

4-[[2-(2,4-Dinitrophenyl)hydrazinylidene]methyl]phenol ethanol hemisolvate

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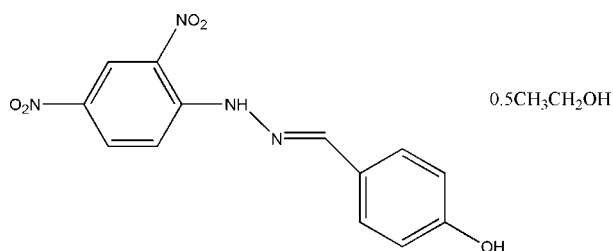
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 Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in solvent or counterion; R factor = 0.064; wR factor = 0.230; data-to-parameter ratio = 12.2.

In the title compound, $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_5 \cdot 0.5\text{C}_2\text{H}_5\text{OH}$, the two benzene rings form a dihedral angle of 4.29 (9°). The ethanol solvent molecule was treated as disordered between two orientations related by symmetry (center of inversion), with occupancies fixed at 0.5. The crystal packing, stabilized by intermolecular $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds and $\pi-\pi$ interactions [indicated by the short distance of 3.7299 (7) Å between the centroids of benzene rings from neighbouring molecules], exhibits short intermolecular $\text{O} \cdots \text{O}$ contacts of 2.8226 (3) Å.

Related literature

For related structures, see: Baughman *et al.* (2004); Shi *et al.* (2008); Ji & Shi (2008). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_5 \cdot 0.5\text{C}_2\text{H}_6\text{O}$
 $M_r = 325.28$

Triclinic, $P\bar{1}$
 $a = 7.0935$ (16) Å
 $b = 7.2888$ (17) Å
 $c = 14.458$ (3) Å
 $\alpha = 100.156$ (4°)
 $\beta = 96.378$ (4°)
 $\gamma = 100.604$ (4°)

$V = 715.2$ (3) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.12$ mm⁻¹
 $T = 295$ K
 $0.15 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 2005)
 $T_{\min} = 0.982$, $T_{\max} = 0.988$

4065 measured reflections
 2776 independent reflections
 1543 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.230$
 $S = 1.04$
 2776 reflections
 227 parameters

3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.46$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1} \cdots \text{O2}$	0.89	1.97	2.605 (3)	127
$\text{O6}-\text{H6A} \cdots \text{O3}$	0.85	1.86	2.702 (9)	174
$\text{O5}-\text{H5} \cdots \text{O6}^i$	0.85	2.26	2.882 (9)	130
$\text{O5}-\text{H5} \cdots \text{O4}^{ii}$	0.85	2.47	3.116 (4)	133
$\text{O5}-\text{H5} \cdots \text{O3}^{ii}$	0.85	2.60	3.404 (4)	159
$\text{N1}-\text{H1} \cdots \text{O2}^{iii}$	0.89	2.63	3.449 (4)	153

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2785).

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supplementary materials

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4-{{2-(2,4-Dinitrophenyl)hydrazinylidene}methyl}phenol ethanol hemisolvate

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Comment

As a contribution to structural studies of 2,4-dinitrophenylhydrazones (Baughman *et al.*, 2004; Shi *et al.*, 2008; Ji *et al.*, 2008;) we present here the crystal structure of the title compound (I).

In (I) (Fig. 1), all bond lengths and angles are normal (Allen *et al.*, 1987). The crystal packing, stabilized by intermolecular O—H...O and N—H...O hydrogen bonds (Table 1) and π — π interactions proved by short distance of 3.7299 (7) Å between the centroids of benzene rings from the neighbouring molecules, exhibits short intermolecular O...O contacts of 2.8226 (3) Å.

Experimental

The title compound was synthesized by the reaction of (2,4-dinitro-phenyl)-hydrazine (1 mmol, 198.1 mg) with 4-hydroxy-benzaldehyde (1 mmol, 122.1 mg) in ethanol (20 ml) under reflux conditions (338 K) for 4 h. The solvent was removed and the solid product recrystallized from ethanol. After five days brown crystals were obtained that were suitable for X-ray diffraction study.

Refinement

All H atoms were placed in idealized positions (C—H = 0.93–0.97 Å, N—H = 0.86 Å) and refined as riding atoms. For those bound to C, $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$, while for those bound to N, $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$. The ethanol solvent molecule has been treated as disordered between two orientations related by symmetry (center of inversion) with occupancies fixed to 0.5 and with C—O, C—C and O...C distances restrained to 1.40 (1), 1.45 (1) and 2.40 (1) Å, respectively.

Figures

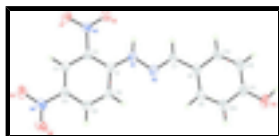


Fig. 1. View of the title compound showing the atomic labeling and 30% probability displacement ellipsoids. Solvent molecule omitted for clarity.

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Crystal data

C₁₃H₁₀N₄O₅·0.5C₂H₆O

$M_r = 325.28$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.0935$ (16) Å

$Z = 2$

$F(000) = 338$

$D_x = 1.510$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 748 reflections

supplementary materials

$b = 7.2888 (17) \text{ \AA}$	$\theta = 2.9\text{--}24.3^\circ$
$c = 14.458 (3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 100.156 (4)^\circ$	$T = 295 \text{ K}$
$\beta = 96.378 (4)^\circ$	Block, brown
$\gamma = 100.604 (4)^\circ$	$0.15 \times 0.12 \times 0.10 \text{ mm}$
$V = 715.2 (3) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	2776 independent reflections
Radiation source: fine-focus sealed tube graphite	1543 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$\theta_{\text{max}} = 26.1^\circ$, $\theta_{\text{min}} = 1.5^\circ$
$T_{\text{min}} = 0.982$, $T_{\text{max}} = 0.988$	$h = -7 \rightarrow 8$
4065 measured reflections	$k = -8 \rightarrow 7$
	$l = -14 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.064$	H-atom parameters constrained
$wR(F^2) = 0.230$	$w = 1/[\sigma^2(F_o^2) + (0.1117P)^2 + 0.1836P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2776 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
227 parameters	$\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$
3 restraints	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXTL</i> (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.017 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.6437 (4)	0.7313 (3)	0.73110 (16)	0.0700 (8)	
O2	0.4959 (4)	0.5632 (3)	0.59767 (16)	0.0683 (8)	
O3	0.7183 (5)	0.4849 (4)	1.00571 (18)	0.0973 (11)	
O4	0.5709 (5)	0.2032 (4)	1.00864 (18)	0.1019 (12)	
O5	-0.1603 (4)	-0.6843 (4)	0.20416 (18)	0.0890 (10)	
H5	-0.1738	-0.6648	0.1478	0.134*	
N1	0.3674 (3)	0.1977 (3)	0.57776 (16)	0.0470 (7)	
H1	0.3863	0.2907	0.5452	0.070*	
N2	0.2771 (3)	0.0174 (4)	0.53066 (17)	0.0479 (7)	
N3	0.5558 (4)	0.5794 (4)	0.68230 (18)	0.0499 (7)	
N4	0.6183 (5)	0.3288 (5)	0.9659 (2)	0.0698 (9)	
C1	0.4286 (4)	0.2316 (4)	0.6718 (2)	0.0412 (7)	
C2	0.5213 (4)	0.4143 (4)	0.7248 (2)	0.0420 (7)	
C3	0.5848 (4)	0.4436 (4)	0.8208 (2)	0.0474 (8)	
H3	0.6479	0.5642	0.8544	0.057*	
C4	0.5548 (5)	0.2961 (4)	0.8656 (2)	0.0493 (8)	
C5	0.4642 (5)	0.1133 (4)	0.8163 (2)	0.0511 (8)	
H5A	0.4453	0.0131	0.8485	0.061*	
C6	0.4040 (4)	0.0821 (4)	0.7223 (2)	0.0467 (8)	
H6	0.3450	-0.0405	0.6899	0.056*	
C7	0.2242 (4)	0.0014 (4)	0.4422 (2)	0.0473 (8)	
H7	0.2487	0.1092	0.4157	0.057*	
C8	0.1273 (4)	-0.1784 (5)	0.3812 (2)	0.0464 (8)	
C9	0.0970 (5)	-0.3493 (5)	0.4128 (2)	0.0551 (9)	
H9	0.1418	-0.3512	0.4755	0.066*	
C10	0.0018 (5)	-0.5148 (5)	0.3525 (2)	0.0612 (9)	
H10	-0.0189	-0.6280	0.3748	0.073*	
C11	-0.0638 (5)	-0.5156 (5)	0.2591 (2)	0.0585 (9)	
C12	-0.0313 (5)	-0.3488 (5)	0.2267 (2)	0.0617 (10)	
H12	-0.0734	-0.3487	0.1635	0.074*	
C13	0.0629 (4)	-0.1817 (5)	0.2868 (2)	0.0530 (8)	
H13	0.0838	-0.0693	0.2638	0.064*	
O6	1.0107 (12)	0.7495 (11)	0.9734 (7)	0.148 (3)	0.50
H6A	0.9238	0.6597	0.9822	0.222*	0.50
C14	0.9498 (18)	0.9229 (13)	0.9968 (12)	0.115 (5)	0.50
H14A	1.0102	0.9845	1.0602	0.138*	0.50
H14B	0.8128	0.8924	0.9983	0.138*	0.50
C15	0.965 (5)	1.042 (3)	0.9313 (12)	0.259 (14)	0.50
H15A	0.9230	1.1573	0.9555	0.388*	0.50
H15B	1.0979	1.0729	0.9223	0.388*	0.50
H15C	0.8861	0.9802	0.8717	0.388*	0.50

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1033 (19)	0.0395 (14)	0.0569 (14)	-0.0028 (12)	0.0025 (13)	0.0063 (11)
O2	0.0965 (19)	0.0546 (15)	0.0477 (14)	0.0023 (13)	-0.0027 (13)	0.0160 (11)
O3	0.137 (3)	0.078 (2)	0.0503 (15)	-0.0157 (18)	-0.0210 (16)	0.0019 (14)
O4	0.172 (3)	0.075 (2)	0.0533 (17)	0.008 (2)	-0.0009 (18)	0.0265 (15)
O5	0.111 (2)	0.0689 (18)	0.0581 (15)	-0.0248 (16)	-0.0010 (15)	-0.0114 (13)
N1	0.0544 (15)	0.0402 (14)	0.0404 (14)	0.0029 (11)	-0.0003 (11)	0.0045 (11)
N2	0.0490 (15)	0.0455 (15)	0.0426 (15)	0.0056 (11)	0.0013 (12)	-0.0009 (11)
N3	0.0627 (17)	0.0373 (15)	0.0473 (16)	0.0055 (12)	0.0062 (13)	0.0090 (11)
N4	0.102 (2)	0.057 (2)	0.0451 (17)	0.0100 (17)	-0.0015 (16)	0.0098 (15)
C1	0.0406 (15)	0.0407 (17)	0.0406 (16)	0.0074 (12)	0.0052 (12)	0.0049 (12)
C2	0.0451 (16)	0.0360 (16)	0.0441 (16)	0.0083 (12)	0.0062 (13)	0.0060 (12)
C3	0.0569 (19)	0.0370 (17)	0.0432 (17)	0.0064 (13)	0.0034 (14)	0.0003 (12)
C4	0.062 (2)	0.0447 (18)	0.0381 (16)	0.0085 (15)	0.0016 (14)	0.0058 (13)
C5	0.066 (2)	0.0380 (17)	0.0498 (18)	0.0065 (14)	0.0117 (15)	0.0129 (13)
C6	0.0561 (18)	0.0354 (16)	0.0456 (17)	0.0047 (13)	0.0054 (14)	0.0066 (13)
C7	0.0487 (17)	0.0467 (18)	0.0433 (17)	0.0051 (14)	0.0039 (14)	0.0080 (13)
C8	0.0381 (16)	0.056 (2)	0.0401 (16)	0.0039 (13)	0.0047 (13)	0.0020 (14)
C9	0.065 (2)	0.054 (2)	0.0402 (17)	0.0030 (16)	0.0031 (15)	0.0072 (14)
C10	0.071 (2)	0.054 (2)	0.054 (2)	0.0004 (17)	0.0107 (17)	0.0075 (16)
C11	0.055 (2)	0.058 (2)	0.0478 (19)	-0.0092 (16)	0.0056 (15)	-0.0063 (16)
C12	0.056 (2)	0.075 (3)	0.0406 (17)	-0.0040 (17)	-0.0054 (15)	0.0027 (16)
C13	0.0516 (18)	0.058 (2)	0.0431 (17)	0.0020 (15)	-0.0005 (14)	0.0091 (14)
O6	0.139 (7)	0.123 (7)	0.176 (8)	-0.003 (5)	0.043 (6)	0.034 (6)
C14	0.113 (9)	0.044 (5)	0.197 (16)	0.026 (5)	0.058 (10)	0.015 (7)
C15	0.35 (4)	0.24 (3)	0.20 (3)	0.10 (2)	0.06 (3)	0.01 (2)

Geometric parameters (\AA , $^\circ$)

O1—N3	1.219 (3)	C7—H7	0.9300
O2—N3	1.227 (3)	C8—C13	1.385 (4)
O3—N4	1.229 (4)	C8—C9	1.390 (5)
O4—N4	1.210 (4)	C9—C10	1.368 (4)
O5—C11	1.356 (4)	C9—H9	0.9300
O5—H5	0.8500	C10—C11	1.376 (5)
N1—C1	1.346 (3)	C10—H10	0.9300
N1—N2	1.370 (3)	C11—C12	1.369 (5)
N1—H1	0.8900	C12—C13	1.372 (4)
N2—C7	1.270 (4)	C12—H12	0.9300
N3—O2	1.227 (3)	C13—H13	0.9300
N3—C2	1.439 (4)	O6—C14	1.407 (8)
N4—O3	1.229 (4)	O6—C15 ⁱ	1.827 (19)
N4—C4	1.435 (4)	O6—H6A	0.8500
C1—C6	1.410 (4)	C14—C15 ⁱ	1.11 (2)
C1—C2	1.413 (4)	C14—C14 ⁱ	1.20 (2)

C2—C3	1.377 (4)	C14—C15	1.394 (9)
C3—C4	1.346 (4)	C14—H14A	0.9600
C3—H3	0.9300	C14—H14B	0.9600
C4—C5	1.394 (4)	C15—C14 ⁱ	1.11 (2)
C5—C6	1.344 (4)	C15—O6 ⁱ	1.828 (19)
C5—H5A	0.9300	C15—H15A	0.9601
C6—H6	0.9300	C15—H15B	0.9600
C7—C8	1.447 (4)	C15—H15C	0.9600
C11—O5—H5	105.5	C9—C10—C11	120.6 (3)
C1—N1—N2	119.9 (3)	C9—C10—H10	119.7
C1—N1—H1	120.9	C11—C10—H10	119.7
N2—N1—H1	119.2	O5—C11—C12	123.4 (3)
C7—N2—N1	114.8 (3)	O5—C11—C10	117.2 (3)
O1—N3—O2	121.8 (3)	C12—C11—C10	119.3 (3)
O1—N3—O2	121.8 (3)	C11—C12—C13	120.5 (3)
O1—N3—C2	119.3 (3)	C11—C12—H12	119.8
O2—N3—C2	119.0 (2)	C13—C12—H12	119.8
O2—N3—C2	119.0 (2)	C12—C13—C8	120.8 (3)
O4—N4—O3	122.2 (3)	C12—C13—H13	119.6
O4—N4—O3	122.2 (3)	C8—C13—H13	119.6
O4—N4—C4	119.2 (3)	C14—O6—H6A	108.9
O3—N4—C4	118.5 (3)	C15 ⁱ —O6—H6A	109.4
O3—N4—C4	118.5 (3)	C15 ⁱ —C14—C14 ⁱ	74.4 (13)
N1—C1—C6	120.5 (3)	C15 ⁱ —C14—C15	124.3 (13)
N1—C1—C2	122.8 (3)	C14 ⁱ —C14—C15	49.9 (12)
C6—C1—C2	116.7 (3)	C15 ⁱ —C14—O6	92.5 (13)
C3—C2—C1	121.3 (3)	C14 ⁱ —C14—O6	124.7 (14)
C3—C2—N3	116.1 (3)	C15—C14—O6	117.0 (10)
C1—C2—N3	122.5 (3)	C14 ⁱ —C14—H14A	65.2
C4—C3—C2	119.4 (3)	C15—C14—H14A	113.8
C4—C3—H3	120.3	O6—C14—H14A	108.3
C2—C3—H3	120.3	C15 ⁱ —C14—H14B	112.3
C3—C4—C5	121.3 (3)	C14 ⁱ —C14—H14B	127.7
C3—C4—N4	119.0 (3)	C15—C14—H14B	102.9
C5—C4—N4	119.7 (3)	O6—C14—H14B	107.2
C6—C5—C4	119.9 (3)	H14A—C14—H14B	106.8
C6—C5—H5A	120.0	C14 ⁱ —C15—C14	55.7 (13)
C4—C5—H5A	120.0	C14 ⁱ —C15—O6 ⁱ	50.3 (8)
C5—C6—C1	121.3 (3)	C14—C15—O6 ⁱ	90.5 (11)
C5—C6—H6	119.3	C14 ⁱ —C15—H15A	81.5
C1—C6—H6	119.3	C14—C15—H15A	109.7
N2—C7—C8	122.5 (3)	C14 ⁱ —C15—H15B	74.1
N2—C7—H7	118.8	C14—C15—H15B	108.2
C8—C7—H7	118.8	O6 ⁱ —C15—H15B	93.5
C13—C8—C9	118.2 (3)	H15A—C15—H15B	109.5

supplementary materials

C13—C8—C7	118.9 (3)	C14 ⁱ —C15—H15C	165.6
C9—C8—C7	122.9 (3)	C14—C15—H15C	110.5
C10—C9—C8	120.5 (3)	O6 ⁱ —C15—H15C	140.8
C10—C9—H9	119.7	H15A—C15—H15C	109.5
C8—C9—H9	119.7	H15B—C15—H15C	109.5

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots O2	0.89	1.97	2.605 (3)	127
O6—H6A \cdots O3	0.85	1.86	2.702 (9)	174
O5—H5 \cdots O6 ⁱⁱ	0.85	2.26	2.882 (9)	130
O5—H5 \cdots O4 ⁱⁱⁱ	0.85	2.47	3.116 (4)	133
O5—H5 \cdots O3 ⁱⁱⁱ	0.85	2.60	3.404 (4)	159
N1—H1 \cdots O2 ^{iv}	0.89	2.63	3.449 (4)	153

Symmetry codes: (ii) $-x+1, -y, -z+1$; (iii) $x-1, y-1, z-1$; (iv) $-x+1, -y+1, -z+1$.

Fig. 1

