# organic papers

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.004 Å

R factor = 0.041

wR factor = 0.100

Data-to-parameter ratio = 19.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

N-(3-Chloro-4-methylphenyl)-N'-hydroxy-2-oxo-2-phenylacetamidine

The title compound, $C_{15}H_{13}ClN_2O_2$, contains two independent molecules in the asymmetric unit. In both molecules, the oxime moiety has an E configuration. Intermolecular O—H$\cdots$N [O$\cdots$N = 2.776 (2) and 2.771 (2) Å] and intramolecular N—H$\cdots$O [N$\cdots$O = 2.532 (3) and 2.534 (3) Å] hydrogen bonds are highly effective in the crystal structure. The O—H$\cdots$N intermolecular hydrogen bonds link the independent molecules into dimers, which are, in turn, interlinked through N—H$\cdots$Cl interactions to form layers parallel to the ab plane.

Comment

Oxime and dioxime derivatives are very important compounds in the chemical industry and medicine (Sevagapandian et al., 2000). The oxime (—C=N—OH) moiety is potentially ambidentate, with possibilities of coordination through the N and/or O atoms. It is a functional group that has not been extensively explored in crystal engineering. In the solid state, oximes are usually associated via O—H$\cdots$N hydrogen bonds of length 2.8 Å. Oxime groups possess stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman et al., 1999), in which intermolecular hydrogen bonding combines moderate strength and directionality (Karle et al., 1996) in linking molecules to form supramolecular structures; this has received considerable attention with respect to directional non-covalent intermolecular interactions (Etter et al., 1990).

The structures of oxime and dioxime derivatives have been the subject of much interest in our laboratory; examples include 2,3-dimethylquinoxaline–dimethylglyoxime (1/1), (II) (Hökelek, Batı et al., 2001), 1-(2,6-dimethylphenylamino)-propane-1,2-dione dioxime, (III) (Hökelek, Zülfikaroğlu et al., 2001), N-hydroxy-2-oxo-2,N'-diphenylacetamidine, (IV) (Büyükgüngör et al., 2003), N-(3,4-dichlorophenyl)-N'-hydroxy-2-oxo-2-phenylacetamidine, (V) (Hökelek, Taş & Batı, 2004), and N-hydroxy-N'-(1-naphthyl)-2-phenyl-acetamidin-2-one, (VI) (Hökelek, Büyükgüngör et al., 2004). The structure determination of the title molecule, (I), was carried out in order to investigate the strength of the hydrogen-bonding capability of the oxime group and to compare the geometry of the oxime moiety with those previously reported.
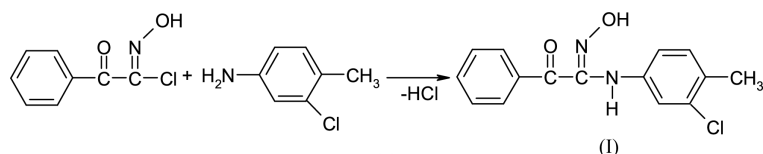
Compound (I) (Fig. 1) consists of 3-chloro-4-methyl-phenylamino and 2-phenylethane-1,2-dione 1-oxime moieties.
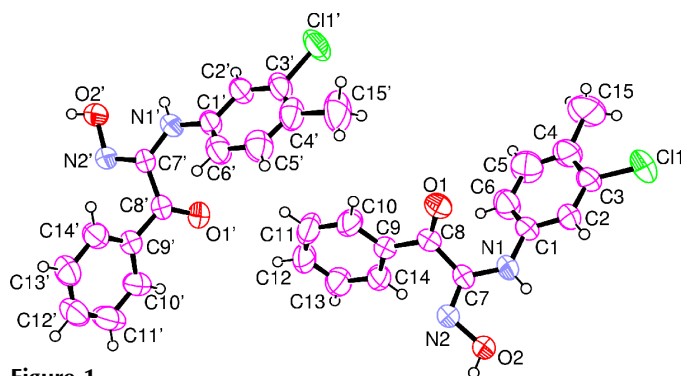
Figure 1
The two molecules in the asymmetric unit of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The asymmetric unit contains two molecules. The dihedral angles between the oxime planes (A: atoms O2/N2/C7; A': atoms O2′/N2′/C7′) and rings B (C1–C6), B' (C1′–C6′), C (C9–C14) and C' (C9′–C14′) are A/B = 37.8 (1), A/C = 59.0 (2), A'/B' = 37.1 (1) and A'/C' = 62.9 (2)°.

The steric effects of the substituents bonded to the C atoms of the oxime group may influence the bond lengths and angles of the oxime moiety (Table 1). In the two independent molecules, corresponding angles have slightly different values. Some significant changes in the geometry of the oxime moiety are evident when the bond lengths and angles are compared with the corresponding values in compounds (II)–(VI) (Table 2).

In both molecules, the oxime moiety has an E configuration [C8—C7—N2—O2 = −170.2 (2)° and C8′—C7′—N2′—O2′ −169.8 (2)°; Chertanova *et al.*, 1994]. In this configuration, the oxime groups are involved as donors in O2—H2···N2′i and O2′—H2′···N2ii intermolecular hydrogen bonds [O2—H2 = 0.82 Å, O2···N2′i = 2.776 (2) Å, H2···N2′i = 2.08 Å and O2—H2···N2′i = 143°; O2′—H2′ = 0.82 Å, O2′···N2ii = 2.771 (2) Å, H2′···N2ii = 2.07 Å and O2′—H2′···N2ii = 143°; symmetry codes: (i) $\frac{1}{2}$ x, $\frac{1}{2}$ + y, z − $\frac{1}{2}$; (ii) $\frac{1}{2}$ − x, y − $\frac{1}{2}$, $\frac{1}{2}$ + z]. There are also N1—H1···O2 and N1′—H1′···O2′ intramolecular hydrogen bonds [N1—H1 = 0.86 Å, N1···O2 = 2.532 (3) Å, H1···O2 = 2.18 Å and N1—H1···O2 = 105°; N1′—H1′ = 0.86 Å, N1′···O2′ = 2.534 (3) Å, H1′···O2′ = 2.20 Å and N1′—H1′···O2′ = 103°].

In the crystal structure, the O—H···N intermolecular hydrogen bonds link the independent molecules into dimers. As can be seen from the packing diagram (Fig. 2), the dimers are stacked along the b axis. Adjacent dimers are linked by H1···Cl1′(−x, 1 − y, z − $\frac{1}{2}$) (2.75 Å) and H1′···Cl1(−x, −y, $\frac{1}{2}$ + z) (2.90 Å) interactions to form layers parallel to the ab plane. Dipole–dipole and van der Waals interactions are also effective in the molecular packing in the crystal structure.

Experimental

A solution of ω-chloroisonitrosoacetophenone (0.015 mol, 2.75 g) in dichloromethane (40 ml) was added dropwise to a solution of 3-chloro-4-methylaniline (0.03 mol, 8.66 g) in dichloromethane (40 ml). The precipitated product was filtered off and the resulting solution

was set aside for crystallization. Five days later, the resulting crystals were washed with ethyl alcohol and then dried.

Crystal data

$C_{15}H_{13}ClN_2O_2$	Mo $K\alpha$ radiation
$M_r = 288.73$	Cell parameters from 13878
Orthorhombic, $Pna2_1$	reflections
$a = 25.6412$ (14) Å	$\theta = 2.3$–26.9°
$b = 4.9773$ (3) Å	$\mu = 0.27$ mm⁻¹
$c = 22.3894$ (16) Å	$T = 293$ (2) K
$V = 2857.4$ (3) Å³	Block, pale yellow
$Z = 8$	$0.40 \times 0.30 \times 0.15$ mm
$D_x = 1.342$ Mg m⁻³	

Data collection

Stoe IPDS-2 diffractometer	$R_{int} = 0.091$
φ scans	$\theta_{max} = 28.2°$
Absorption correction: none	$h = -34 \rightarrow 33$
32785 measured reflections	$k = -6 \rightarrow 5$
7041 independent reflections	$l = -29 \rightarrow 29$
3175 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$\Delta\rho_{max} = 0.16$ e Å⁻³
$wR(F^2) = 0.100$	$\Delta\rho_{min} = -0.15$ e Å⁻³
$S = 0.75$	Extinction correction: *SHELXL*97
7041 reflections	Extinction coefficient: 0.0088 (5)
367 parameters	Absolute structure: Flack (1983);
H-atom parameters constrained	3418 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$	Flack parameter = 0.42 (6)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cl1—C3	1.734 (3)	Cl1′—C3′	1.742 (3)
O1—C8	1.210 (3)	O1′—C8′	1.217 (3)
O2—N2	1.416 (3)	O2′—N2′	1.397 (3)
N1—C7	1.355 (3)	N1′—C7′	1.361 (3)
N1—C1	1.413 (3)	N1′—C1′	1.406 (3)
N2—C7	1.282 (3)	N2′—C7′	1.289 (3)
C7—C8	1.501 (4)	C7′—C8′	1.502 (4)
C8—C9	1.487 (3)	C8′—C9′	1.482 (3)
C7—N1—C1	127.8 (2)	C7′—N1′—C1′	126.8 (2)
C7—N2—O2	110.65 (18)	C7′—N2′—O2′	111.09 (18)
C6—C1—N1	122.4 (2)	C6′—C1′—N1′	122.9 (2)
C2—C1—N1	117.6 (3)	C2′—C1′—N1′	117.5 (3)
C4—C3—Cl1	119.6 (2)	C4′—C3′—Cl1′	119.2 (2)
C2—C3—Cl1	117.9 (3)	C2′—C3′—Cl1′	117.4 (3)
C3—C4—C15	122.9 (3)	C3′—C4′—C15′	123.7 (4)
C5—C4—C15	120.5 (4)	C5′—C4′—C15′	120.2 (4)
N2—C7—N1	123.3 (2)	N2′—C7′—N1′	122.8 (2)
N2—C7—C8	114.4 (2)	N2′—C7′—C8′	113.44 (19)
N1—C7—C8	121.7 (2)	N1′—C7′—C8′	122.7 (2)
O1—C8—C9	122.3 (3)	O1′—C8′—C9′	122.0 (2)
O1—C8—C7	118.5 (2)	O1′—C8′—C7′	119.0 (2)
C9—C8—C7	119.1 (2)	C9′—C8′—C7′	118.9 (2)
C14—C9—C8	123.2 (2)	C10′—C9′—C8′	118.9 (3)
C10—C9—C8	117.6 (2)	C14′—C9′—C8′	122.3 (2)
O2—N2—C7—C8	−170.2 (2)	O2′—N2′—C7′—C8′	−169.8 (2)
C1—N1—C7—N2	168.1 (3)	C1′—N1′—C7′—N2′	164.3 (3)
N2—C7—C8—O1	133.0 (3)	N2′—C7′—C8′—O1′	134.9 (3)
N1—C7—C8—O1	−37.6 (4)	N1′—C7′—C8′—O1′	−33.5 (4)
N2—C7—C8—C9	−43.3 (4)	N2′—C7′—C8′—C9′	−41.2 (4)
N1—C7—C8—C9	146.0 (3)	N1′—C7′—C8′—C9′	150.5 (2)
O1—C8—C9—C14	159.4 (3)	O1′—C8′—C9′—C10′	−25.5 (4)
C7—C8—C9—C14	−24.4 (4)	C7′—C8′—C9′—C10′	150.4 (3)
O1—C8—C9—C10	−20.0 (4)	O1′—C8′—C9′—C14′	153.2 (3)
C7—C8—C9—C10	156.2 (3)	C7′—C8′—C9′—C14′	−30.8 (4)

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Table 2
Comparison of bond lengths and angles (Å,°) in the oxime moieties of (I) with the corresponding values in the related compounds (II)–(VI).

|	(I)	(II)	(III)	(V)	(VI)
N2—O2	1.416 (3)	1.403 (2)	1.423 (3)	1.429 (4)	1.424 (2)
	1.397 (3)	1.396 (2)	1.396 (3)		
N2—C7	1.282 (3)	1.281 (2)	1.290 (3)	1.241 (6)	1.289 (2)
	1.289 (3)	1.281 (2)	1.282 (3)		
C7—C8	1.501 (4)	1.477 (3)	1.489 (3)	1.551 (7)	1.513 (2)
	1.502 (4)	1.473 (3)			
C8—C7—N2	114.4 (2)	115.2 (2)	116.6 (2)	118.3 (5)	113.2 (1)
	113.4 (2)	115.0 (2)	115.0 (2)		
C7—N2—O2	110.7 (2)	112.4 (1)	109.4 (2)	112.2 (4)	110.6 (1)
	111.1 (2)	112.2 (1)	111.5 (2)		

The positions of the H atoms were calculated geometrically at distances of 0.82 (OH), 0.86 (NH), 0.93 (CH) and 0.96 Å (CH$_3$) from the carrier atoms, and a riding model was used during the refinement process. A rotating-group model was used for methyl and OH groups. The U_{iso} values were constrained to be 1.2 (1.5 for hydroxy and methyl groups) times U_{eq} of the carrier atom. The refined Flack (1983) parameter for the structure is significantly greater than zero, indicating that some inversion twinning is present.

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).

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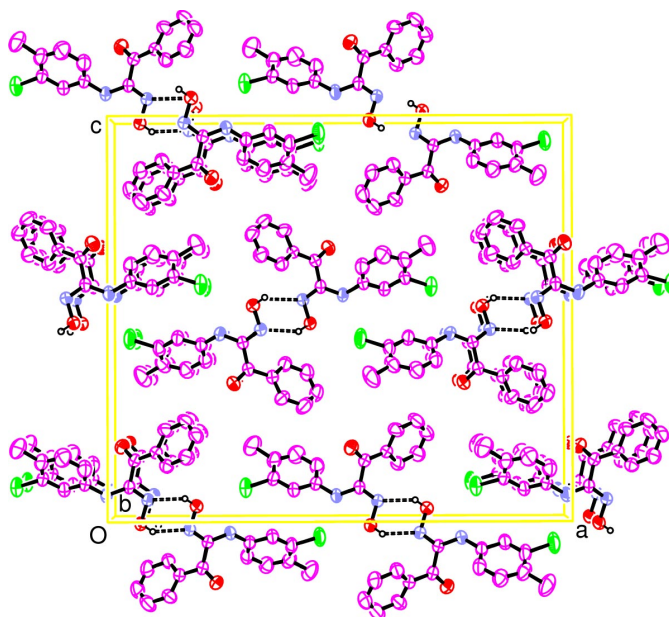
Figure 2
Packing diagram, viewed down the *b* axis. H atoms not involved in hydrogen bonding have been omitted; hydrogen bonds are shown as dashed lines.

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