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2-Methylamino-5-nitrobenzoic acid

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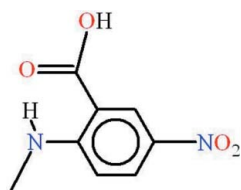
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.051; wR factor = 0.156; data-to-parameter ratio = 12.9.

The title compound, $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$, is almost planar (r.m.s. deviation = 0.037 Å) and an intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond generates an $S(6)$ ring. In the crystal, inversion dimers linked by pairs of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds generate $R_2^2(8)$ loops. Intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (involving the same H atom that forms the intramolecular hydrogen bond) link the dimers into infinite sheets lying parallel to (102).

Related literature

For background to the medicinal properties of benzodiazepines, see: Blank *et al.* (2009); Kamal *et al.* (2010). For a related structure, see: Dhaneshwar & Pant (1972). For graph-set theory, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$ $M_r = 196.16$ Monoclinic, $P2_1/c$ $a = 7.2541$ (12) Å $b = 14.037$ (2) Å $c = 8.5972$ (14) Å $\beta = 103.673$ (6)° $V = 850.6$ (2) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.13$ mm⁻¹ $T = 296$ K $0.34 \times 0.12 \times 0.10$ mm

Data collection

Bruker Kappa APEXII CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.979$, $T_{\max} = 0.988$

6739 measured reflections

1667 independent reflections

931 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.051$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.051$ $wR(F^2) = 0.156$ $S = 0.95$

1667 reflections

129 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.86	2.03	2.694 (3)	134
$\text{N1}-\text{H1}\cdots\text{O4}^{\text{i}}$	0.86	2.52	3.165 (3)	133
$\text{O2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.82	1.86	2.679 (3)	177

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5463).

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2-Methylamino-5-nitrobenzoic acid

Abdul Rauf Raza, Syeda Laila Rubab and M. Nawaz Tahir

S1. Comment

The benzodiazepines constitute a very diverse class of heterocyclic compounds with plethora of biological activities such as anti-cancer (Kamal *et al.*, 2010) and anti-HIV (Blank *et al.*, 2009) agent. The title compound (I, Fig. 1) was synthesized as a precursor for the synthesis of benzodiazepine derivative and it will also be utilized for the metal complexation.

The crystal structures of *N*-methylantranilic acid (II) (Dhaneshwar & Pant, 1972) has been published. The title compound differs from (II) due to substitution of nitro group at at position five.

The asymmetric unit of title compound is essentially planar with r. m. s. deviation of 0.0366 Å from the least square plane of (C1—C8/N1/N2/O1/O2/O3). There exist a S(6) ring motif (Bernstein *et al.*, 1995) due to N—H \cdots O type of intramolecular H-bondings. The molecules are dimerised due to inversion related O—H \cdots O type of H-bondings with R₂²(8) ring motifs. The dimers are interlinked in the form of infinite two dimensional polymeric sheets due to H-bonding of N—H \cdots O type (Fig. 2).

S2. Experimental

To HNO₃ (1.83 g, 0.03 mol) taken in an ice chilled round bottom flask the H₂SO₄ (2.6 g, 0.026 mol) was added as drops with constant stirring. A solution of *N*-methylantranilic acid (2 g, 0.01 mol) in EtOAc (25 ml) was added as drops to the nitrating mixture in ice chilled water bath and stirred for half an hour followed by 3 hours reflux. The reaction mixture was neutralized and extracted with EtOAc (3 × 30 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduce pressure that afforded purple needles of (I) upon standing.

S3. Refinement

Although H atoms were appeared in difference Fourier map but were positioned geometrically with (C-H = 0.93–0.96 and O-H = 0.82 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl and hydroxy H-atoms and $x = 1.2$ for other H atoms.

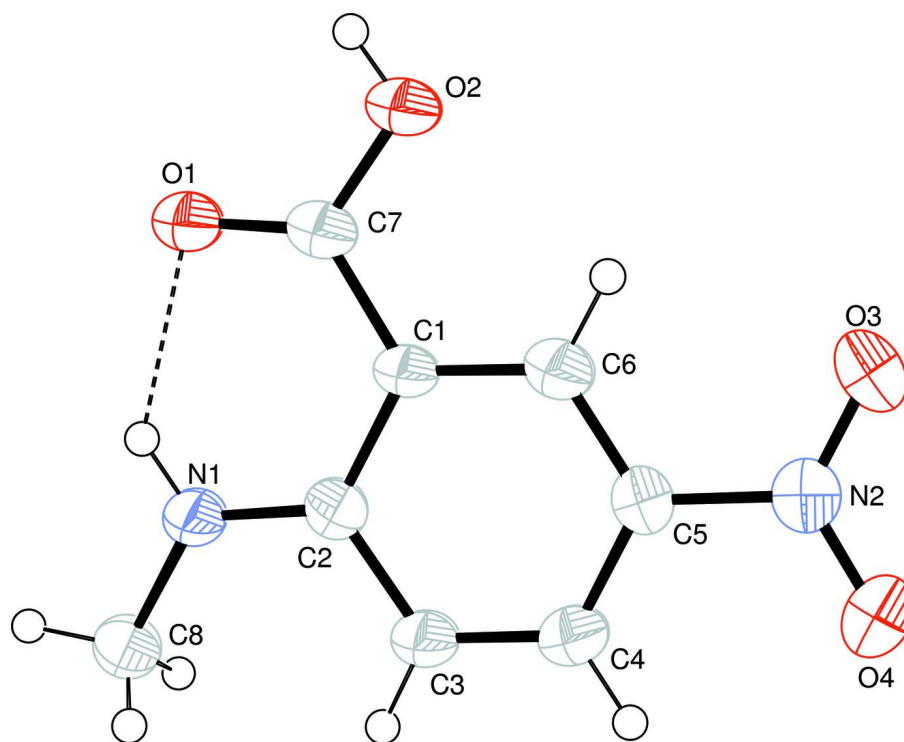


Figure 1

View of (I) with displacement ellipsoids drawn at the 50% probability level. The dotted line indicate the intramolecular H-bond.

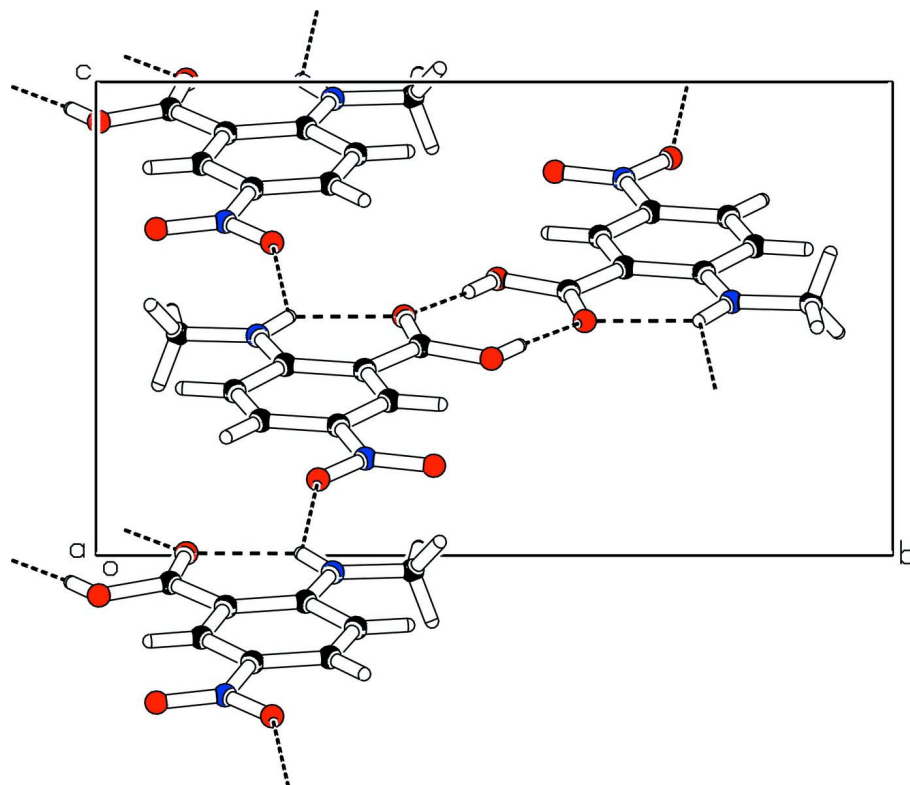


Figure 2

The partial packing diagram of (I), which shows that molecules form polymeric chains extending along the b-axis.

2-Methylamino-5-nitrobenzoic acid

Crystal data

$C_8H_8N_2O_4$

$M_r = 196.16$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 7.2541$ (12) Å

$b = 14.037$ (2) Å

$c = 8.5972$ (14) Å

$\beta = 103.673$ (6)°

$V = 850.6$ (2) Å³

$Z = 4$

$F(000) = 408$

$D_x = 1.532$ Mg m⁻³

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

Cell parameters from 931 reflections

$\theta = 2.8$ – 26.0 °

$\mu = 0.13$ mm⁻¹

$T = 296$ K

Needle, colorless

$0.34 \times 0.12 \times 0.10$ mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 7.50 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2005)

$T_{\min} = 0.979$, $T_{\max} = 0.988$

6739 measured reflections

1667 independent reflections

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

$R_{\text{int}} = 0.051$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 2.8$ °

$h = -8 \rightarrow 8$

$k = -17 \rightarrow 12$

$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.156$
 $S = 0.95$
 1667 reflections
 129 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0901P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.5419 (3)	0.38658 (12)	0.5049 (2)	0.0518 (7)
O2	0.7127 (3)	0.49628 (11)	0.4158 (3)	0.0573 (8)
O3	1.2269 (3)	0.42409 (14)	0.1896 (3)	0.0729 (9)
O4	1.3096 (3)	0.27893 (14)	0.1606 (3)	0.0672 (8)
N1	0.6259 (3)	0.20268 (13)	0.4642 (3)	0.0468 (8)
N2	1.2080 (3)	0.33798 (16)	0.2050 (3)	0.0520 (9)
C1	0.7967 (3)	0.33700 (15)	0.3914 (3)	0.0356 (8)
C2	0.7635 (3)	0.23711 (16)	0.4028 (3)	0.0380 (8)
C3	0.8868 (3)	0.17368 (17)	0.3470 (3)	0.0421 (9)
C4	1.0304 (4)	0.20647 (17)	0.2851 (3)	0.0445 (9)
C5	1.0588 (3)	0.30381 (17)	0.2745 (3)	0.0412 (9)
C6	0.9435 (4)	0.36766 (16)	0.3270 (3)	0.0405 (8)
C7	0.6728 (4)	0.40694 (16)	0.4424 (3)	0.0404 (9)
C8	0.5800 (4)	0.10286 (17)	0.4683 (4)	0.0530 (11)
H1	0.55963	0.24247	0.50427	0.0562*
H2	0.63612	0.53160	0.44325	0.0859*
H3	0.86864	0.10833	0.35312	0.0505*
H4	1.10970	0.16375	0.24988	0.0534*
H6	0.96473	0.43263	0.31904	0.0486*
H8A	0.68822	0.06878	0.52857	0.0796*
H8B	0.54575	0.07839	0.36101	0.0796*
H8C	0.47552	0.09499	0.51789	0.0796*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0570 (13)	0.0296 (10)	0.0792 (14)	0.0016 (8)	0.0367 (11)	0.0003 (9)
O2	0.0657 (13)	0.0256 (11)	0.0921 (16)	0.0005 (9)	0.0418 (12)	-0.0015 (9)
O3	0.0793 (16)	0.0436 (12)	0.1119 (19)	-0.0089 (10)	0.0550 (14)	0.0108 (12)
O4	0.0582 (13)	0.0610 (13)	0.0958 (17)	0.0082 (10)	0.0448 (12)	0.0052 (12)
N1	0.0541 (14)	0.0254 (11)	0.0716 (16)	-0.0034 (10)	0.0363 (13)	-0.0040 (10)
N2	0.0497 (15)	0.0443 (14)	0.0687 (17)	0.0010 (12)	0.0273 (13)	0.0050 (12)
C1	0.0406 (15)	0.0224 (12)	0.0464 (16)	0.0003 (10)	0.0156 (12)	-0.0020 (10)
C2	0.0416 (15)	0.0307 (13)	0.0447 (15)	-0.0026 (11)	0.0160 (13)	-0.0013 (11)
C3	0.0464 (16)	0.0261 (12)	0.0584 (17)	0.0005 (11)	0.0216 (14)	-0.0032 (12)
C4	0.0461 (16)	0.0333 (15)	0.0586 (18)	0.0050 (12)	0.0212 (14)	-0.0029 (12)
C5	0.0414 (15)	0.0366 (15)	0.0497 (16)	-0.0023 (11)	0.0190 (13)	0.0030 (12)
C6	0.0438 (15)	0.0288 (13)	0.0502 (16)	-0.0012 (11)	0.0137 (13)	-0.0003 (11)
C7	0.0467 (16)	0.0264 (14)	0.0494 (16)	-0.0001 (11)	0.0141 (14)	-0.0006 (12)
C8	0.069 (2)	0.0257 (14)	0.076 (2)	-0.0092 (12)	0.0404 (16)	-0.0070 (13)

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

O1—C7	1.230 (4)	C1—C6	1.380 (4)
O2—C7	1.319 (3)	C2—C3	1.423 (3)
O3—N2	1.227 (3)	C3—C4	1.357 (4)
O4—N2	1.228 (3)	C4—C5	1.388 (3)
O2—H2	0.8200	C5—C6	1.373 (4)
N1—C8	1.443 (3)	C3—H3	0.9300
N1—C2	1.326 (3)	C4—H4	0.9300
N2—C5	1.437 (3)	C6—H6	0.9300
N1—H1	0.8600	C8—H8A	0.9600
C1—C7	1.466 (3)	C8—H8B	0.9600
C1—C2	1.430 (3)	C8—H8C	0.9600
C7—O2—H2	109.00	N2—C5—C6	119.7 (2)
C2—N1—C8	124.3 (2)	C1—C6—C5	121.1 (2)
O3—N2—C5	119.2 (2)	O1—C7—O2	121.4 (2)
O4—N2—C5	118.1 (2)	O1—C7—C1	124.5 (2)
O3—N2—O4	122.7 (2)	O2—C7—C1	114.2 (2)
C2—N1—H1	118.00	C2—C3—H3	119.00
C8—N1—H1	118.00	C4—C3—H3	119.00
C6—C1—C7	119.8 (2)	C3—C4—H4	120.00
C2—C1—C6	119.5 (2)	C5—C4—H4	120.00
C2—C1—C7	120.7 (2)	C1—C6—H6	119.00
N1—C2—C3	119.9 (2)	C5—C6—H6	119.00
N1—C2—C1	122.7 (2)	N1—C8—H8A	109.00
C1—C2—C3	117.4 (2)	N1—C8—H8B	109.00
C2—C3—C4	121.5 (2)	N1—C8—H8C	109.00
C3—C4—C5	119.9 (2)	H8A—C8—H8B	109.00
C4—C5—C6	120.6 (2)	H8A—C8—H8C	110.00

N2—C5—C4	119.6 (2)	H8B—C8—H8C	109.00
C8—N1—C2—C1	175.8 (3)	C2—C1—C7—O1	4.1 (4)
C8—N1—C2—C3	-5.1 (4)	C2—C1—C7—O2	-175.9 (2)
O3—N2—C5—C4	176.8 (3)	C6—C1—C7—O1	-178.0 (2)
O3—N2—C5—C6	-2.0 (4)	C6—C1—C7—O2	2.0 (4)
O4—N2—C5—C4	-1.9 (4)	N1—C2—C3—C4	-179.3 (2)
O4—N2—C5—C6	179.4 (3)	C1—C2—C3—C4	-0.1 (4)
C6—C1—C2—N1	179.6 (2)	C2—C3—C4—C5	-0.3 (4)
C6—C1—C2—C3	0.4 (4)	C3—C4—C5—N2	-178.4 (2)
C7—C1—C2—N1	-2.5 (4)	C3—C4—C5—C6	0.4 (4)
C7—C1—C2—C3	178.4 (2)	N2—C5—C6—C1	178.7 (2)
C2—C1—C6—C5	-0.4 (4)	C4—C5—C6—C1	0.0 (4)
C7—C1—C6—C5	-178.3 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1	0.86	2.03	2.694 (3)	134
N1—H1...O4 ⁱ	0.86	2.52	3.165 (3)	133
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Symmetry codes: (i) $x-1, -y+1/2, z+1/2$; (ii) $-x+1, -y+1, -z+1$.