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2-Hydroxy-5-nitrobenzaldehyde phenylhydrazone

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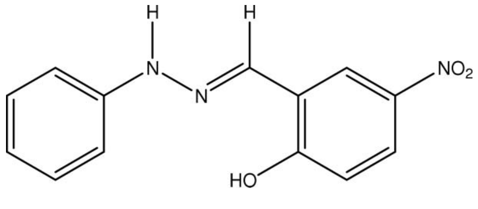
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.068; wR factor = 0.152; data-to-parameter ratio = 19.3.

In the title compound, $C_{13}H_{11}N_3O_3$, the molecule is essentially planar, the dihedral angle between the benzene rings being 5.31 (10)°. The nitro group *meta* to the phenylhydrazone substituent is almost coplanar with the ring to which it is attached, with a dihedral angle of 3.09 (12)° between the plane of the nitro group and the phenol ring plane. In the crystal structure, intermolecular N—H···O and C—H···O interactions interconnect the molecules into a three-dimensional framework. In addition, the crystal packing is stabilized by weak π–π interactions [centroid–centroid distance = 3.7279 (11) Å].

Related literature

For related literature on hydrogen-bond motifs, see Bernstein *et al.* (1995) and on values of bond lengths and angles, see Allen *et al.* (1987). For related structures, see Shan *et al.* (2003); Shan *et al.* (2004); Tameem *et al.*, 2006; Tameem *et al.*, 2007. For related literature, see: Raj & Kurup (2006); Suliman & Soma (2002); Vogel *et al.* (2000).



Experimental

Crystal data

$C_{13}H_{11}N_3O_3$
M_r = 257.25
Monoclinic, $P2_1/c$
a = 12.9019 (5) Å
b = 7.9909 (3) Å
c = 12.5323 (5) Å
β = 113.418 (2)°
V = 1185.63 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100.0 (1) K
0.35 × 0.29 × 0.03 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{\min}$ = 0.939, $T_{\max}$ = 0.997
12742 measured reflections
3480 independent reflections
2265 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.152
S = 1.04
3480 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.42 e Å^{-3}
$\Delta\rho_{\min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···N2	0.85 (2)	1.81 (2)	2.613 (2)	156 (2)
N1—H1C···O3$^{\rm i}$	0.85 (2)	2.12 (2)	2.961 (2)	170 (2)
C9—H9A···O1$^{\rm ii}$	0.93	2.54	3.430 (2)	161

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2291).

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supplementary materials

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2-Hydroxy-5-nitrobenzaldehyde phenylhydrazone

A. A. Tameem, A. Salhin, B. Saad, S.-L. Ng and **H.-K. Fun**

Comment

Several phenylhydrazone derivatives have been reported and were found to have versatile coordinating abilities towards different metal ions (Raj *et al.*, 2006). Some of these compounds were used as monitors or detectors for formaldehyde (Suliman *et al.*, 2001) and are also used to determine airbone aldehydes and ketones (Vogel *et al.*, 2000). Phenylhydrazone and nitrophenylhydrazone derivatives have also been synthesized in our laboratory in order to investigate their structures and analytical application. The title compound (I) whose structure is reported here, (Fig. 1) is one of the series of related phenylhdrazone derivatives that we have prepared; the X-ray structures of two of this series have been studied previously (Tameem *et al.*, 2006; Tameem *et al.*, 2007).

The bond lengths and angles in (I) have normal values (Allen *et al.*, 1987) and are comparable with those in the related structures (Shan *et al.*, 2003; Shan *et al.*, 2004). The molecule is essentially planar with the dihedral angle between the two benzene rings (C1—C6 and C8—C13) being 5.31 (10)°. The nitro group in the title compound, benzaldehyde 2-nitro-5-hydroxyphenylhydrazone, is attached at C10, meta to the phenylhydrazone substituent in the phenol ring [torsion angle of O2—N3—C10—C11 = -2.7 (3)°]. However, the corresponding nitro group in salicylaldehyde 4-nitrophenylhydrazone (Shan *et al.*, 2003) is attached at C4 in para-position to the hydrazone group [torsion angle of O1—N1—C4—C5 = -6.2 (5)°].

An intramolecular O1—H1B···N2 interaction (Table 1 and Figure 1) generates an S(6) ring motif (Bernstein *et al.*, 1995). In the crystal structure, the molecules are linked by intermolecular N1—H1C···O3^{i} and C9—H9A···O1^{ii} interactions into a three-dimensional framework (Figure 2). In addition, the crystal packing is stabilized by weak intermolecular π···π interactions involving the C8—C13 (Centroid Cg1) benzene ring with a Cg1···Cg1^{iii} distance of 3.7279 (11)Å [symmetry code : (iii) 1-x, 2-y, -z].

Experimental

The title compound (I) was prepared by the slow addition of phenylhydrazine (350 mg, 3.2 mmol) dissolved in 5 ml concentrated sulfuric acid to a 2-hydroxy-5-nitrobenzaldehyde (540 mg, 3.2 mmol) dissloved in 20 ml of 95% ethanol. The mixture was stirred for 15 min, and then left to stand at room temperature form 30 min. The resulting product was filtered off and washed with 20 ml 95% ethanol and an orange powder product was collected. Crystals suitable for X-ray diffraction analysis were grown by the slow evaporation of a saturated solution of the resultant product in ethanol.

Refinement

The H atoms on the N and O atoms were located in a difference map and refined isotropically, with N—H = 0.85 (2)Å and O—H = 0.85 (3) Å. The remaining H atoms were positioned geometrically and treated as riding, with C—H = 0.93Å and the $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

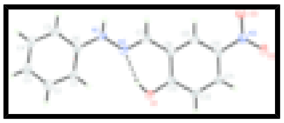

Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom numbering. A dashed line indicates an intramolecular hydrogen bond.

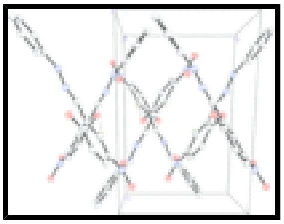

Fig. 2. The crystal packing of (I), viewed down the *c* axis. The intermolecular N—H···O and C—H···O hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

2-Hydroxy-5-nitrobenzaldehyde phenylhydrazone

Crystal data

$C_{13}H_{11}N_3O_3$

$M_r = 257.25$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.9019$ (5) Å

$b = 7.9909$ (3) Å

$c = 12.5323$ (5) Å

$\beta = 113.418$ (2)°

$V = 1185.63$ (8) Å^3

$Z = 4$

$F_{000} = 536$

$D_x = 1.441$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 2685 reflections

$\theta = 1.7$–30.2°

$\mu = 0.11$ mm^{-1}

$T = 100.0$ (1) K

Plate, orange

0.35 × 0.29 × 0.03 mm

Data collection

Bruker SMART APEX2 CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 8.33 pixels mm^{-1}

$T = 297(2)$ K

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{min} = 0.939$, $T_{max} = 0.997$

12742 measured reflections

3480 independent reflections

2265 reflections with $I > 2\sigma(I)$

$R_{int} = 0.050$

$\theta_{max} = 30.2$°

$\theta_{min} = 1.7$°

$h = -18 \rightarrow 16$

$k = -9 \rightarrow 11$

$l = -16 \rightarrow 17$

Refinement

Refinement on F^2

H atoms treated by a mixture of independent and constrained refinement

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.068$

$wR(F^2) = 0.152$

$S = 1.04$

3480 reflections

180 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.5968P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}

$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Extinction correction: none

Special details

Experimental. The data was collected with the Oxford Cyrosystem Cobra low-temperature attachment.

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 > 2sigma(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*	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.48565 (12)	0.68203 (19)	0.15079 (12)	0.0262 (4)
O2	0.84393 (11)	1.10514 (19)	0.05297 (12)	0.0308 (4)
O3	0.73542 (12)	1.0344 (2)	−0.12240 (12)	0.0387 (4)
N1	0.25322 (13)	0.5634 (2)	−0.14691 (14)	0.0231 (4)
N2	0.34887 (12)	0.6265 (2)	−0.06494 (13)	0.0200 (4)
N3	0.76112 (13)	1.0327 (2)	−0.01671 (14)	0.0236 (4)
C1	0.18662 (16)	0.4549 (3)	−0.00323 (16)	0.0236 (4)
H1A	0.2441	0.5097	0.0569	0.028*
C2	0.10905 (17)	0.3587 (3)	0.02002 (18)	0.0289 (5)
H2A	0.1152	0.3485	0.0962	0.035*
C3	0.02226 (17)	0.2773 (3)	−0.06842 (19)	0.0302 (5)
H3A	−0.0287	0.2112	−0.0517	0.036*
C4	0.01232 (17)	0.2953 (3)	−0.18153 (18)	0.0283 (5)
H4A	−0.0467	0.2428	−0.2415	0.034*
C5	0.08898 (16)	0.3903 (2)	−0.20658 (17)	0.0235 (4)
H5A	0.0814	0.4019	−0.2832	0.028*
C6	0.17827 (15)	0.4695 (2)	−0.11688 (16)	0.0205 (4)
C7	0.41932 (15)	0.7005 (2)	−0.09859 (15)	0.0200 (4)
H7A	0.4046	0.7061	−0.1774	0.024*

C8	0.52188 (15)	0.7755 (2)	−0.01390 (15)	0.0184 (4)
C9	0.59248 (15)	0.8645 (2)	−0.05285 (16)	0.0197 (4)
H9A	0.5749	0.8741	−0.1321	0.024*
C10	0.68939 (15)	0.9392 (2)	0.02689 (16)	0.0194 (4)
C11	0.71885 (15)	0.9287 (2)	0.14548 (16)	0.0218 (4)
H11A	0.7842	0.9799	0.1974	0.026*
C12	0.64949 (15)	0.8409 (3)	0.18517 (16)	0.0227 (4)
H12A	0.6684	0.8320	0.2647	0.027*
C13	0.55093 (15)	0.7649 (2)	0.10712 (15)	0.0199 (4)
H1C	0.2504 (16)	0.564 (3)	−0.2155 (19)	0.017 (5)*
H1B	0.431 (2)	0.649 (3)	0.090 (2)	0.051 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0238 (7)	0.0336 (9)	0.0177 (7)	−0.0076 (6)	0.0046 (6)	0.0003 (6)
O2	0.0240 (7)	0.0339 (9)	0.0311 (8)	−0.0097 (6)	0.0073 (6)	−0.0029 (7)
O3	0.0321 (8)	0.0616 (12)	0.0211 (7)	−0.0113 (8)	0.0091 (6)	0.0048 (7)
N1	0.0214 (8)	0.0300 (10)	0.0143 (8)	−0.0056 (7)	0.0033 (6)	−0.0018 (7)
N2	0.0170 (7)	0.0214 (9)	0.0170 (7)	0.0004 (6)	0.0019 (6)	−0.0022 (6)
N3	0.0196 (8)	0.0263 (9)	0.0234 (8)	0.0011 (7)	0.0071 (7)	0.0024 (7)
C1	0.0181 (9)	0.0245 (11)	0.0221 (9)	−0.0020 (8)	0.0016 (7)	−0.0010 (8)
C2	0.0258 (10)	0.0342 (13)	0.0253 (10)	0.0001 (9)	0.0088 (8)	0.0036 (9)
C3	0.0234 (10)	0.0261 (11)	0.0386 (12)	−0.0028 (9)	0.0096 (9)	0.0031 (9)
C4	0.0208 (10)	0.0227 (11)	0.0329 (11)	−0.0031 (8)	0.0017 (8)	−0.0033 (9)
C5	0.0223 (9)	0.0219 (10)	0.0200 (9)	0.0002 (8)	0.0018 (7)	−0.0007 (8)
C6	0.0183 (9)	0.0180 (9)	0.0217 (9)	0.0011 (7)	0.0042 (7)	−0.0002 (8)
C7	0.0188 (9)	0.0231 (10)	0.0147 (8)	0.0021 (8)	0.0030 (7)	−0.0004 (7)
C8	0.0176 (8)	0.0182 (9)	0.0163 (8)	0.0033 (7)	0.0034 (7)	0.0002 (7)
C9	0.0201 (9)	0.0211 (10)	0.0168 (8)	0.0030 (8)	0.0063 (7)	−0.0004 (7)
C10	0.0161 (8)	0.0199 (10)	0.0220 (9)	0.0022 (7)	0.0072 (7)	0.0013 (8)
C11	0.0170 (9)	0.0220 (10)	0.0211 (9)	0.0007 (8)	0.0020 (7)	0.0000 (8)
C12	0.0219 (9)	0.0283 (11)	0.0135 (8)	−0.0001 (8)	0.0025 (7)	0.0004 (8)
C13	0.0194 (9)	0.0206 (10)	0.0183 (9)	0.0021 (8)	0.0062 (7)	0.0017 (7)

Geometric parameters (Å, °)

O1—C13	1.347 (2)	C4—C5	1.379 (3)
O1—H1B	0.85 (3)	C4—H4A	0.9300
O2—N3	1.224 (2)	C5—C6	1.401 (3)
O3—N3	1.231 (2)	C5—H5A	0.9300
N1—N2	1.351 (2)	C7—C8	1.456 (2)
N1—C6	1.389 (3)	C7—H7A	0.9300
N1—H1C	0.85 (2)	C8—C9	1.389 (3)
N2—C7	1.288 (2)	C8—C13	1.413 (2)
N3—C10	1.454 (2)	C9—C10	1.387 (2)
C1—C2	1.382 (3)	C9—H9A	0.9300
C1—C6	1.390 (3)	C10—C11	1.383 (3)
C1—H1A	0.9300	C11—C12	1.376 (3)

C2—C3	1.385 (3)	C11—H11A	0.9300
C2—H2A	0.9300	C12—C13	1.398 (2)
C3—C4	1.379 (3)	C12—H12A	0.9300
C3—H3A	0.9300		

C13—O1—H1B	103.0 (19)	N1—C6—C5	117.75 (17)
N2—N1—C6	121.31 (16)	C1—C6—C5	119.26 (18)
N2—N1—H1C	115.4 (14)	N2—C7—C8	120.37 (17)
C6—N1—H1C	121.6 (14)	N2—C7—H7A	119.8
C7—N2—N1	118.22 (16)	C8—C7—H7A	119.8
O2—N3—O3	123.23 (17)	C9—C8—C13	118.48 (16)
O2—N3—C10	118.71 (16)	C9—C8—C7	119.19 (16)
O3—N3—C10	118.06 (15)	C13—C8—C7	122.30 (17)
C2—C1—C6	119.67 (18)	C10—C9—C8	119.77 (17)
C2—C1—H1A	120.2	C10—C9—H9A	120.1
C6—C1—H1A	120.2	C8—C9—H9A	120.1
C1—C2—C3	121.0 (2)	C11—C10—C9	122.15 (18)
C1—C2—H2A	119.5	C11—C10—N3	119.41 (16)
C3—C2—H2A	119.5	C9—C10—N3	118.44 (17)
C4—C3—C2	119.3 (2)	C12—C11—C10	118.63 (17)
C4—C3—H3A	120.4	C12—C11—H11A	120.7
C2—C3—H3A	120.4	C10—C11—H11A	120.7
C5—C4—C3	120.63 (19)	C11—C12—C13	120.66 (17)
C5—C4—H4A	119.7	C11—C12—H12A	119.7
C3—C4—H4A	119.7	C13—C12—H12A	119.7
C4—C5—C6	120.11 (19)	O1—C13—C12	118.11 (16)
C4—C5—H5A	119.9	O1—C13—C8	121.58 (16)
C6—C5—H5A	119.9	C12—C13—C8	120.31 (18)
N1—C6—C1	122.96 (16)		

C6—N1—N2—C7	174.30 (18)	C8—C9—C10—C11	−0.2 (3)
C6—C1—C2—C3	−0.5 (3)	C8—C9—C10—N3	−179.55 (17)
C1—C2—C3—C4	−1.1 (3)	O2—N3—C10—C11	−2.7 (3)
C2—C3—C4—C5	1.3 (3)	O3—N3—C10—C11	177.10 (18)
C3—C4—C5—C6	0.2 (3)	O2—N3—C10—C9	176.73 (17)
N2—N1—C6—C1	10.0 (3)	O3—N3—C10—C9	−3.5 (3)
N2—N1—C6—C5	−171.80 (18)	C9—C10—C11—C12	0.1 (3)
C2—C1—C6—N1	−179.80 (19)	N3—C10—C11—C12	179.47 (17)
C2—C1—C6—C5	2.0 (3)	C10—C11—C12—C13	−0.4 (3)
C4—C5—C6—N1	179.86 (18)	C11—C12—C13—O1	−179.33 (18)
C4—C5—C6—C1	−1.8 (3)	C11—C12—C13—C8	0.8 (3)
N1—N2—C7—C8	177.97 (17)	C9—C8—C13—O1	179.28 (17)
N2—C7—C8—C9	−175.53 (18)	C7—C8—C13—O1	1.1 (3)
N2—C7—C8—C13	2.7 (3)	C9—C8—C13—C12	−0.9 (3)
C13—C8—C9—C10	0.5 (3)	C7—C8—C13—C12	−179.07 (18)
C7—C8—C9—C10	178.80 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1B···N2	0.85 (2)	1.81 (2)	2.613 (2)	156 (2)

N1—H1C···O3^{i}	0.85 (2)	2.12 (2)	2.961 (2)	170 (2)
C9—H9A···O1^{ii}	0.93	2.54	3.430 (2)	161

Symmetry codes: (i) $-x+1, y-1/2, -z-1/2$; (ii) $x, -y+3/2, z-1/2$.

Fig. 1

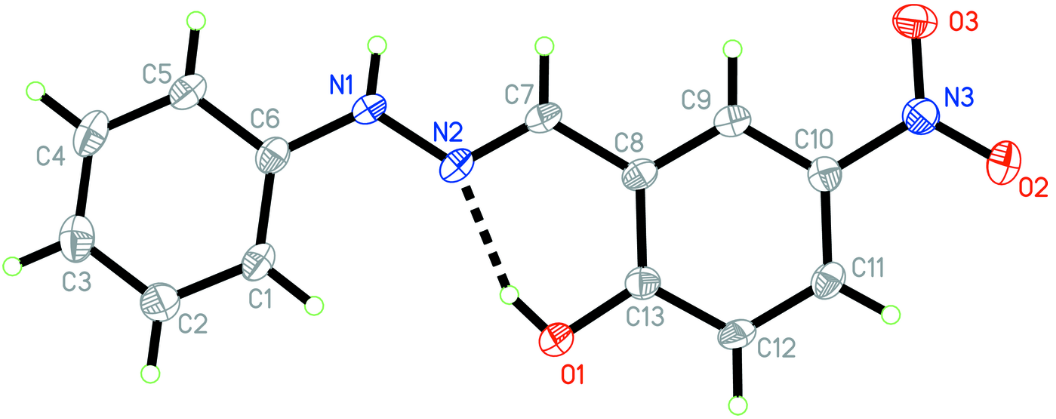

Fig. 2