organic compounds

(E)-4-Nitrobenzaldehyde oxime

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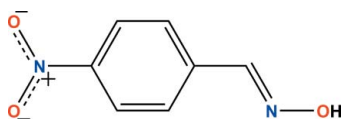Correspondence e-mail: profazmi@hotmail.com

In the title compound, $C_7H_6N_2O_3$, the planes containing the CNO and ONO atoms subtend dihedral angles of 5.47 (5) and 8.31 (5)°, respectively, with the benzene ring. In the crystal structure, intermolecular O—H⋯N hydrogen bonds link the molecules into centrosymmetric dimers with an $R_2^2(6)$ graph-set motif.

Related literature

For oximes as therapeutic agents in organophosphorus poisoning, see: Jokanovic et al. (2009); Marrs et al. (2006). For their use as protecting groups in organic synthesis, see: Greene et al. (1999); Shinada et al. (1995). For graph-set notation, see: Etter et al. (1990); Bernstein et al. (1995). For bond lengths in similar structures, see: Xing, Ding et al. (2007); Xing, Wang et al. (2007).

Experimental

Crystal data

$C_7H_6N_2O_3$	$c = 28.6651$ (14) Å
$M_r = 166.14$	$\beta = 91.237$ (3)°
Monoclinic, $P2_1/n$	$V = 760.96$ (6) Å^3
$a = 3.7737$ (2) Å	$Z = 4$
$b = 7.0363$ (3) Å	Mo $K\alpha$ radiation

$\mu = 0.12$ mm^{-1}	$0.49 \times 0.41 \times 0.16$ mm
$T = 296$ K	

Data collection

Bruker APEXII CCD area-detector diffractometer	7222 measured reflections
	1869 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1340 reflections with $I > 2\sigma(I)$
$T_{min} = 0.945$, $T_{max} = 0.982$	$R_{int} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$	110 parameters
$wR(F^2) = 0.175$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
1869 reflections	$\Delta\rho_{min} = -0.20$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯N2[i]	0.82	2.12	2.841 (3)	146

Symmetry code: (i) $-x + 2, -y + 2, -z$.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: publCIF (Westrip, 2010).

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supporting information

(*E*)-4-Nitrobenzaldehyde oxime

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S1. Comment

Thousands of deaths are caused by acute organophosphorus pesticide poisoning each year. Oximes are accepted therapeutic agents in organophosphorus poisoning (Jokanovic *et al.*, 2009, Marrs *et al.*, 2006). Oximes can act as useful protecting groups (Greene *et al.*, 1999) and have served for the protection of carbonyl groups in the syntheses of erythromycin derivatives and perhydrohistrionicotoxin (Shinada *et al.*, 1995). Oximes are also used for the purification and characterization of carbonyl compounds. As part of our interest in the study of oxime derivatives, we report here the crystal structure of the title compound (I). A depiction of the molecule is given in Fig. 1. In the crystal structure of the title compound, molecules are connected via intermolecular O—H···N hydrogen bonds (see Table 1 and Fig. 2) to form two-dimensional dimers. The oxime group has an *E* configuration [C3—C7—N2—O3 = 179.1 (2)°] and the planes containing the CNO and ONO atoms subtend dihedral angles of 5.47 (5)° and 8.31 (5)° with the phenyl C(1–6) ring. which is less than that reported for similar structures (Xing & Ding *et al.*, 2007; Xing & Wang *et al.*, 2007). Each molecule is connected to a symmetry-related molecule through an inversion center by O—H···N hydrogen bonds, building an $R_2^2(6)$ graph-set motif in Fig. 2 (Etter *et al.*, 1990; Bernstein *et al.*, 1995;).

S2. Experimental

To a warm solution of 4-nitrobenzaldehyde (0.907 g , 0.005 mol) in 25 ml e thanol, hydroxylamine hydrochloride (0.417 g, 0.006 mol) and sodium acetate trihydrate (2.04 g, 0.015 mol) were added and the mixture was heated under reflux until completion of the reaction. The concentrated reaction mixture was cooled down and water was added. The precipitated oxime was separated by filtration, washed with excess of water and dried. The crude product was recrystallized from ethanol to get the title compound (I).

S3. Refinement

All H atoms were placed in calculated position and treated as riding on their parent atoms with C—H = 0.93Å or O—H = 0.82Å with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$ for the hydroxyl H atom.
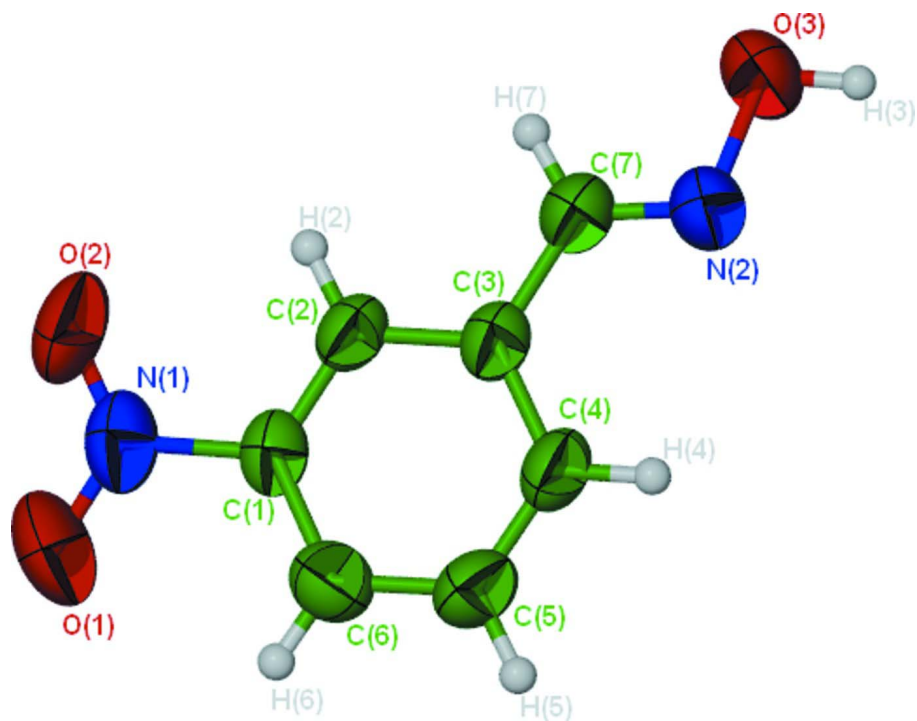
Figure 1

Molecular structure of (I) showing atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
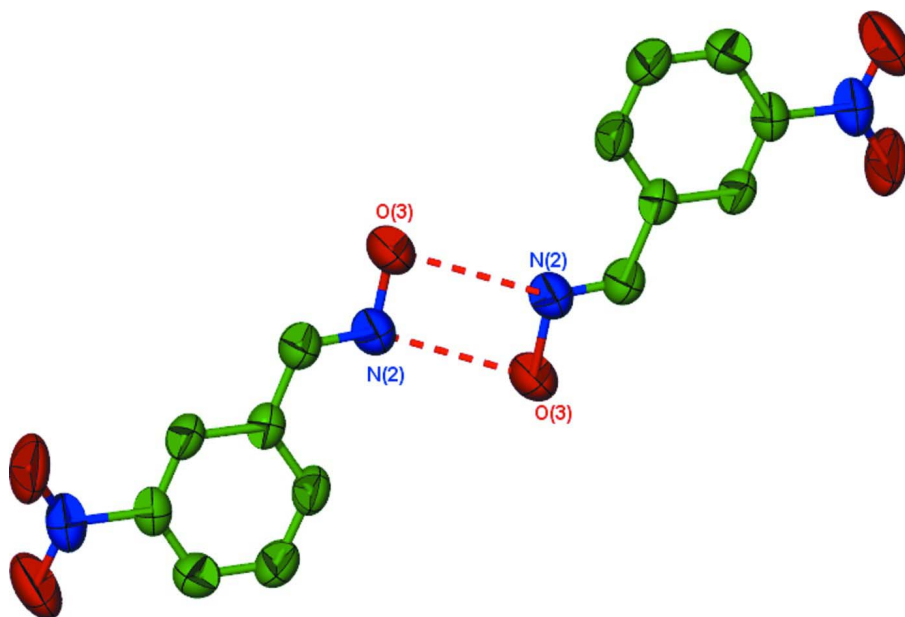

Figure 2

Hydrogen bonds shown as dashed lines, forming dimers through R22(6) graph set motif.

(*E*)-4-Nitrobenzaldehyde oxime

Crystal data

$C_7H_6N_2O_3$	$F(000) = 344$
$M_r = 166.14$	$D_x = 1.450$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 1727 reflections
$a = 3.7737$ (2) Å	$\theta = 2.8–25.1°$
$b = 7.0363$ (3) Å	$\mu = 0.12$ mm^{-1}
$c = 28.6651$ (14) Å	$T = 296$ K
$\beta = 91.237$ (3)°	Block, colorless
$V = 760.96$ (6) Å^3	$0.49 \times 0.41 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD area-detector diffractometer	7222 measured reflections
Radiation source: fine-focus sealed tube	1869 independent reflections
Graphite monochromator	1340 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$\theta_{max} = 28.2°$, $\theta_{min} = 2.8°$
	$h = -5\rightarrow4$
$T_{min} = 0.945$, $T_{max} = 0.982$	$k = -9\rightarrow9$
	$l = -38\rightarrow37$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.066$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.175$	
$S = 1.09$	H-atom parameters constrained
1869 reflections	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.435P]$ where $P = (F_o^2 + 2F_c^2)/3$
110 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.20$ e Å^{-3}
	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > \sigma(F^2)$ 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}
O3	0.9103 (8)	0.7939 (3)	−0.02398 (6)	0.0848 (8)
H3	0.9673	0.8950	−0.0359	0.127*
O2	0.2494 (7)	0.1865 (3)	0.14956 (8)	0.0857 (8)
N1	0.3651 (6)	0.3009 (3)	0.17705 (8)	0.0575 (6)

N2	0.8746 (6)	0.8191 (3)	0.02418 (7)	0.0562 (6)
C1	0.5229 (6)	0.4774 (3)	0.15885 (8)	0.0425 (5)
C2	0.5707 (6)	0.4913 (3)	0.11163 (8)	0.0426 (5)
H2	0.5092	0.3912	0.0919	0.051*
C3	0.7126 (6)	0.6576 (3)	0.09400 (8)	0.0415 (5)
C7	0.7669 (7)	0.6696 (3)	0.04381 (9)	0.0529 (6)
H7	0.7205	0.5629	0.0255	0.063*
C6	0.6116 (7)	0.6200 (3)	0.18954 (8)	0.0509 (6)
H6	0.5788	0.6059	0.2214	0.061*
C5	0.7516 (7)	0.7856 (3)	0.17149 (9)	0.0549 (6)
H5	0.8135	0.8850	0.1914	0.066*
C4	0.7997 (6)	0.8040 (3)	0.12444 (8)	0.0474 (6)
H4	0.8922	0.9165	0.1128	0.057*
O1	0.3545 (8)	0.2798 (4)	0.21888 (8)	0.1044 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.143 (2)	0.0654 (13)	0.0469 (11)	−0.0300 (13)	0.0171 (12)	0.0024 (9)
O2	0.1130 (19)	0.0472 (11)	0.0966 (17)	−0.0354 (12)	−0.0037 (13)	0.0100 (10)
N1	0.0583 (13)	0.0447 (11)	0.0694 (15)	−0.0043 (10)	0.0033 (11)	0.0160 (10)
N2	0.0732 (15)	0.0490 (11)	0.0467 (11)	−0.0115 (10)	0.0070 (10)	0.0029 (9)
C1	0.0405 (11)	0.0353 (10)	0.0518 (13)	−0.0014 (9)	0.0023 (9)	0.0071 (9)
C2	0.0467 (12)	0.0318 (10)	0.0491 (12)	−0.0054 (9)	−0.0020 (9)	−0.0028 (9)
C3	0.0432 (12)	0.0335 (10)	0.0478 (12)	−0.0031 (9)	−0.0004 (9)	0.0015 (9)
C7	0.0677 (16)	0.0416 (12)	0.0496 (14)	−0.0128 (11)	0.0028 (11)	−0.0025 (10)
C6	0.0586 (15)	0.0501 (13)	0.0442 (12)	0.0019 (11)	0.0022 (10)	0.0012 (10)
C5	0.0706 (17)	0.0410 (12)	0.0528 (14)	−0.0082 (11)	−0.0034 (12)	−0.0077 (10)
C4	0.0543 (14)	0.0332 (10)	0.0544 (14)	−0.0095 (9)	−0.0020 (10)	0.0008 (9)
O1	0.155 (3)	0.0918 (17)	0.0674 (15)	−0.0365 (17)	0.0135 (14)	0.0309 (12)

Geometric parameters (Å, º)

O3—N2	1.401 (3)	C2—H2	0.9300
O3—H3	0.8200	C3—C4	1.385 (3)
O2—N1	1.202 (3)	C3—C7	1.460 (3)
N1—O1	1.210 (3)	C7—H7	0.9300
N1—C1	1.477 (3)	C6—C5	1.385 (3)
N2—C7	1.264 (3)	C6—H6	0.9300
C1—C6	1.371 (3)	C5—C4	1.371 (3)
C1—C2	1.373 (3)	C5—H5	0.9300
C2—C3	1.387 (3)	C4—H4	0.9300
N2—O3—H3	109.5	C2—C3—C7	118.11 (19)
O2—N1—O1	123.2 (2)	N2—C7—C3	122.7 (2)
O2—N1—C1	118.4 (2)	N2—C7—H7	118.7
O1—N1—C1	118.4 (2)	C3—C7—H7	118.7
C7—N2—O3	111.8 (2)	C1—C6—C5	117.8 (2)

C6—C1—C2	123.0 (2)	C1—C6—H6	121.1
C6—C1—N1	118.9 (2)	C5—C6—H6	121.1
C2—C1—N1	118.1 (2)	C4—C5—C6	120.4 (2)
C1—C2—C3	118.63 (19)	C4—C5—H5	119.8
C1—C2—H2	120.7	C6—C5—H5	119.8
C3—C2—H2	120.7	C5—C4—C3	121.0 (2)
C4—C3—C2	119.1 (2)	C5—C4—H4	119.5
C4—C3—C7	122.78 (19)	C3—C4—H4	119.5
O2—N1—C1—C6	171.2 (2)	C4—C3—C7—N2	−5.0 (4)
O1—N1—C1—C6	−7.8 (4)	C2—C3—C7—N2	175.6 (3)
O2—N1—C1—C2	−8.2 (3)	C2—C1—C6—C5	0.8 (4)
O1—N1—C1—C2	172.8 (3)	N1—C1—C6—C5	−178.6 (2)
C6—C1—C2—C3	−0.5 (3)	C1—C6—C5—C4	−0.2 (4)
N1—C1—C2—C3	178.8 (2)	C6—C5—C4—C3	−0.5 (4)
C1—C2—C3—C4	−0.3 (3)	C2—C3—C4—C5	0.8 (4)
C1—C2—C3—C7	179.1 (2)	C7—C3—C4—C5	−178.6 (2)
O3—N2—C7—C3	179.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···N2[i]	0.82	2.12	2.841 (3)	146

Symmetry code: (i) −x+2, −y+2, −z.