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N^1-(2,6-Dimethylphenyl)-N^2-hydroxy-α-oxo-α-phenylacetamidine

Serkan Soylu,[a]* Murat Taş,[b] Hanife Saraçoĝlu,[a] Hümeyra Batı,[b] Nezihe Çalışkan[a] and Orhan Büyükgüngör[a]

[a]Department of Physics, Art and Science Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, and [b]Department of Chemistry, Art and Science Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey
Correspondence e-mail: mssoylu@omu.edu.tr

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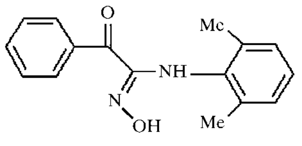
The structure of the title compound, $C_{16}H_{16}N_2O_2$, consists of a dimeric arrangement around an inversion centre of acetamidine molecules linked *via* O—H···N hydrogen bonds. There are also H···π-ring interactions. All these interactions result in the formation of infinite chains parallel to the (101) axis. The oxime group has an *E* conformation.

Comment

Intermolecular hydrogen bonding has received considerable attention as one of the available directional non-covalent intermolecular interactions (Etter *et al.*, 1990) which combine moderate strength and directionality (Karle *et al.*, 1996) in linking molecules to form supramolecular structures. With the aim of investigating the versatility of oximes in coordination chemistry and further researching their involvement in supramolecular polymer chemistry, successful syntheses with oximate groups have been carried out (Liu *et al.*, 2002). The oxime (C═N—OH) group possesses stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman *et al.*, 1999). Hydrogen bonding plays a key role in molecular recognition in chemical engineering (Bertolasi *et al.*, 1982; Gilli *et al.*, 1983; Hökelek *et al.*, 2001).

The crystal structure determination of the title compound, (I), was carried out not only to determine the strength of the hydrogen-bonding capabilities of the oxime groups and the π-ring interactions between the molecules, but also to compare the geometry of the oxime moiety with that found in *N*-(3-chloro-4-methoxyphenyl)-*N*′-hydroxy-2-oxo-2-phenylacetamidine, (II) (Soylu *et al.*, 2003), *N*-hydroxy-2-oxo-2-diphenylacetamidine, (III) (Büyükgüngör *et al.*, 2003) and *N*-(3,4-dichlorophenyl)-*N*′-hydroxy-2-oxo-2-phenylacetamidine, (IV) (Hökelek *et al.*, 2004).

Compound (I) consists of two aromatic rings linked through a monooxime group (Fig. 1). The dihedral angles between oxime plane *A* (O2/N2/C7) and benzene rings *B* (C1–C6) and *C* (C9–C14) are *A*/*B* = 73.37 (11)°, *A*/*C* = 50.10 (14)° and *B*/*C* = 89.19 (6)°, *i.e.* rings *B* and *C* are nearly perpendicular to each other. Ring *C* is linked to the oxime group *via* atom C8(O1), whereas ring *B* is linked to the same functional group *via* atom N1. The steric effects of the bulky phenyl substituent bonded to the oxime group may influence the bond lengths and angles of the oxime moiety, as indicated in Table 1. A comparison of bond lengths and angles of (I) with those in the related compounds (II), (III) and (IV) is shown in Table 3. One can note significant changes in the geometry of the oxime moiety, which are certainly due to the steric effect of the 2,6-dimethylphenyl group.



(I)

The oxime moiety in (I) has an *E* conformation, with a C8—C7—N2—O2 torsion angle of −174.6 (2)°, which deviates slightly from the values reported in other studies (Soylu *et al.*, 2003; Hökelek *et al.*, 2001). In this conformation, atom O2 of the oxime group behaves as a donor, resulting in the formation of O—H···N hydrogen bonds which link two molecules related by an inversion centre (Fig. 2). There is also an intramolecular N1—H···O2 hydrogen bond.

Of greater interest are the intermolecular π-ring interactions with the NH group, which contribute to the crystal packing by forming an infinite chain of dimers (Fig. 2). These π-ring interactions with the NH group are characterized by four parameters, as follows: (i) the distance between atom H1 and the centre of aromatic ring *B* (C1–C6) of 2.98 Å; (ii) the distance between atom H1 and the plane of ring *B* of 2.643 (3) Å; (iii) the angle between the line connecting atom H1 and the centre of ring *B*, *M*, and the normal to the *B* plane of 27.55°; (iv) the angle N1—H1···*M* of 145.4°.

The results obtained in this study indicate that there are significant differences when comparing the geometry of (I) with the geometry of other oxime groups, such as (II), (III)

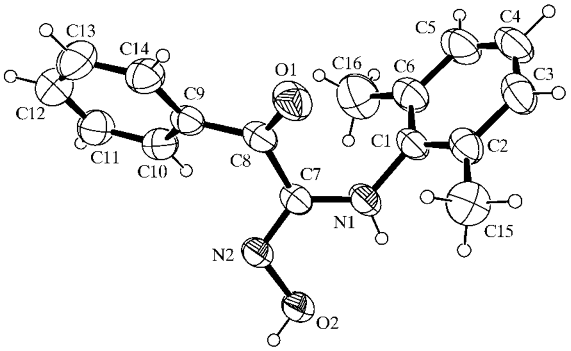


Figure 1
A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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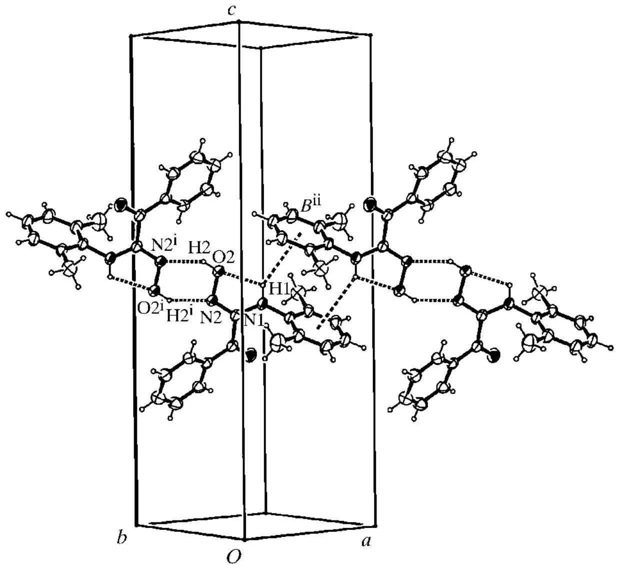

Figure 2
Diagram showing the hydrogen-bonding and π-ring interactions in (I). Displacement ellipsoids are drawn at the 20% probability level. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$.]

and (IV). In these previously reported studies, the crystal packing is mainly stabilized by intermolecular hydrogen bonds, which are highly effective in forming polymeric chains. From the results presented in this paper, it can be said that O—H···N hydrogen bonds link two molecules through an inversion centre to form a dimers. Besides these hydrogen bonds, there is an interesting π-ring interaction which stabilizes the crystal structure. Dipole–dipole and van der Waals interactions are also effective in the molecular packing in the crystal structure.

Experimental

The title compound was prepared from a mixture of ω-chloroisonitrosoacetophenone (2.75 g, 0.015 mol) and 2,6-dimethylaniline (1.82 g, 0.015 mol) in ethanol (20 ml). The precipitate was stirred for 1 h and filtered. The crystallized product was filtered off, washed with ethanol and dried.

Crystal data

$C_{16}H_{16}N_2O_2$
$M_r = 268.31$
Monoclinic, $P2_1/n$
$a = 8.1002$ (10) Å
$b = 7.8837$ (10) Å
$c = 23.108$ (3) Å
$\beta = 90.828$ (10)°
$V = 1475.5$ (3) Å^3
$Z = 4$

$D_x = 1.208$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8969 reflections
$\theta = 1.8$–$23.7°$
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.36 × 0.33 × 0.29 mm

Data collection

Stoe IPDS-2 diffractometer
φ scans
10 735 measured reflections
2566 independent reflections
1316 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.060$
$\theta_{\rm max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 0.87$
2566 reflections
184 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0593P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.11$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—N2	1.413 (2)	C7—C8	1.499 (3)
N2—C7	1.292 (2)	N1—C1	1.420 (2)
C9—C8	1.473 (3)	C8—O1	1.212 (2)
C7—N1	1.349 (2)		
C7—N2—O2	109.89 (15)	C2—C1—N1	117.8 (2)
C10—C9—C8	123.6 (2)	C6—C1—N1	119.8 (2)
C14—C9—C8	118.6 (2)	O1—C8—C9	121.5 (2)
N2—C7—N1	122.81 (19)	O1—C8—C7	118.0 (2)
N1—C7—C8	121.37 (19)	C9—C8—C7	120.5 (2)
C7—N1—C1	128.37 (18)		
O2—N2—C7—C8	−174.53 (17)	C9—C14—C8—O1	164.5 (2)
N2—C7—N1—C1	176.4 (2)	N2—C7—C8—O1	141.4 (2)
C7—N1—C1—C8	5.08 (18)	C7—N1—C8—O1	151.4 (3)
C7—N1—C1—C2	112.4 (2)	N2—C9—C7—C8	−147.8 (2)
C10—C9—C8—O1	160.7 (2)	C9—C7—N1—C8	25.47 (18)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···$N2^i$	0.82	2.02	2.737 (2)	145
N1—H1···O2	0.86	2.13	2.512 (2)	107

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 3
Comparison of geometrical parameters (Å, °) in the oxime moiety of (I) with those in the related compounds (II), (III) and (IV).

	(I)	(II)	(III)	(IV)
N2—O2	1.413 (3)	1.4063 (17)	1.4167 (10)	1.429 (4)
N2—C7	1.295 (3)	1.282 (2)	1.2897 (12)	1.241 (6)
C7—C8	1.494 (4)	1.502 (2)	1.5098 (13)	1.551 (7)
C7—C8—N2	115.6 (2)	113.75 (15)	114.32 (8)	118.3 (5)
C7—N2—O2	109.97 (19)	111.00 (14)	110.66 (8)	112.2 (4)

All H atoms were fixed at localized positions, with C—H distances in the range 0.93–0.96 Å, an N—H distance of 0.86 Å and an O—H distance of 0.82 Å. A riding isotropic displacement parameter was used for all H atoms, with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(parent atom).

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, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996; Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN1035). Services for accessing these data are described at the back of the journal.

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