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4-Nitrophenol–piperazine (2/1)

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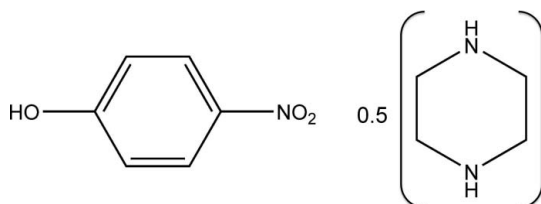
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.111; data-to-parameter ratio = 14.0.

In the title adduct, $\text{C}_6\text{H}_5\text{NO}_3 \cdot 0.5\text{C}_4\text{H}_{10}\text{N}_2$, the piperazine ring possesses inversion symmetry and has a *chair* conformation. Its mean plane makes a dihedral angle of 65.45 (7) $^\circ$ with the 4-nitrophenol ring. In the crystal, the piperazine ring is linked to two 4-nitrophenol molecules *via* $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The molecules are also linked *via* bifurcated $\text{N}-\text{H} \cdots (\text{O}, \text{O})$ hydrogen bonds involving the NO_2 O atoms, forming a two-dimensional network lying parallel to (102). The networks are linked *via* $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds, forming a three-dimensional structure.

Related literature

For the biological properties of piperazine compounds, see: Foroumadi *et al.* (2007); Upadhyaya *et al.* (2004); Chen *et al.* (2006); Cunico *et al.* (2009); Smits *et al.* (2008); Becker *et al.* (2006).



Experimental

Crystal data

 $\text{C}_6\text{H}_5\text{NO}_3 \cdot 0.5\text{C}_4\text{H}_{10}\text{N}_2$ $M_r = 182.18$ Monoclinic, $P2_1/c$ $a = 6.1879$ (2) Å $b = 19.9274$ (7) Å $c = 6.9846$ (2) Å $\beta = 91.199$ (1) $^\circ$ $V = 861.07$ (5) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.11$ mm⁻¹ $T = 293$ K $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.968$, $T_{\max} = 0.979$

12570 measured reflections
1763 independent reflections
1437 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.111$ $S = 1.04$

1763 reflections

126 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O3}-\text{H3A} \cdots \text{N2}^i$	0.82	1.82	2.6210 (16)	167
$\text{N2}-\text{H2A} \cdots \text{O1}$	0.796 (19)	2.58 (2)	3.2437 (17)	141.4 (17)
$\text{N2}-\text{H2A} \cdots \text{O2}$	0.796 (19)	2.557 (19)	3.2273 (17)	142.8 (19)
$\text{C2}-\text{H2} \cdots \text{O1}^i$	0.93	2.51	3.3428 (17)	149
$\text{C6}-\text{H6} \cdots \text{O3}^{ii}$	0.93	2.57	3.5035 (17)	179

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

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: ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2605).

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supporting information

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4-Nitrophenol–piperazine (2/1)

**Perumal Nagapandiselvi, Srinivasan Muralidharan, Thothadri Srinivasan, Rengaswamy
Goplal Krishnan and Devadasan Velmurugan**

S1. Comment

Piperazine-based research has attracted considerable attention in recent years. A broad range of compounds displaying antibacterial (Foroumadi *et al.*, 2007), antifungal (Upadhayaya *et al.*, 2004), anticancer (Chen *et al.*, 2006), antiparasitic (Cunico *et al.*, 2009), antihistamin (Smits *et al.*, 2008), and antidepressive activities (Becker *et al.*, 2006) have been found to contain this versatile core. In view of these important properties, we have undertaken the X-ray diffraction study of the title compound.

In the title adduct, $C_6H_5N_1O_3 \cdot 0.5(C_4H_{10}N_2)$, the piperazine ring (N2/C7/C8/N2a/C7a/C8a) possesses inversion symmetry. It adopts a *chair* conformation and its mean plane makes a dihedral angle of 65.45 (7)° with the 4-nitrophenol ring (C1–C6).

In the crystal, the piperazine ring is linked to two 4-nitrophenol molecules via O–H⋯N hydrogen bonds (Table 1 and Fig 2). The molecules are also linked via bifurcated N–H⋯O/O hydrogen bonds, involving the NO₂ O atoms, forming a two-dimensional network lying parallel to (102). These networks are linked via C–H⋯O hydrogen bonds forming a three-dimensional structure (Table 1).

S2. Experimental

Piperazine 4-nitrophenol was synthesized by mixing an equimolar mixture (1:1) of anhydrous piperazine and 4-nitrophenol in methanol. The resultant solution was stirred magnetically at room temperature and filtered into a clean beaker. The filtrate was kept in a constant temperature bath at 308 K. Yellow block-like crystals suitable for x-ray diffraction were harvested from the solution within a day.

S3. Refinement

The OH and C-bound H atoms were positioned geometrically and refined using a riding model: O—H = 0.82 Å, C—H = 0.93 and 0.97 Å for aryl and methylene H-atoms, respectively, with $U_{iso}(H) = 1.5U_{eq}(O)$ and $= 1.2U_{eq}(C,N)$.

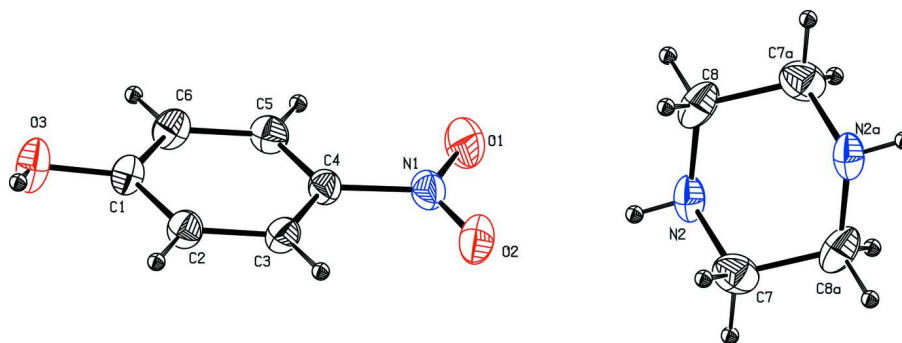


Figure 1

The molecular structure of the title compound, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level (symmetry code: (a) = $-x+2, -y, -z+1$).

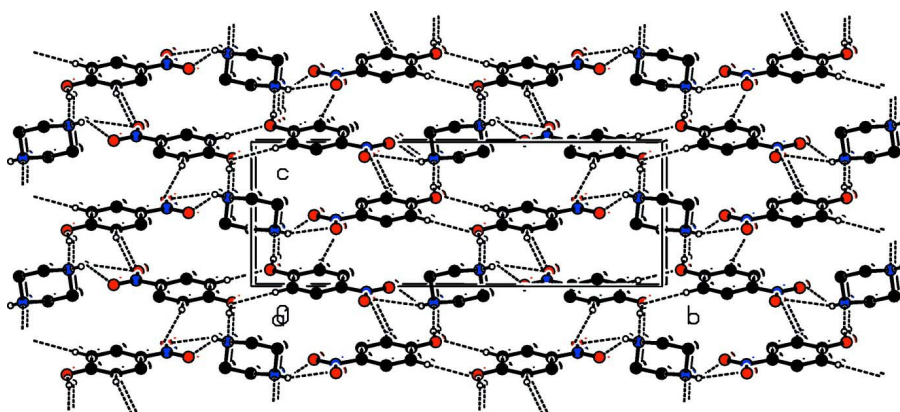


Figure 2

The crystal packing of the title compound viewed along the a axis. The N-H \cdots O, O-H \cdots N and C-H \cdots O hydrogen bonds are shown as dashed lines; see Table 1 for details. The H atoms not involved in hydrogen bonding have been omitted for clarity.

4-Nitrophenol–piperazine (2/1)

Crystal data

$C_6H_5NO_3 \cdot 0.5C_4H_{10}N_2$

$M_r = 182.18$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2ybc$

$a = 6.1879$ (2) Å

$b = 19.9274$ (7) Å

$c = 6.9846$ (2) Å

$\beta = 91.199$ (1) $^\circ$

$V = 861.07$ (5) Å 3

$Z = 4$

$F(000) = 384$

$D_x = 1.405$ Mg m $^{-3}$

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

Cell parameters from 1763 reflections

$\theta = 2.0$ – 26.4 $^\circ$

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

$T = 293$ K

Block, yellow

$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART APEXII area-detector
diffractometer

Radiation source: fine-focus sealed tube
Graphite monochromator

ω and ϕ scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.968$, $T_{\max} = 0.979$

12570 measured reflections
 1763 independent reflections
 1437 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 26.4^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -7 \rightarrow 7$
 $k = -24 \rightarrow 24$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.111$
 $S = 1.04$
 1763 reflections
 126 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.1751P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.17 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL*,
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.022 (4)

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3284 (2)	0.39314 (6)	0.57841 (18)	0.0431 (3)
C2	0.2308 (2)	0.33121 (6)	0.61501 (19)	0.0446 (3)
H2	0.0929	0.3300	0.6654	0.053*
C3	0.3365 (2)	0.27233 (6)	0.57715 (19)	0.0436 (3)
H3	0.2711	0.2313	0.6019	0.052*
C4	0.5409 (2)	0.27456 (6)	0.50202 (18)	0.0412 (3)
C5	0.6389 (2)	0.33516 (7)	0.45997 (18)	0.0460 (3)
H5	0.7756	0.3359	0.4072	0.055*
C6	0.5330 (2)	0.39403 (7)	0.4966 (2)	0.0474 (3)
H6	0.5974	0.4348	0.4670	0.057*
C7	0.8041 (2)	-0.00321 (8)	0.3919 (2)	0.0604 (4)
H7A	0.7274	-0.0085	0.2703	0.073*
H7B	0.6982	0.0024	0.4911	0.073*
C8	1.0620 (3)	0.06407 (7)	0.5674 (2)	0.0615 (4)
H8A	0.9605	0.0707	0.6697	0.074*
H8B	1.1545	0.1033	0.5618	0.074*
N1	0.65536 (19)	0.21262 (6)	0.46944 (16)	0.0506 (3)
N2	0.9439 (2)	0.05619 (6)	0.38520 (18)	0.0515 (3)
O1	0.84102 (19)	0.21550 (6)	0.4113 (2)	0.0764 (4)

O2	0.56486 (19)	0.15891 (5)	0.50020 (17)	0.0672 (3)
O3	0.23383 (18)	0.45125 (5)	0.61778 (16)	0.0628 (3)
H3A	0.1330	0.4447	0.6898	0.094*
H2A	0.867 (3)	0.0873 (10)	0.362 (3)	0.071 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0508 (7)	0.0362 (6)	0.0425 (7)	0.0028 (5)	0.0080 (5)	-0.0010 (5)
C2	0.0394 (6)	0.0439 (7)	0.0507 (7)	0.0000 (5)	0.0092 (5)	-0.0019 (5)
C3	0.0464 (7)	0.0370 (6)	0.0473 (7)	-0.0033 (5)	0.0015 (6)	-0.0022 (5)
C4	0.0439 (7)	0.0420 (7)	0.0376 (6)	0.0076 (5)	-0.0014 (5)	-0.0052 (5)
C5	0.0397 (7)	0.0547 (8)	0.0438 (7)	0.0013 (5)	0.0079 (5)	-0.0017 (6)
C6	0.0521 (8)	0.0420 (7)	0.0486 (7)	-0.0058 (6)	0.0106 (6)	0.0011 (5)
C7	0.0445 (7)	0.0688 (10)	0.0680 (9)	-0.0099 (7)	0.0014 (6)	0.0101 (8)
C8	0.0785 (10)	0.0362 (7)	0.0703 (10)	-0.0139 (7)	0.0146 (8)	-0.0050 (6)
N1	0.0530 (7)	0.0529 (7)	0.0458 (6)	0.0152 (5)	-0.0031 (5)	-0.0079 (5)
N2	0.0537 (7)	0.0356 (6)	0.0658 (8)	0.0096 (5)	0.0141 (6)	0.0094 (5)
O1	0.0564 (7)	0.0762 (8)	0.0972 (10)	0.0210 (6)	0.0138 (6)	-0.0163 (6)
O2	0.0812 (8)	0.0428 (6)	0.0776 (8)	0.0125 (5)	0.0034 (6)	-0.0018 (5)
O3	0.0740 (7)	0.0385 (5)	0.0772 (8)	0.0080 (5)	0.0329 (6)	0.0014 (5)

Geometric parameters (Å, °)

C1—O3	1.3290 (15)	C7—N2	1.4673 (18)
C1—C6	1.3995 (19)	C7—C8 ⁱ	1.493 (2)
C1—C2	1.4000 (17)	C7—H7A	0.9700
C2—C3	1.3720 (18)	C7—H7B	0.9700
C2—H2	0.9300	C8—N2	1.463 (2)
C3—C4	1.3799 (19)	C8—C7 ⁱ	1.493 (2)
C3—H3	0.9300	C8—H8A	0.9700
C4—C5	1.3855 (18)	C8—H8B	0.9700
C4—N1	1.4434 (16)	N1—O1	1.2279 (16)
C5—C6	1.3706 (18)	N1—O2	1.2290 (16)
C5—H5	0.9300	N2—H2A	0.80 (2)
C6—H6	0.9300	O3—H3A	0.8200
O3—C1—C6	118.65 (11)	N2—C7—H7A	109.7
O3—C1—C2	122.45 (12)	C8 ⁱ —C7—H7A	109.7
C6—C1—C2	118.90 (11)	N2—C7—H7B	109.7
C3—C2—C1	120.60 (12)	C8 ⁱ —C7—H7B	109.7
C3—C2—H2	119.7	H7A—C7—H7B	108.2
C1—C2—H2	119.7	N2—C8—C7 ⁱ	110.09 (12)
C2—C3—C4	119.37 (12)	N2—C8—H8A	109.6
C2—C3—H3	120.3	C7 ⁱ —C8—H8A	109.6
C4—C3—H3	120.3	N2—C8—H8B	109.6
C3—C4—C5	121.15 (11)	C7 ⁱ —C8—H8B	109.6
C3—C4—N1	119.28 (12)	H8A—C8—H8B	108.2

C5—C4—N1	119.57 (12)	O1—N1—O2	122.10 (12)
C6—C5—C4	119.55 (12)	O1—N1—C4	118.54 (12)
C6—C5—H5	120.2	O2—N1—C4	119.36 (12)
C4—C5—H5	120.2	C8—N2—C7	110.05 (11)
C5—C6—C1	120.37 (12)	C8—N2—H2A	112.3 (14)
C5—C6—H6	119.8	C7—N2—H2A	106.6 (14)
C1—C6—H6	119.8	C1—O3—H3A	109.5
N2—C7—C8 ⁱ	109.63 (11)		
O3—C1—C2—C3	-178.17 (12)	O3—C1—C6—C5	177.78 (12)
C6—C1—C2—C3	2.1 (2)	C2—C1—C6—C5	-2.5 (2)
C1—C2—C3—C4	-0.1 (2)	C3—C4—N1—O1	-176.52 (12)
C2—C3—C4—C5	-1.5 (2)	C5—C4—N1—O1	2.59 (19)
C2—C3—C4—N1	177.55 (11)	C3—C4—N1—O2	3.58 (19)
C3—C4—C5—C6	1.2 (2)	C5—C4—N1—O2	-177.31 (11)
N1—C4—C5—C6	-177.93 (11)	C7 ⁱ —C8—N2—C7	59.04 (16)
C4—C5—C6—C1	0.9 (2)	C8 ⁱ —C7—N2—C8	-58.77 (17)

Symmetry code: (i) $-x+2, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3A...N2 ⁱⁱ	0.82	1.82	2.6210 (16)	167
N2—H2A...O1	0.796 (19)	2.58 (2)	3.2437 (17)	141.4 (17)
N2—H2A...O2	0.796 (19)	2.557 (19)	3.2273 (17)	142.8 (19)
C2—H2...O1 ⁱⁱ	0.93	2.51	3.3428 (17)	149
C6—H6...O3 ⁱⁱⁱ	0.93	2.57	3.5035 (17)	179

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