3-[(2,4-Dinitrophenyl)hydrazono]butan-2-one oxime

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.050
wR factor = 0.132
Data-to-parameter ratio = 11.6

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

The title compound, $C_{10}H_{11}N_5O_5$, contains of dinitrophenyl, monooxime and hydrazone groups. The molecules are linked through O—H···N and C—H···O hydrogen bonds. There are also π–π interactions and intramolecular hydrogen bonds. All these hydrogen bonds are highly effective in forming dimeric chains, thereby stabilizing the crystal structure. The monooxime and hydrazone groups both have an E configuration.

Comment

Various hydrazone compounds possess strong bactericidal, herbicidal, insecticidal and fungicidal properties (Sahni *et al.*, 1977). Some phenylhydrazone derivatives have been shown to be potentially DNA-damaging and are mutagenic agents (Okabe *et al.*, 1993). In addition, hydrazones have analytical applications (Heit & Ryan, 1966; Jensen & Pflaum, 1967; Dey *et al.*, 1985). Hydrazones have interesting ligational properties due to the presence of several potential coordination sites (Dutta & Hossain, 1985), and both transition and non-transition metal complexes of these ligands have been synthesized previously (Dey *et al.*, 1992).


(I)
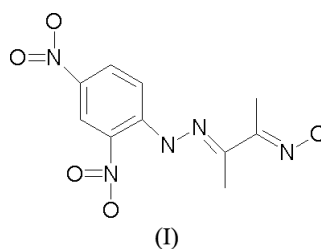
Oximes and their derivatives are very important compounds for the chemical industry, and in medicine as a result of their biological activity. The oxime group possesses stronger hydrogen-bonding capabilities than alcohol, phenol and carboxylic acid groups (Marsman *et al.*, 1999). Hydrogen bonding plays a key role in molecular recognition in crystal engineering (Bertolasi *et al.*, 1982; Gilli *et al.*, 1983).

The crystal structure determination of the title compound, (I), was carried out to determine the strength of the hydrogen-bonding capabilities of the oxime (C=N—OH) and hydrazone (HN—N=C) groups, as well as to establish the molecular arrangement; the aim also was to compare the geometry of oxime and hydrazone moieties with those found in 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazino]thiazole and its reduction product 4-methyl-2-[*N*-(3,4-methylenedioxybenzylidene)hydrazono]-4,5-dihydrothiazole, (II) (Wouters *et al.*, 2002), propiophenone 2,4-dinitrophenylhydrazone, (III) (Shan *et al.*, 2002*a*), and acetophenone (2,4-dinitrophenyl)hydrazone, (IV) (Shan *et al.*, 2002*b*).
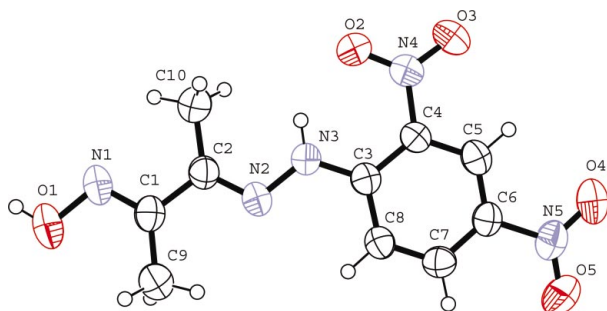
Figure 1
A view of the molecular structure of (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.
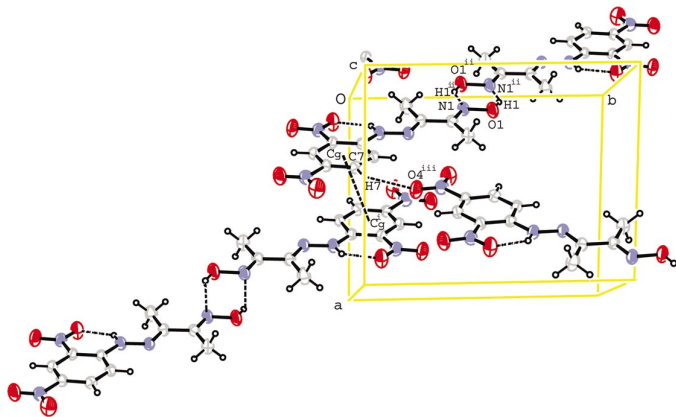
Figure 2
Diagram showing the hydrogen-bonding and π–π interactions in (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, 1-y, -z$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.]

Compound (I) contains three moieties: dinitrophenyl, monooxime and hydrazone (Fig. 1). The dihedral angles between oxime plane A (O1/N1/C1), hydrazone plane B (C2/N2/N3) and benzene plane C (C3–C8) are $A/B = 1.91\ (26)°$, $A/C = 4.49\ (17)°$ and $B/C = 4.74\ (17)°$. The molecule has an approximately planar structure. Oxime and dinitrophenyl groups are linked through a hydrazone moiety. The bond lengths and angles of the oxime and hydrazone moieties are given in Table 1 and a comparison of bond lengths and angles of (I) with those in the related compounds (II), (III) and (IV) is given in Table 3. Both the oxime and hydrazone moieties in (I) have an E configuration [O1—N1—C1—C2 = $-179.4\ (3)°$ and N3—N2—C2—C1 = $-178.5\ (3)°$]. In these groups, atom O1 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. Atom C7 of the benzene ring also behaves as a donor, resulting in the formation of C—H⋯O hydrogen bonds which link another two molecules to form the supramolecular layered structure (Fig. 2). There is also an intramolecular N3—H⋯O2 hydrogen bond, as found in many other studies (Vickery *et al.*, 1985)

In addition, there is an intermolecular π–π interaction between the benzene rings. The rings are oriented in such a way that the perpendicular distance from C3—C8 to the C3^{i}–

C8^{i} ring is 3.292 Å [symmetry code: (i) $1-x, -y, 1-z$] and the distance between the ring centroids is 3.538 (3) Å. An uneven distribution of π-electron density in the aromatic ring is probably responsible for the mutual orientation of these rings (Bogdanović *et al.*, 2002).

Experimental

2,4-Dinitrophenylhydrazine (1 mmol, 0.198 g) was dissolved by heating in ethanol (5 ml). H_2SO_4 (98%, 1 ml) solution was added to this, giving a clear orange solution at 373 K. Butane-2,3-dione monooxime (1 mmol, 0.101 g) in ethanol (4 ml) was added dropwise with stirring and the mixture refluxed for 2 h. The product was filtered off and dried before being dissolved in ethanol and left at room temperature to yield orange crystals.

Crystal data

$C_{10}H_{11}N_5O_5$	$D_x = 1.503$ Mg m^{-3}
$M_r = 281.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8500
$a = 10.1400\ (16)$ Å	reflections
$b = 12.3079\ (19)$ Å	$\theta = 2.0–26.8°$
$c = 10.6624\ (18)$ Å	$\mu = 0.12$ mm^{-1}
$\beta = 110.950\ (12)°$	$T = 293\ (2)$ K
$V = 1242.7\ (3)$ Å^3	Prism, orange
$Z = 4$	$0.35 \times 0.23 \times 0.12$ mm

Data collection

Stoe IPDS-2 diffractometer	$R_{int} = 0.103$
ω and φ scans	$\theta_{max} = 25.0°$
Absorption correction: none	$h = -12 \rightarrow 11$
12 323 measured reflections	$k = -14 \rightarrow 14$
2180 independent reflections	$l = -12 \rightarrow 12$
1207 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.132$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.87$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
2180 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
188 parameters	Extinction correction: *SHELXL*97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.018 (4)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.292 (3)	N4—C4	1.454 (3)
N1—O1	1.396 (3)	N5—C6	1.467 (3)
N2—C2	1.290 (3)	C1—C2	1.473 (4)
N2—N3	1.373 (3)	C1—C9	1.477 (4)
N3—C3	1.358 (3)	C2—C10	1.492 (4)
C1—N1—O1	111.6 (2)	N1—C1—C9	124.7 (2)
C2—N2—N3	114.2 (2)	N2—C2—C1	115.9 (2)
C3—N3—N2	122.5 (2)	N3—C3—C4	121.9 (2)
N1—C1—C2	113.9 (3)	N3—C3—C8	120.9 (2)
C2—N2—N3—C3	−175.4 (2)	N1—C1—C2—C10	−0.9 (4)
O1—N1—C1—C2	−179.47 (19)	C9—C1—C2—C10	−179.8 (3)
O1—N1—C1—C9	−0.6 (4)	N2—N3—C3—C4	178.0 (2)
N3—N2—C2—C1	−178.4 (2)	N2—N3—C3—C8	−1.4 (4)
N1—C1—C2—N2	179.3 (2)	N3—C3—C4—N4	1.1 (4)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1$\cdots$N1^{ii}	0.82	2.22	2.932 (3)	146
C7—H7$\cdots$O4^{iii}	0.93	2.54	3.230 (4)	131
N3—H3$\cdots$O2	0.85 (3)	1.92 (3)	2.587 (3)	135 (2)

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

Table 3
Geometrical parameters (Å, °) in the hydrazone moiety of (I) compared with those in the related compounds (II), (III) and (IV).

Bonds	(I)	(II)	(III)	(IV)
N3—C3	1.358 (3)	1.356 (2)	1.343 (3)	1.351 (3)
N2—N3	1.373 (3)	1.3714 (18)	1.379 (3)	1.367 (3)
N2—C2	1.290 (3)	1.276 (2)	1.289 (3)	1.286 (3)
C3—N3—N2	122.5 (2)	116.11 (13)	119.1 (2)	120.39 (19)
C2—N2—N3	114.2 (2)	116.83 (14)	117.0 (2)	116.7 (2)

The H atom bound to N3 was found in a difference map and refined freely; the other H atoms were placed in calculated positions and constrained to an idealized geometry, with an O—H distance of 0.82 Å, and C—H distances of 0.93 and 0.96 Å. The $U_{iso}(H)$ values were constrained to be 1.2 (1.5 for hydroxy and methyl groups) times U_{eq} of the carrier atom.

References

Bertolasi, V., Gilli, G. & Veronese, A. C. (1982). *Acta Cryst.* B**38**, 502–511.
Bogdanović, G. A., Miadragovic, D. U. & Malinar, M. J. (2002). *Acta Cryst.* C**58**, m338–m340.
Dey, K., Mandal, K. & Bandyopadhyay, D. (1992). *Indian J. Chem. Sect. A*, **31**, 937–942.
Dey, K., Ray, S. B., Bhattacharya, P. K., Gangopadhyay, A., Bhasin, K. K. & Verma, R. D. (1985). *J. Indian Chem. Soc.* **62**, 809–814.
Dutta, R. L. & Hossain, M. (1985). *J. Sci. Ind. Res.* **44**, 635–674.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gilli, G., Bertolasi, V. & Veronese, A. C. (1983). *Acta Cryst.* B**39**, 450–456.
Heit, M. L. & Ryan, D. E. (1966). *Anal. Chim. Acta*, **34**, 407–411.
Jensen, R. E. & Pflaum, R. T. (1967). *Anal. Chim. Acta*, **37**, 397–400.
Marsman, A. W., Leussink, E. D., Zwikker, J. W. & Jenneskens, L. W. (1999). *Chem. Mater.* **11**, 1484–1491.
Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* C**49**, 1678–1680.
Sahni, S. K., Sangal, S. K., Gupta, S. P. & Rana, V. B. (1977). *J. Inorg. Nucl. Chem.* **39**, 1098–1100.
Shan, S., Xu, D., Wu, J. & Chiang, M. (2002a). *Acta Cryst.* E**58**, o1444–o1445.
Shan, S., Xu, D., Wu, J. & Chiang, M. (2002b). *Acta Cryst.* E**58**, o1333–o1335.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Vickery, B., Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* C**41**, 1072–1075.
Wouters, J., Norberg, B. & Guccione, S. (2002). *Acta Cryst.* C**58**, o69–o71.