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N^1-(4-*tert*-Butylphenyl)-N^2-hydroxy-*α*-oxo-*α*-phenylacetamidine and N^2-hydroxy-N^1-(4-nitrophenyl)-*α*-oxo-*α*-phenylacetamidine hemihydrate

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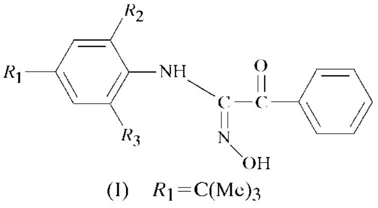
In the title compounds, $C_{18}H_{20}N_2O_2$, (I), and $C_{14}H_{11}N_3O_4\cdot0.5H_2O$, (II), respectively, the oxime groups have an *E* configuration. In (I), the molecules exist as polymers bound by intermolecular C—H···O and O—H···N hydrogen bonds around inversion centres. In (II), intermolecular O*W*—H···N, O*W*—H···O and O—H···O*W* interactions stabilize the molecular packing.

Comment

The oxime group (C═N—OH) possesses stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman *et al.*, 1999). Intermolecular hydrogen bonding has received considerable attention among the range of directional non-covalent intermolecular interactions, which combine moderate strength and directionality, in the design of compounds with supramolecular structures (Karle *et al.*, 1996). The crystal structure determination of the title compounds, N^1-(4-*tert*-butylphenyl)-N^2-hydroxy-*α*-oxo-*α*-phenylacetamidine, (I), and N^2-hydroxy-N^1-(4-nitrophenyl)-*α*-oxo-*α*-phenylacetamidine hemihydrate, (II*A*) and (II*B*) (two independent molecules), were carried out to determine the strength of the hydrogen-bonding capabilities of the oxime group, to establish the molecular arrangements, and also to compare the geometry of the oxime moiety with those found in the related compounds 2-[benzoyl(hydroxyimino)methylamino]benzoic acid, (III) (Soylu, Taş, Batı *et al.*, 2004), and N^1-(2,6-dimethylphenyl)-N^2-hydroxy-*α*-oxo-*α*-phenylacetamidine, (IV) (Soylu, Taş, Saraçoğlu *et al.*, 2004).



(I) R_1=C(Me)$_3$
(II) R_1=NO$_2$, +0.5H$_2$O
(III) R_2=COOH
(IV) R_2=R_3=Me

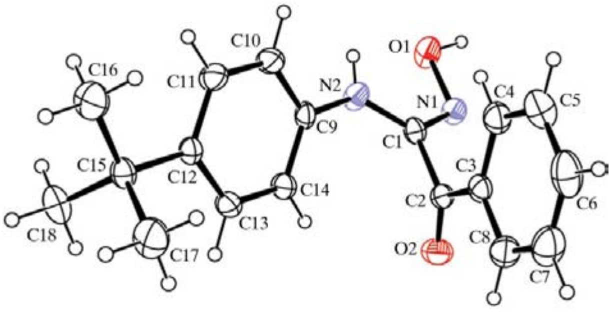


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

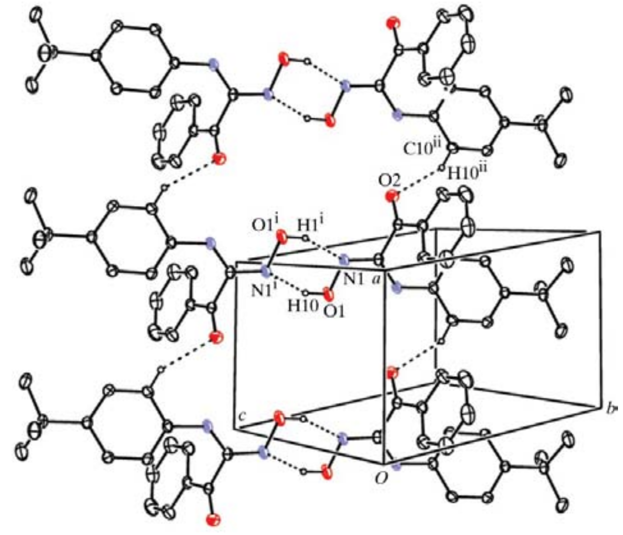


Figure 2
A view of the hydrogen-bonding interactions in (I). For the sake of clarity, all H atoms, except for H8 and H1O, have been omitted. [Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $1 + x, y, z$.]

Compound (I) crystallizes in the triclinic space group $P\overline{1}$ (Fig. 1), whereas compound (II) crystallizes in the monoclinic space group $P2_1/n$, with two independent molecules in the asymmetric unit (Fig. 3). Both compounds consist of two benzene rings linked through an oxime moiety. The interplanar angles between the oxime moiety and the benzene rings are listed in Table 3.

While benzene rings *B* (C3–C8) and *C* (C9–C14) are nearly perpendicular to one another in these and the above-mentioned related compounds, those in molecules (II*A*) and (II*B*) are much more coplanar than those in (I). The oxime moiety in (I), (II*A*) and (II*B*) has an *E* conformation, with appropriate C2—C1═N1—O1 torsion angles. There are no

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significant differences in the C1=N1 bond distances or in the C2—C1=N1 bond angles (Table 3). The bond lengths and angles of the oxime moiety in (I) are in close accord with the reported values for (III).

Analysis of the crystal packing of (I) and (II) shows significant differences. The molecules of (I) are linked by a nearly linear O—H···N hydrogen bond and a rather weak C—H···O hydrogen bond (Table 1). Atom O1 of the oxime group behaves as a donor, resulting in the formation of O1—H1O···N1 hydrogen bonds which link two molecules related by an inversion centre in an $R_2^2(6)$-type dimeric arrangement; the intermolecular C10—H10···O2($x-1$, y, z) hydrogen bond is of type $C_1^1(7)$ (Bernstein *et al.*, 1995). This interaction links the dimers along the *a* axis and, as a consequence of this hydrogen bond, the molecules form interesting polymers approximately along the *a* axis in the crystal, as illustrated in Fig. 2.

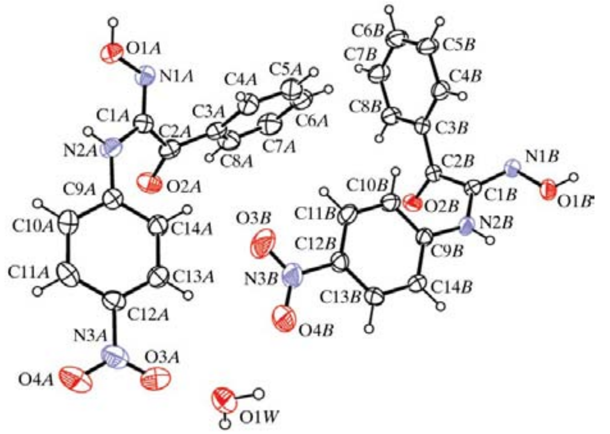

Figure 3

A view of the asymmetric unit of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

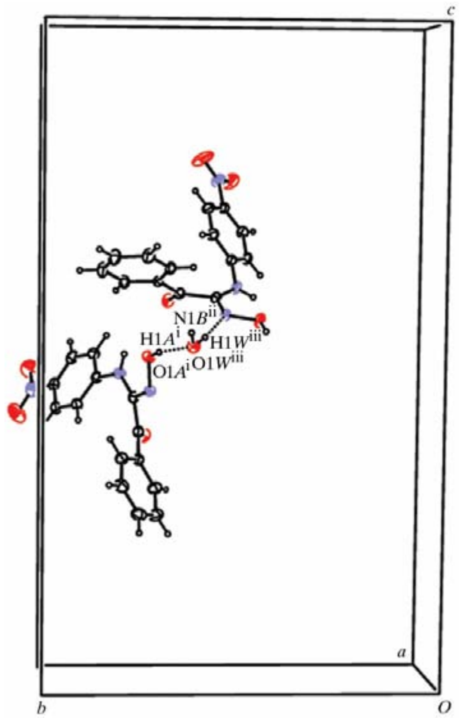

Figure 4

A view of the hydrogen-bonding interactions in (II). For the sake of clarity, H atoms bonded to C atoms have been omitted. [Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $2-x, 1-y, 1-z$; (iv) x, y, z; (v) $x-1, y, z$].

In compound (II), the water O atom, O1*W*, is involved in four hydrogen bonds, in two as a donor and in two as an acceptor (Table 2 and Fig. 4). There are close contacts between the water and hydroxy groups (H1*A*···H1*W* and H1*B*···H2*W*). This may relate to the observed disorder of the water H atoms. The crystal packing is therefore stabilized by intermolecular hydrogen bonds, which form a polymeric arrangement parallel to the *a* axis. While compound (I) forms a polymeric arrangement of symmetry-related molecules, compound (II) arranges polymeric chains of molecules with solvate water molecules, suggesting that the hydrogen-bonding interactions in (II) are stronger than those in (I). Weak dipole–dipole and van der Waals interactions are also present in both compounds.

Experimental

To a solution of 4-*tert*-butylaniline (0.15 mol, 2.24 g) in ethanol (10 ml) was added dropwise a solution of ω-chloroisonitrosoacetophenone (2.75 g, 0.015 mol) in ethanol (20 ml). $NaHCO_3$ (1.10 g) was added to the solution. The precipated product, *viz*. compound (I), was filtered off and the resulting solution was allowed to stand for 1 h at room temperature for crystallization to occur. Compound (II) was prepared from a mixture of ω-chloroisonitrosoacetophenone (2.75 g, 0.015 mol) and $NaHCO_3$ (1.10 g, 0.015 mol) in *p*-nitroaniline (0.015 mol, 1.38 g) dissolved in ethanol (10 ml). The precipitate was stirred for 4 h and dissolved in water (10 ml). The crystallized product was filtered off, washed with ethanol and dried.

Compound (I)

Crystal data

$C_{18}H_{20}N_2O_2$
$M_r = 296.36$
Triclinic, $P\bar{1}$
$a = 6.4331$ (10) Å
$b = 10.7150$ (15) Å
$c = 12.299$ (2) Å
$\alpha = 75.054$ (12)°
$\beta = 82.120$ (12)°
$\gamma = 77.258$ (11)°
$V = 796.0$ (2) Å^3
$Z = 2$

$D_x = 1.236$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4848 reflections
$\theta = 2.0$–26.8°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Rod, yellow
0.42 × 0.19 × 0.05 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
10 299 measured reflections
2808 independent reflections
1403 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.093$
$\theta_{\rm max} = 25.0°$
$h = -7 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.114$
$S = 0.95$
2808 reflections
207 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···N1^{i}	0.91 (4)	1.95 (4)	2.801 (3)	155 (4)
C10—H10···O2^{ii}	0.93	2.50	3.351 (4)	152

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

Compound (II)

Crystal data

$C_{14}H_{11}N_3O_4 \cdot 0.5H_2O$
$M_r = 294.27$
Monoclinic, $P2_1/n$
$a = 6.8298$ (5) Å
$b = 15.5454$ (15) Å
$c = 26.097$ (2) Å
$\beta = 92.080$ (7)°
$V = 2769.0$ (4) Å^3
$Z = 8$

$D_x = 1.412$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 5334 reflections
$\theta = 1.5$–24.0°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Rod, yellow
0.40 × 0.22 × 0.12 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
17 727 measured reflections
4876 independent reflections
1986 reflections with $I > 2\sigma(I)$

$R_{int} = 0.067$
$\theta_{max} = 25.0°$
$h = -8 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -30 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.047$
$S = 0.81$
4876 reflections
402 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.005P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.13$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···O1W^{i}	0.82	2.00	2.808 (3)	167
O1B—H1B···O1W^{ii}	0.82	1.93	2.750 (2)	173
O1W—H1W···N1B^{iii}	0.82 (2)	2.02 (2)	2.838 (2)	176 (2)
O1W—H2W···O2B^{iv}	0.81 (2)	2.00 (2)	2.787 (2)	166 (2)

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

Table 3
Comparison of geometric parameters (Å, °) for (I) and (II) with those in the related compounds (III) and (VI).

A is the ring O1/N1/C1, B is the ring C3–C8 and C is the ring C9–C14.

Bond	(I)	(IIA)	(IIB)	(III)	(IV)
C1—N1	1.283 (3)	1.290 (3)	1.299 (3)	1.288 (2)	1.295 (3)
N1—O1	1.418 (3)	1.402 (2)	1.404 (2)	1.4093 (18)	1.413 (3)
C2—C1	1.518 (4)	1.500 (3)	1.516 (3)	1.501 (2)	1.494 (4)
C1—N1—O1	110.1 (3)	108.68 (19)	109.47 (18)	111.51 (13)	109.97 (19)
C2—C1—N1	113.2 (3)	112.7 (2)	116.4 (2)	113.21 (15)	115.6 (2)
C2—C1—N1—O1	−178.0 (3)	169.90 (17)	−172.33 (18)	169.11 (14)	−174.6 (2)
A/B	82.8 (3)	60.3 (2)	56.6 (2)	58.61 (10)	50.10 (14)
A/C	39.7 (3)	35.2 (2)	44.6 (2)	30.13 (11)	73.37 (11)
B/C	72.30 (18)	81.43 (13)	76.07 (12)	75.30 (9)	89.19 (6)

In compound (I), C-bound H atoms were positioned geometrically and refined using a riding model, with C—H distances in the range 0.93–0.96 Å and with $U_{iso}(H) = 1.2U_{eq}$ or $1.5U_{eq}$ of the parent atom. The remaining H atoms were located by difference Fourier methods and refined with isotropic displacement parameters. In the final stages of refinement for compound (II), the H atoms on O1A, O1B and the phenyl groups were placed in calculated positions and refined using a riding model, with X—H distances of 0.82 and 0.93 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}$ of the parent atom. The water H atoms were disordered and restraints were applied [O—H = 0.82 (1) Å and H···H = 1.30 (1) Å]. They were located by difference Fourier methods and refined with isotropic displacement parameters.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA1061). Services for accessing these data are described at the back of the journal.

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