearly the keto tautomer. The same conclusion may be drawn from a comparable analysis of the relevant bond distances for (II). The full lists of DFT-calculated and experimental bond lengths are shown in Tables 1 and 4. Collectively, the bond lengths of the calculated keto tautomers of (I) and (II) are in excellent agreement with the corresponding X-ray data, confirming that the keto tautomers are favoured in the solid state. Interestingly, the present calculations show that the keto tautomers are favoured over the enol tautomers by 20.55 and 18.86 kJ mol^{-1} for (I) and (II), respectively. Lastly, the present DFT calculations support the conclusions drawn from the semi-empirical calculations performed on the parent compound (Kabak *et al.*, 1998).

Experimental

Pentane-2,4-dione (1.00 g, 9.99 mmol) was added to 2-amino-4-(ethylsulfonyl)phenol (2.01 g, 9.99 mmol) in ethanol (30 ml) and the solution was refluxed for 1 h. The reaction mixture was then left undisturbed and brown crystals of (I) formed by slow evaporation (yield: 1.565 g, 55%). ^{1}H NMR (400 MHz, DMSO-d_6, 303 K): δ 1.08 (t, ^3J = 7.3 Hz, 3H, CH$_2$CH_3), 2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.21 (q, ^3J = 7.4 Hz, 2H, CH_2CH$_3$), 5.29 (s, 1H, CH), 7.10 (d, ^3J = 8.4 Hz, 1H, aromatic CH), 7.50 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1H, aromatic CH), 7.60 (d, ^4J = 2.4 Hz, 1H, aromatic CH), 11.16 (s, 1H, OH), 12.22 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl$_3$, 303 K): δ 7.76, 20.04, 29.50, 49.94, 99.01, 116.16, 122.00, 126.33, 127.55, 128.91, 154.99, 159.31, 195.64.

Pentane-2,4-dione (0.607 g, 6.06 mmol) was added to 2-amino-4-*tert*-butylphenol (1.00 g, 6.05 mmol) in ethanol (30 ml) and the solution was refluxed for 2 h. The solution was then cooled to 273 K for 30 min, resulting in the formation of a cream precipitate. The precipitate was filtered off and air dried, yielding a cream-coloured powder of (II) (yield: 0.752 g, 51%). Single colourless crystals were grown by liquid–liquid diffusion of hexane into a dichloromethane solution of (II). ^{1}H NMR (400 MHz, DMSO-d_6, 303 K): δ 1.24 (s, 9H, CH_3), 1.95 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 5.19 (s, 1H, CH), 6.83 (d, ^3J = 8.5 Hz, 1H, aromatic CH), 7.04 (dd, ^3J = 8.5 Hz, ^4J = 2.5 Hz, 1H, aromatic CH), 7.09 (d, ^4J= 2.5 Hz, 1H, aromatic CH), 9.62 (s, 1H, OH), 12.10 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl$_3$, 303 K): δ 19.81, 29.30, 31.74, 34.19, 97.37, 115.75, 122.97, 123.37, 125.77, 141.97, 148.70, 160.86, 194.55.

Compound (I)

Crystal data

$C_{13}H_{17}NO_4S$
M_r = 283.34
Orthorhombic, $P2_12_12_1$
a = 6.2335 (6) Å
b = 8.9651 (8) Å
c = 24.747 (2) Å

V = 1383.0 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 100 K
0.45 × 0.40 × 0.40 mm

Data collection

Bruker APEX DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
$T_{\min}$ = 0.898, $T_{\max}$ = 0.909

6386 measured reflections
2703 independent reflections
2673 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.060
S = 1.11
2703 reflections
183 parameters
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), with 1051 Friedel pairs
Flack parameter: 0.13 (6)

Compound (II)

Crystal data

$C_{15}H_{21}NO_2$
M_r = 247.33
Monoclinic, $P2_1/c$
a = 12.3617 (7) Å
b = 8.3063 (5) Å
c = 14.1054 (8) Å
β = 104.114 (2)°

V = 1404.62 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 100 K
0.40 × 0.25 × 0.18 mm

Table 1
Comparison of experimental and DFT-calculated bond lengths (Å) for (I).

Bond	X-ray	Keto tautomer	Enol tautomer
C2—O1	1.2630 (18)	1.238	1.323
C2—C3	1.4165 (19)	1.447	1.370
C3—C4	1.3937 (19)	1.376	1.441
C4—N1	1.3441 (18)	1.365	1.305
N1—C6	1.4153 (17)	1.396	1.395

Table 2
Selected geometric parameters (Å, °) for (I).

C7—O2	1.3530 (16)	O3—S1	1.4435 (11)
C10—S1	1.7673 (14)	O4—S1	1.4441 (10)
C12—S1	1.7745 (15)		
O1—C2—C3	122.55 (13)	O4—S1—C10	109.53 (6)
O1—C2—C1	119.35 (13)	O3—S1—C12	108.61 (7)
C4—N1—C6	130.38 (13)	O4—S1—C12	108.25 (7)
O3—S1—C10	107.85 (7)	C10—S1—C12	103.81 (7)

Table 3
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H100···O1	0.83 (2)	1.98 (2)	2.657 (2)	139 (2)
N1—H100···O2	0.83 (2)	2.24 (2)	2.622 (2)	108 (2)
O2—H200···O1$^{\rm i}$	0.90 (2)	1.70 (2)	2.601 (1)	175 (2)
C1—H1B···O2$^{\rm ii}$	0.98	2.48	3.457 (2)	172
C12—H12B···O4$^{\rm iii}$	0.99	2.38	3.267 (2)	149
C13—H13B···O3$^{\rm iv}$	0.98	2.55	3.372 (2)	142

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

Table 4
Comparison of experimental and DFT-calculated bond lengths (Å) for (II).

Bond	X-ray	Keto tautomer	Enol tautomer
C2—O1	1.2686 (15)	1.251	1.326
C2—C3	1.4116 (17)	1.437	1.372
C3—C4	1.3945 (17)	1.385	1.443
C4—N1	1.3356 (16)	1.355	1.308
N1—C6	1.4298 (15)	1.417	1.408

Table 5
Selected geometric parameters (Å, °) for (II).

O2—C7	1.3570 (14)		
C4—N1—C6	126.89 (11)	O1—C2—C1	117.96 (11)
O1—C2—C3	122.63 (11)		

Table 6
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H100···O1	0.89 (2)	1.89 (2)	2.628 (2)	138 (2)
O2—H200···O1$^{\rm i}$	0.92 (2)	1.72 (2)	2.633 (1)	172 (2)

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

Data collection

Bruker APEX DUO diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
$T_{\min} = 0.970$, $T_{\max} = 0.986$
10867 measured reflections
2709 independent reflections
2476 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 1.06$
2709 reflections
176 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

The positions of all C-bonded H atoms were calculated using a standard riding model, with aromatic C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, methylene C—H = 0.99 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, and methyl C—H = 0.96 Å and $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. The amino and hydroxy H atoms were located in difference density maps and allowed to refine isotropically.

For both compounds, data collection: *APEX2* (Bruker, 2010); cell refinement: *SAINT* (Bruker, 2010); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: YP3023). Services for accessing these data are described at the back of the journal.

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supplementary materials

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An X-ray crystallographic and density functional theory study of (3*Z*)-4-(5-ethylsulfonyl-2-hydroxyanilino)pent-3-en-2-one and (3*Z*)-4-(5-*tert*-butyl-2-hydroxyanilino)pent-3-en-2-one

Kate J. Akerman and Orde Q. Munro

(I) (3*Z*)-4-(5-Ethylsulfonyl-2-hydroxyanilino)pent-3-en-2-one

Crystal data

$C_{13}H_{17}NO_4S$
$M_r = 283.34$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.2335$ (6) Å
$b = 8.9651$ (8) Å
$c = 24.747$ (2) Å
$V = 1383.0$ (2) Å^3
$Z = 4$
$F(000) = 600$
$D_x = 1.361$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2673 reflections
$\theta = 1.6$–$26.4°$
$\mu = 0.24$ mm^{-1}
$T = 100$ K
Block, brown
0.45 × 0.40 × 0.40 mm

Data collection

Bruker APEX DUO diffractometer
Radiation source: Incoatec Microsource
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)
$T_{min} = 0.898$, $T_{max} = 0.909$
6386 measured reflections
2703 independent reflections
2673 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26.4°$, $\theta_{min} = 1.7°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 11$
$l = -23 \rightarrow 30$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.060$
$S = 1.11$
2703 reflections
183 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0281P)^2 + 0.3817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), with 1051 Friedel pairs
Flack parameter: 0.13 (6)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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_{iso}*/U_{eq}
H100	0.227 (3)	−0.114 (2)	0.1744 (8)	0.038 (5)*
H200	−0.052 (4)	0.095 (2)	0.2469 (9)	0.047 (6)*
C1	0.4679 (3)	−0.51084 (15)	0.21444 (6)	0.0201 (3)
H1A	0.3649	−0.5502	0.2407	0.030*
H1B	0.6099	−0.5036	0.2312	0.030*
H1C	0.4752	−0.5778	0.1832	0.030*
C2	0.3968 (2)	−0.35844 (16)	0.19618 (5)	0.0152 (3)
C3	0.5422 (2)	−0.27171 (15)	0.16540 (5)	0.0146 (3)
H3	0.6789	−0.3137	0.1579	0.018*
C4	0.5001 (2)	−0.12949 (15)	0.14527 (5)	0.0142 (3)
C5	0.6695 (2)	−0.04891 (16)	0.11455 (6)	0.0213 (3)
H5A	0.6372	−0.0536	0.0758	0.032*
H5B	0.8090	−0.0956	0.1214	0.032*
H5C	0.6737	0.0555	0.1262	0.032*
C6	0.2341 (2)	0.07980 (14)	0.14310 (5)	0.0140 (3)
C7	0.0890 (2)	0.13863 (16)	0.18152 (5)	0.0145 (3)
C8	0.0004 (2)	0.27918 (15)	0.17414 (6)	0.0179 (3)
H8	−0.0949	0.3189	0.2004	0.022*
C9	0.0506 (2)	0.36179 (16)	0.12850 (6)	0.0180 (3)
H9	−0.0101	0.4579	0.1233	0.022*
C10	0.1906 (2)	0.30273 (16)	0.09038 (5)	0.0155 (3)
C11	0.2823 (2)	0.16203 (14)	0.09684 (5)	0.0149 (3)
H11	0.3761	0.1228	0.0701	0.018*
C12	0.5068 (2)	0.48763 (15)	0.04731 (6)	0.0181 (3)
H12A	0.4995	0.5397	0.0825	0.022*
H12B	0.6152	0.4073	0.0503	0.022*
C13	0.5745 (3)	0.59713 (18)	0.00375 (7)	0.0270 (3)
H13A	0.5657	0.5487	−0.0317	0.040*
H13B	0.7224	0.6294	0.0104	0.040*
H13C	0.4791	0.6840	0.0044	0.040*
N1	0.30742 (19)	−0.06660 (13)	0.15389 (5)	0.0150 (2)
O1	0.21083 (16)	−0.31335 (11)	0.20818 (4)	0.0205 (2)
O2	0.04168 (17)	0.05041 (11)	0.22424 (4)	0.0188 (2)
O3	0.09742 (17)	0.52721 (12)	0.02798 (5)	0.0251 (2)
O4	0.27808 (18)	0.30992 (11)	−0.01354 (4)	0.0207 (2)
S1	0.25292 (6)	0.40846 (3)	0.032180 (13)	0.01536 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0209 (7)	0.0172 (7)	0.0221 (7)	0.0003 (6)	−0.0018 (6)	0.0054 (6)
C2	0.0175 (7)	0.0161 (6)	0.0120 (6)	−0.0003 (5)	−0.0016 (5)	−0.0022 (5)
C3	0.0147 (7)	0.0155 (6)	0.0137 (6)	0.0026 (5)	0.0023 (5)	−0.0008 (5)
C4	0.0161 (6)	0.0162 (6)	0.0103 (6)	−0.0016 (5)	0.0002 (5)	−0.0021 (5)
C5	0.0159 (6)	0.0202 (7)	0.0279 (8)	0.0007 (6)	0.0048 (6)	0.0076 (6)
C6	0.0132 (6)	0.0135 (6)	0.0153 (6)	−0.0005 (6)	−0.0011 (5)	−0.0017 (5)
C7	0.0136 (6)	0.0160 (6)	0.0138 (6)	−0.0011 (5)	0.0011 (5)	−0.0007 (5)
C8	0.0156 (7)	0.0182 (7)	0.0200 (7)	0.0030 (6)	0.0037 (6)	−0.0026 (6)
C9	0.0186 (7)	0.0139 (6)	0.0215 (7)	0.0040 (5)	−0.0016 (6)	0.0000 (6)
C10	0.0155 (7)	0.0164 (6)	0.0145 (6)	−0.0010 (5)	−0.0023 (5)	0.0012 (5)
C11	0.0148 (7)	0.0158 (6)	0.0140 (6)	0.0001 (5)	0.0000 (5)	−0.0004 (5)
C12	0.0170 (7)	0.0143 (6)	0.0230 (7)	−0.0011 (6)	−0.0034 (6)	−0.0015 (6)
C13	0.0190 (7)	0.0209 (7)	0.0411 (9)	−0.0022 (7)	0.0015 (7)	0.0069 (7)
N1	0.0172 (6)	0.0128 (5)	0.0150 (5)	0.0010 (5)	0.0047 (5)	0.0024 (4)
O1	0.0209 (6)	0.0182 (5)	0.0223 (5)	0.0022 (4)	0.0087 (4)	0.0044 (4)
O2	0.0204 (5)	0.0188 (5)	0.0173 (5)	0.0042 (4)	0.0070 (4)	0.0024 (4)
O3	0.0185 (5)	0.0246 (5)	0.0321 (6)	0.0047 (5)	0.0010 (5)	0.0125 (5)
O4	0.0258 (6)	0.0209 (5)	0.0154 (5)	−0.0056 (5)	−0.0028 (4)	0.0016 (4)
S1	0.01550 (16)	0.01435 (15)	0.01623 (15)	−0.00002 (14)	−0.00236 (14)	0.00376 (11)

Geometric parameters (Å, º)

C1—C2	1.5057 (19)	C8—C9	1.387 (2)
C1—H1A	0.9800	C8—H8	0.9500
C1—H1B	0.9800	C9—C10	1.390 (2)
C1—H1C	0.9800	C9—H9	0.9500
C2—O1	1.2630 (18)	C10—C11	1.3941 (19)
C2—C3	1.4165 (19)	C10—S1	1.7673 (14)
C3—C4	1.3937 (19)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.518 (2)
C4—N1	1.3441 (18)	C12—S1	1.7745 (15)
C4—C5	1.4879 (19)	C12—H12A	0.9900
C5—H5A	0.9800	C12—H12B	0.9900
C5—H5B	0.9800	C13—H13A	0.9800
C5—H5C	0.9800	C13—H13B	0.9800
C6—C11	1.3944 (18)	C13—H13C	0.9800
C6—C7	1.4141 (19)	N1—H100	0.83 (2)
C6—N1	1.4153 (17)	O2—H200	0.90 (2)
C7—O2	1.3530 (16)	O3—S1	1.4435 (11)
C7—C8	1.388 (2)	O4—S1	1.4441 (10)
C2—C1—H1A	109.5	C8—C9—H9	120.3
C2—C1—H1B	109.5	C10—C9—H9	120.3
H1A—C1—H1B	109.5	C9—C10—C11	121.61 (13)
C2—C1—H1C	109.5	C9—C10—S1	119.14 (11)
H1A—C1—H1C	109.5	C11—C10—S1	119.25 (11)
H1B—C1—H1C	109.5	C10—C11—C6	118.96 (12)

O1—C2—C3	122.55 (13)	C10—C11—H11	120.5
O1—C2—C1	119.35 (13)	C6—C11—H11	120.5
C3—C2—C1	118.10 (13)	C13—C12—S1	110.90 (10)
C4—C3—C2	125.03 (13)	C13—C12—H12A	109.5
C4—C3—H3	117.5	S1—C12—H12A	109.5
C2—C3—H3	117.5	C13—C12—H12B	109.5
N1—C4—C3	119.68 (13)	S1—C12—H12B	109.5
N1—C4—C5	120.76 (13)	H12A—C12—H12B	108.0
C3—C4—C5	119.56 (13)	C12—C13—H13A	109.5
C4—C5—H5A	109.5	C12—C13—H13B	109.5
C4—C5—H5B	109.5	H13A—C13—H13B	109.5
H5A—C5—H5B	109.5	C12—C13—H13C	109.5
C4—C5—H5C	109.5	H13A—C13—H13C	109.5
H5A—C5—H5C	109.5	H13B—C13—H13C	109.5
H5B—C5—H5C	109.5	C4—N1—C6	130.38 (13)
C11—C6—C7	119.51 (12)	C4—N1—H100	115.0 (14)
C11—C6—N1	125.14 (12)	C6—N1—H100	113.3 (14)
C7—C6—N1	115.19 (12)	C7—O2—H200	111.5 (14)
O2—C7—C8	123.15 (12)	O3—S1—O4	117.88 (7)
O2—C7—C6	116.54 (12)	O3—S1—C10	107.85 (7)
C8—C7—C6	120.31 (13)	O4—S1—C10	109.53 (6)
C9—C8—C7	120.15 (13)	O3—S1—C12	108.61 (7)
C9—C8—H8	119.9	O4—S1—C12	108.25 (7)
C7—C8—H8	119.9	C10—S1—C12	103.81 (7)
C8—C9—C10	119.43 (13)		

O1—C2—C3—C4	0.3 (2)	C7—C6—C11—C10	1.86 (19)
C1—C2—C3—C4	179.55 (13)	N1—C6—C11—C10	177.04 (13)
C2—C3—C4—N1	−1.3 (2)	C3—C4—N1—C6	172.26 (13)
C2—C3—C4—C5	178.54 (13)	C5—C4—N1—C6	−7.6 (2)
C11—C6—C7—O2	177.09 (12)	C11—C6—N1—C4	40.5 (2)
N1—C6—C7—O2	1.45 (18)	C7—C6—N1—C4	−144.18 (14)
C11—C6—C7—C8	−2.0 (2)	C9—C10—S1—O3	−15.06 (13)
N1—C6—C7—C8	−177.69 (12)	C11—C10—S1—O3	164.72 (11)
O2—C7—C8—C9	−177.90 (13)	C9—C10—S1—O4	−144.52 (11)
C6—C7—C8—C9	1.2 (2)	C11—C10—S1—O4	35.25 (13)
C7—C8—C9—C10	−0.1 (2)	C9—C10—S1—C12	100.05 (12)
C8—C9—C10—C11	0.0 (2)	C11—C10—S1—C12	−80.17 (12)
C8—C9—C10—S1	179.75 (11)	C13—C12—S1—O3	−59.05 (12)
C9—C10—C11—C6	−0.8 (2)	C13—C12—S1—O4	70.04 (12)
S1—C10—C11—C6	179.38 (10)	C13—C12—S1—C10	−173.62 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H100···O1	0.83 (2)	1.98 (2)	2.657 (2)	139 (2)
N1—H100···O2	0.83 (2)	2.24 (2)	2.622 (2)	108 (2)
O2—H200···O1$^{\rm i}$	0.90 (2)	1.70 (2)	2.601 (1)	175 (2)
C1—H1*B*···O2$^{\rm ii}$	0.98	2.48	3.457 (2)	172

C12—H12*B*···O4^{iii}	0.99	2.38	3.267 (2)	149
C13—H13*B*···O3^{iv}	0.98	2.55	3.372 (2)	142

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

(II) (3*Z*)-4-(5-*tert*-Butyl-2-hydroxyanilino)pent-3-en-2-one

Crystal data

$C_{15}H_{21}NO_2$	$F(000) = 536$
$M_r = 247.33$	$D_x = 1.170$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2476 reflections
$a = 12.3617$ (7) Å	$\theta = 1.7$–$26.0°$
$b = 8.3063$ (5) Å	$\mu = 0.08$ mm^{-1}
$c = 14.1054$ (8) Å	$T = 100$ K
$\beta = 104.114$ (2)°	Needle, colourless
$V = 1404.62$ (14) Å^3	0.40 × 0.25 × 0.18 mm
$Z = 4$	

Data collection

Bruker APEX DUO diffractometer	10867 measured reflections
Radiation source: Incoatec microsource	2709 independent reflections
Graphite monochromator	2476 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\rm int} = 0.016$
Absorption correction: multi-scan (*SADABS*; Bruker, 2010)	$\theta_{\rm max} = 26.0°$, $\theta_{\rm min} = 1.7°$
$T_{\rm min} = 0.970$, $T_{\rm max} = 0.986$	$h = -15\rightarrow12$
	$k = -9\rightarrow10$
	$l = -11\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.825P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\rm max} = 0.010$
2709 reflections	$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
176 parameters	$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	0.83957 (7)	0.29365 (12)	0.98641 (7)	0.0192 (2)
O1	0.86652 (7)	0.10651 (11)	0.66786 (6)	0.0169 (2)
N1	0.78093 (8)	0.09934 (13)	0.82105 (8)	0.0148 (2)
C15	0.29802 (10)	0.25200 (18)	0.85609 (10)	0.0236 (3)
H15A	0.3083	0.3645	0.8393	0.035*
H15B	0.3118	0.2414	0.9272	0.035*
H15C	0.2215	0.2184	0.8255	0.035*
C12	0.38003 (10)	0.14538 (15)	0.81904 (10)	0.0186 (3)
C10	0.50147 (10)	0.19556 (15)	0.86262 (9)	0.0157 (3)
C11	0.58701 (10)	0.12996 (15)	0.82546 (9)	0.0156 (3)
H11	0.5680	0.0609	0.7702	0.019*
C6	0.69864 (10)	0.16257 (15)	0.86668 (9)	0.0146 (3)
C4	0.86111 (10)	−0.00646 (15)	0.85914 (9)	0.0150 (3)
C3	0.93860 (10)	−0.05218 (15)	0.80706 (9)	0.0158 (3)
H3	0.9953	−0.1263	0.8368	0.019*
C2	0.93769 (10)	0.00529 (15)	0.71269 (9)	0.0153 (3)
C1	1.02283 (11)	−0.05663 (19)	0.66153 (10)	0.0250 (3)
H1A	0.9849	−0.1138	0.6019	0.038*
H1B	1.0739	−0.1304	0.7049	0.038*
H1C	1.0652	0.0340	0.6444	0.038*
C13	0.36577 (12)	−0.02851 (18)	0.85116 (14)	0.0337 (4)
H13A	0.3834	−0.0338	0.9227	0.051*
H13B	0.4163	−0.0995	0.8268	0.051*
H13C	0.2885	−0.0631	0.8244	0.051*
C9	0.53385 (10)	0.29864 (15)	0.94273 (9)	0.0166 (3)
H9	0.4780	0.3468	0.9693	0.020*
C8	0.64531 (10)	0.33288 (15)	0.98480 (9)	0.0166 (3)
H8	0.6642	0.4037	1.0392	0.020*
C7	0.72958 (10)	0.26451 (15)	0.94800 (9)	0.0150 (3)
C5	0.86327 (11)	−0.07976 (17)	0.95670 (9)	0.0200 (3)
H5A	0.8799	0.0038	1.0072	0.030*
H5B	0.9209	−0.1633	0.9716	0.030*
H5C	0.7904	−0.1278	0.9551	0.030*
C14	0.35188 (11)	0.15514 (19)	0.70700 (10)	0.0262 (3)
H14A	0.2731	0.1282	0.6806	0.039*
H14B	0.3986	0.0789	0.6818	0.039*
H14C	0.3660	0.2646	0.6870	0.039*
H100	0.7804 (13)	0.133 (2)	0.7608 (13)	0.027 (4)*
H200	0.8488 (16)	0.338 (2)	1.0476 (16)	0.046 (5)*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0148 (4)	0.0276 (5)	0.0156 (5)	−0.0046 (4)	0.0046 (3)	−0.0064 (4)
O1	0.0166 (4)	0.0208 (5)	0.0136 (4)	0.0018 (3)	0.0040 (3)	0.0018 (3)
N1	0.0153 (5)	0.0192 (5)	0.0105 (5)	0.0006 (4)	0.0045 (4)	−0.0009 (4)
C15	0.0149 (6)	0.0289 (7)	0.0264 (7)	0.0032 (5)	0.0040 (5)	0.0003 (6)

C12	0.0142 (6)	0.0166 (6)	0.0243 (7)	0.0008 (5)	0.0033 (5)	0.0013 (5)
C10	0.0155 (6)	0.0137 (6)	0.0173 (6)	0.0015 (5)	0.0031 (5)	0.0038 (5)
C11	0.0181 (6)	0.0145 (6)	0.0136 (6)	0.0007 (5)	0.0029 (5)	−0.0003 (5)
C6	0.0162 (6)	0.0161 (6)	0.0124 (6)	0.0015 (5)	0.0054 (5)	0.0013 (5)
C4	0.0144 (6)	0.0165 (6)	0.0128 (6)	−0.0029 (4)	0.0004 (4)	−0.0016 (5)
C3	0.0138 (6)	0.0176 (6)	0.0150 (6)	0.0016 (5)	0.0014 (5)	−0.0010 (5)
C2	0.0127 (5)	0.0165 (6)	0.0161 (6)	−0.0021 (5)	0.0028 (5)	−0.0030 (5)
C1	0.0223 (7)	0.0316 (8)	0.0240 (7)	0.0065 (6)	0.0113 (5)	0.0014 (6)
C13	0.0198 (7)	0.0203 (7)	0.0580 (11)	−0.0022 (5)	0.0036 (7)	0.0090 (7)
C9	0.0173 (6)	0.0156 (6)	0.0185 (6)	0.0031 (5)	0.0072 (5)	0.0017 (5)
C8	0.0210 (6)	0.0150 (6)	0.0143 (6)	0.0001 (5)	0.0053 (5)	−0.0019 (5)
C7	0.0154 (6)	0.0169 (6)	0.0129 (6)	−0.0016 (5)	0.0038 (4)	0.0022 (5)
C5	0.0202 (6)	0.0244 (7)	0.0151 (6)	0.0002 (5)	0.0038 (5)	0.0030 (5)
C14	0.0171 (6)	0.0340 (8)	0.0246 (7)	−0.0006 (6)	−0.0004 (5)	−0.0070 (6)

Geometric parameters (Å, º)

O2—C7	1.3570 (14)	C3—C2	1.4116 (17)
O2—H200	0.92 (2)	C3—H3	0.9500
O1—C2	1.2686 (15)	C2—C1	1.5045 (17)
N1—C4	1.3356 (16)	C1—H1A	0.9800
N1—C6	1.4298 (15)	C1—H1B	0.9800
N1—H100	0.894 (18)	C1—H1C	0.9800
C15—C12	1.5309 (18)	C13—H13A	0.9800
C15—H15A	0.9800	C13—H13B	0.9800
C15—H15B	0.9800	C13—H13C	0.9800
C15—H15C	0.9800	C9—C8	1.3903 (17)
C12—C10	1.5346 (17)	C9—H9	0.9500
C12—C14	1.5353 (19)	C8—C7	1.3931 (17)
C12—C13	1.5367 (19)	C8—H8	0.9500
C10—C9	1.3962 (18)	C5—H5A	0.9800
C10—C11	1.4001 (17)	C5—H5B	0.9800
C11—C6	1.3873 (17)	C5—H5C	0.9800
C11—H11	0.9500	C14—H14A	0.9800
C6—C7	1.4018 (17)	C14—H14B	0.9800
C4—C3	1.3945 (17)	C14—H14C	0.9800
C4—C5	1.4991 (17)		

C7—O2—H200	109.2 (12)	C2—C1—H1A	109.5
C4—N1—C6	126.89 (11)	C2—C1—H1B	109.5
C4—N1—H100	115.0 (11)	H1A—C1—H1B	109.5
C6—N1—H100	118.1 (10)	C2—C1—H1C	109.5
C12—C15—H15A	109.5	H1A—C1—H1C	109.5
C12—C15—H15B	109.5	H1B—C1—H1C	109.5
H15A—C15—H15B	109.5	C12—C13—H13A	109.5
C12—C15—H15C	109.5	C12—C13—H13B	109.5
H15A—C15—H15C	109.5	H13A—C13—H13B	109.5
H15B—C15—H15C	109.5	C12—C13—H13C	109.5
C15—C12—C10	111.75 (11)	H13A—C13—H13C	109.5
C15—C12—C14	108.55 (11)	H13B—C13—H13C	109.5

C10—C12—C14	110.61 (10)	C8—C9—C10	121.98 (11)
C15—C12—C13	108.06 (11)	C8—C9—H9	119.0
C10—C12—C13	107.97 (10)	C10—C9—H9	119.0
C14—C12—C13	109.85 (12)	C9—C8—C7	120.73 (11)
C9—C10—C11	116.61 (11)	C9—C8—H8	119.6
C9—C10—C12	123.38 (11)	C7—C8—H8	119.6
C11—C10—C12	119.91 (11)	O2—C7—C8	123.09 (11)
C6—C11—C10	122.14 (11)	O2—C7—C6	118.77 (11)
C6—C11—H11	118.9	C8—C7—C6	118.13 (11)
C10—C11—H11	118.9	C4—C5—H5A	109.5
C11—C6—C7	120.40 (11)	C4—C5—H5B	109.5
C11—C6—N1	118.93 (11)	H5A—C5—H5B	109.5
C7—C6—N1	120.54 (10)	C4—C5—H5C	109.5
N1—C4—C3	120.33 (11)	H5A—C5—H5C	109.5
N1—C4—C5	118.81 (11)	H5B—C5—H5C	109.5
C3—C4—C5	120.81 (11)	C12—C14—H14A	109.5
C4—C3—C2	123.79 (11)	C12—C14—H14B	109.5
C4—C3—H3	118.1	H14A—C14—H14B	109.5
C2—C3—H3	118.1	C12—C14—H14C	109.5
O1—C2—C3	122.63 (11)	H14A—C14—H14C	109.5
O1—C2—C1	117.96 (11)	H14B—C14—H14C	109.5
C3—C2—C1	119.41 (11)		

C15—C12—C10—C9	14.20 (17)	N1—C4—C3—C2	−1.04 (19)
C14—C12—C10—C9	135.27 (13)	C5—C4—C3—C2	176.43 (11)
C13—C12—C10—C9	−104.50 (15)	C4—C3—C2—O1	1.24 (19)
C15—C12—C10—C11	−169.52 (11)	C4—C3—C2—C1	−177.78 (12)
C14—C12—C10—C11	−48.46 (16)	C11—C10—C9—C8	−1.00 (18)
C13—C12—C10—C11	71.77 (15)	C12—C10—C9—C8	175.39 (11)
C9—C10—C11—C6	1.15 (18)	C10—C9—C8—C7	−0.05 (19)
C12—C10—C11—C6	−175.38 (11)	C9—C8—C7—O2	−179.87 (11)
C10—C11—C6—C7	−0.24 (19)	C9—C8—C7—C6	0.98 (18)
C10—C11—C6—N1	−176.12 (11)	C11—C6—C7—O2	179.98 (11)
C4—N1—C6—C11	−116.71 (14)	N1—C6—C7—O2	−4.21 (17)
C4—N1—C6—C7	67.42 (17)	C11—C6—C7—C8	−0.83 (18)
C6—N1—C4—C3	−177.34 (11)	N1—C6—C7—C8	174.98 (11)
C6—N1—C4—C5	5.14 (18)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H100···O1	0.89 (2)	1.89 (2)	2.628 (2)	138 (2)
O2—H200···O1^{i}	0.92 (2)	1.72 (2)	2.633 (1)	172 (2)

Symmetry code: (i) *x*, −*y*+1/2, *z*+1/2.

Comparison of experimental and DFT-calculated bond lengths (Å) for (I)

Bond	X-ray	Keto tautomer	Enol tautomer
C2—O1	1.263 (2)	1.238	1.323
C2—C3	1.416 (2)	1.447	1.370

C3—C4	1.394 (2)	1.376	1.441
C4—N1	1.344 (2)	1.365	1.305
N1—C6	1.415 (2)	1.396	1.395

Comparison of experimental and DFT-calculated bond lengths (Å) for (II)

Bond	X-ray	Keto tautomer	Enol tautomer
C2—O1	1.268 (1)	1.251	1.326
C2—C3	1.411 (2)	1.437	1.372
C3—C4	1.395 (2)	1.385	1.443
C4—N1	1.335 (2)	1.355	1.308
N1—C6	1.430 (2)	1.417	1.408