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 4-*tert*-Butylamino-3-nitrobenzoic acid

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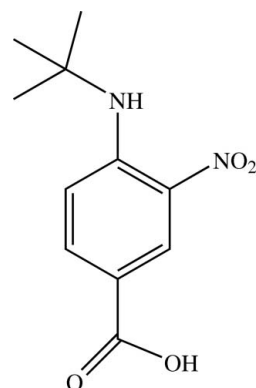
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.065; wR factor = 0.153; data-to-parameter ratio = 13.3.

In the title compound, $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$, all non-H atoms lie in a mirror plane except for one of the methyl groups which deviates from the mirror plane by 0.919 (3) Å and is twisted by a torsion angle of 62.9 (2)°. An intramolecular N—H...O hydrogen bond generates an $S(6)$ ring motif. In the crystal packing, the molecules are linked together by O—H...O hydrogen bonds, forming dimers with graph-set motif $R_2^2(8)$ which propagate along the a -axis direction. C—H...O contacts link adjacent dimers with a graph-set motif $C_2^2(7)$, forming chains along b , and further consolidate the structure into a three-dimensional network. The crystal packing is further strengthened by short intermolecular O...O=C [2.655 (4) Å] contacts.

Related literature

Nitro benzoic acid derivatives are important intermediates for the synthesis of various heterocyclic compounds of pharmaceutical interest, see: Brouillette *et al.* (1999); Williams *et al.* (1995). For the structure of 4-(*tert*-butylamino)-3-nitrobenzoate, see: Mohd Maidin *et al.* (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$
 $M_r = 238.24$
 Monoclinic, $C2/m$
 $a = 20.8125$ (15) Å
 $b = 6.7412$ (5) Å
 $c = 8.0793$ (5) Å
 $\beta = 90.863$ (6)°
 $V = 1133.41$ (14) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 100$ K
 $0.39 \times 0.10 \times 0.03$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.959$, $T_{\max} = 0.997$
 6267 measured reflections
 1418 independent reflections
 985 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.153$
 $S = 1.11$
 1418 reflections
 107 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O1...O2 ⁱ	0.82 (4)	1.83 (4)	2.655 (4)	178 (4)
C1—H1A...O3 ⁱⁱ	0.93	2.52	3.407 (4)	161
N2—H1N2...O4	0.81 (4)	1.97 (4)	2.641 (4)	139 (4)
C9—H9C...O2 ⁱⁱⁱ	0.96	2.53	3.437 (3)	158

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

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 and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2439).

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S1. Comment

Nitro benzoic acid derivatives are important intermediates for the synthesis of various heterocyclic compounds of pharmacological interest (Brouillette *et al.*, 1999; Williams *et al.*, 1995). As a part of our ongoing study on such compounds, in this paper, we present the crystal structure of the title compound (I) which was synthesized as an intermediate.

In the asymmetric unit of (I), all non-hydrogen atoms lie in a mirror plane except the methyl-C9A moiety, which is deviated from the mean plane by 0.919 (3) Å and twisted by a torsion angle C6–N2–C7–C9 of 62.9 (2) Å.

An intramolecular N—H···O hydrogen bond generates a ring of motif S(6) (Bernstein *et al.*, 1995) (Fig. 1). In the crystal packing, the molecules are linked together by O—H···O hydrogen bonds to form dimers with the graph set motif $R_2^2(8)$ which propagate along the a-direction (Table 1). C—H···O contacts link adjacent dimers with a graph set motif $C_2^2(7)$ (Fig. 2) to form chains along the b-direction and further consolidate the structure into a 3D network. The crystal packing is further strengthened by short intermolecular O···Oⁱ⁻ⁱⁱ = 2.655 (4) Å contacts; symmetry code: (i) 1-x, y, 1-z; (ii) 1-x, 1-y, 1-z.

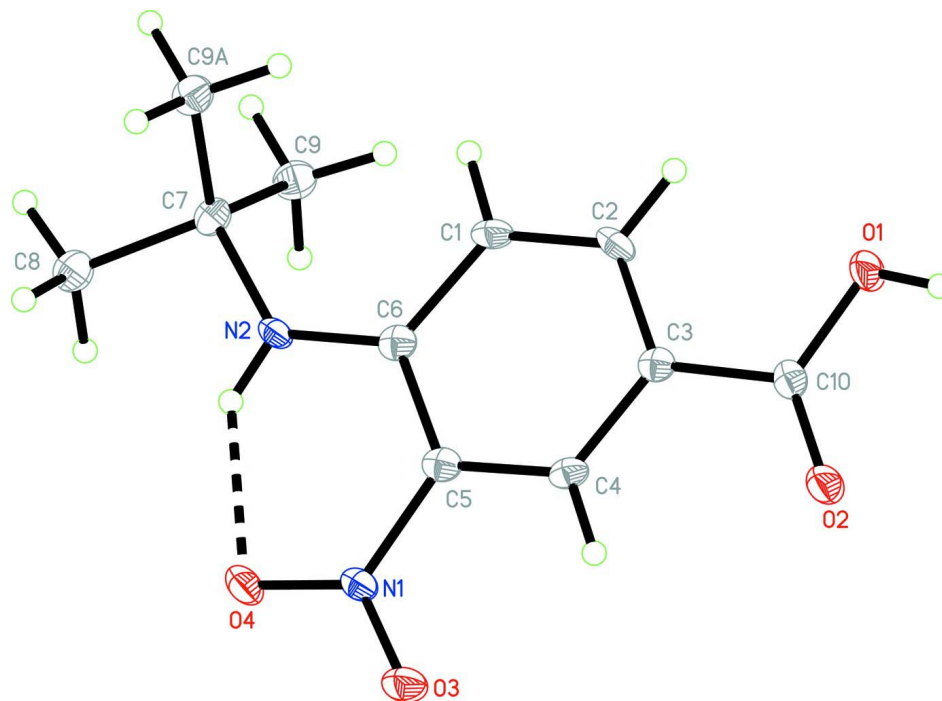
S2. Experimental

Compound (I) was prepared by refluxing ethyl 4-(*tert*-butylamino)-3-nitrobenzoate (0.7 g, 0.0026 mol) (Mohd Maidin *et al.*, 2008) and KOH (0.14 g, 0.0026 mol) in aqueous ethanol (10 ml) for 3 h. Ethanol was then removed *in vacuo* and the reaction mixture was diluted with water (15 ml). The aqueous layer was washed with dichloromethane (10 ml × 2) and acidified with concentrated hydrochloric acid to bring about the precipitation of the desired benzoic acid.

Recrystallization of the precipitate with hot ethyl acetate afforded yellow crystals of the title compound (I).

S3. Refinement

H atoms were positioned geometrically [C–H = 0.93–0.96 Å] and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{methyl C})$. A rotating-group model was used for the methyl groups. The O- and N-bound hydrogen atoms were located from the Fourier map and allowed to refine freely.

**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom numbering scheme.

Intramolecular hydrogen bonding is shown as a dashed line. [Symmetry code used to generate methyl moiety C9A: $x, -y + 1, z$]

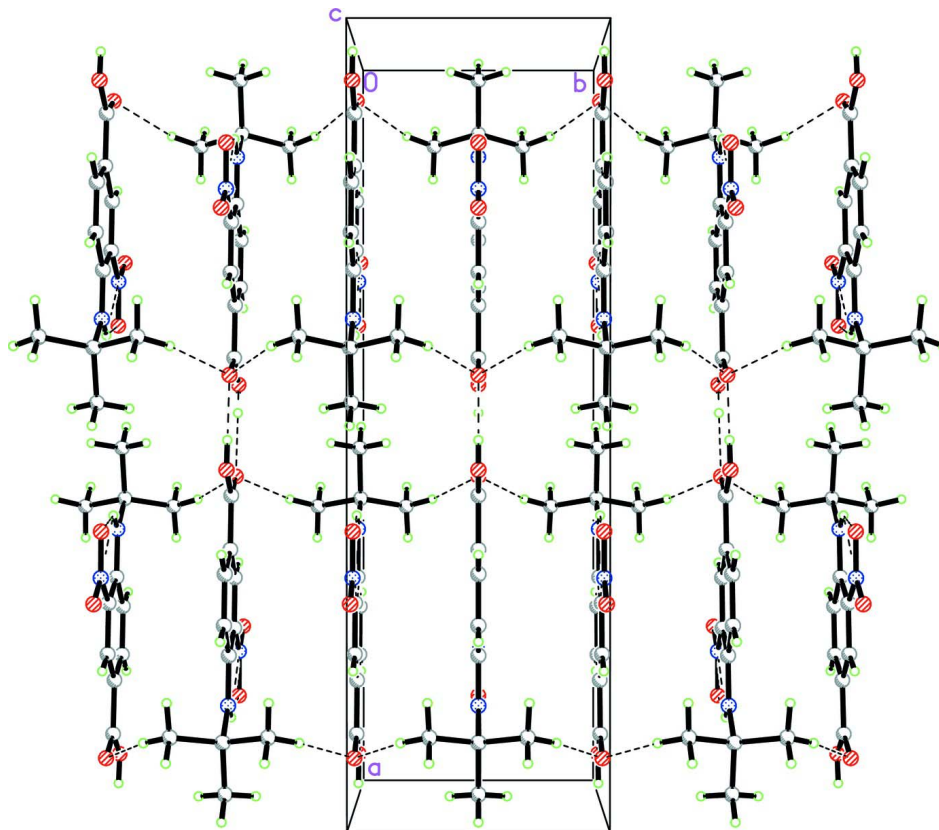


Figure 2

The crystal packing of (I), viewed along the *c* axis. Dashed lines indicate the hydrogen bonding and C—H···O contacts.

(I)

Crystal data $C_{11}H_{14}N_2O_4$ $M_r = 238.24$ Monoclinic, $C2/m$ Hall symbol: $-C\ 2y$ $a = 20.8125\ (15)\ \text{\AA}$ $b = 6.7412\ (5)\ \text{\AA}$ $c = 8.0793\ (5)\ \text{\AA}$ $\beta = 90.863\ (6)^\circ$ $V = 1133.41\ (14)\ \text{\AA}^3$ $Z = 4$ $F(000) = 504$ $D_x = 1.396\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1829 reflections

 $\theta = 3.2\text{--}30.6^\circ$ $\mu = 0.11\ \text{mm}^{-1}$ $T = 100\ \text{K}$

Plate, yellow

 $0.39 \times 0.10 \times 0.03\ \text{mm}$ *Data collection*Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2005)

 $T_{\min} = 0.959$, $T_{\max} = 0.997$

6267 measured reflections

1418 independent reflections

985 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.057$ $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.0^\circ$ $h = -26 \rightarrow 26$ $k = -8 \rightarrow 8$ $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.153$
 $S = 1.11$
 1418 reflections
 107 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
 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 2.3728P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.44372 (12)	0.5000	0.3166 (3)	0.0189 (6)
O2	0.43314 (11)	0.5000	0.5919 (3)	0.0185 (6)
O3	0.22447 (11)	0.5000	0.8193 (3)	0.0198 (6)
O4	0.13560 (11)	0.5000	0.6766 (3)	0.0187 (6)
N1	0.19540 (13)	0.5000	0.6848 (3)	0.0130 (6)
N2	0.13842 (13)	0.5000	0.3497 (4)	0.0131 (6)
C1	0.24626 (16)	0.5000	0.2381 (4)	0.0142 (7)
H1A	0.2298	0.5000	0.1304	0.017*
C2	0.31116 (16)	0.5000	0.2615 (4)	0.0145 (7)
H2A	0.3377	0.5000	0.1700	0.017*
C3	0.33894 (15)	0.5000	0.4217 (4)	0.0122 (7)
C4	0.29869 (16)	0.5000	0.5563 (4)	0.0126 (7)
H4A	0.3163	0.5000	0.6628	0.015*
C5	0.23216 (16)	0.5000	0.5349 (4)	0.0130 (7)
C6	0.20244 (16)	0.5000	0.3726 (4)	0.0129 (7)
C7	0.09935 (16)	0.5000	0.1929 (4)	0.0145 (7)
C8	0.02967 (16)	0.5000	0.2518 (4)	0.0184 (8)
H8B	0.0008	0.5000	0.1581	0.028*
H8C	0.0228	0.3861	0.3206	0.028*
C9	0.11138 (11)	0.3105 (4)	0.0926 (3)	0.0169 (6)
H9A	0.1558	0.3044	0.0627	0.025*
H9B	0.0850	0.3120	-0.0060	0.025*

H9C	0.1008	0.1966	0.1581	0.025*
C10	0.40933 (15)	0.5000	0.4522 (4)	0.0132 (7)
H1N2	0.1189 (18)	0.5000	0.435 (5)	0.015 (10)*
H1O1	0.4804 (19)	0.5000	0.341 (5)	0.010 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0086 (13)	0.0327 (15)	0.0154 (14)	0.000	0.0005 (10)	0.000
O2	0.0121 (12)	0.0293 (14)	0.0142 (13)	0.000	0.0012 (10)	0.000
O3	0.0207 (13)	0.0282 (14)	0.0104 (12)	0.000	0.0002 (10)	0.000
O4	0.0130 (13)	0.0279 (14)	0.0153 (13)	0.000	0.0045 (10)	0.000
N1	0.0154 (15)	0.0119 (14)	0.0117 (15)	0.000	0.0033 (11)	0.000
N2	0.0113 (15)	0.0189 (15)	0.0092 (15)	0.000	0.0029 (12)	0.000
C1	0.0197 (18)	0.0147 (17)	0.0082 (17)	0.000	-0.0002 (14)	0.000
C2	0.0176 (18)	0.0131 (16)	0.0129 (18)	0.000	0.0074 (14)	0.000
C3	0.0155 (17)	0.0082 (15)	0.0128 (17)	0.000	0.0004 (13)	0.000
C4	0.0172 (17)	0.0109 (16)	0.0096 (17)	0.000	-0.0014 (13)	0.000
C5	0.0178 (18)	0.0085 (15)	0.0126 (17)	0.000	0.0016 (13)	0.000
C6	0.0166 (17)	0.0088 (15)	0.0134 (17)	0.000	0.0003 (14)	0.000
C7	0.0132 (17)	0.0158 (17)	0.0142 (17)	0.000	-0.0026 (13)	0.000
C8	0.0173 (18)	0.0215 (18)	0.0164 (18)	0.000	-0.0021 (14)	0.000
C9	0.0184 (12)	0.0163 (12)	0.0160 (12)	-0.0014 (10)	-0.0014 (10)	0.0003 (10)
C10	0.0134 (17)	0.0093 (16)	0.0170 (18)	0.000	0.0027 (14)	0.000

Geometric parameters (Å, °)

O1—C10	1.318 (4)	C3—C4	1.383 (5)
O1—H1O1	0.79 (4)	C3—C10	1.482 (5)
O2—C10	1.226 (4)	C4—C5	1.393 (5)
O3—N1	1.236 (4)	C4—H4A	0.9300
O4—N1	1.245 (4)	C5—C6	1.441 (5)
N1—C5	1.442 (4)	C7—C8	1.533 (5)
N2—C6	1.343 (4)	C7—C9	1.536 (3)
N2—C7	1.495 (4)	C7—C9 ⁱ	1.536 (3)
N2—H1N2	0.80 (4)	C8—H8B	0.9595
C1—C2	1.361 (5)	C8—H8C	0.9600
C1—C6	1.429 (5)	C9—H9A	0.9600
C1—H1A	0.9300	C9—H9B	0.9600
C2—C3	1.409 (5)	C9—H9C	0.9600
C2—H2A	0.9300		
C10—O1—H1O1	109 (3)	N2—C6—C1	122.6 (3)
O3—N1—O4	121.5 (3)	N2—C6—C5	122.5 (3)
O3—N1—C5	118.6 (3)	C1—C6—C5	114.9 (3)
O4—N1—C5	119.9 (3)	N2—C7—C8	104.0 (3)
C6—N2—C7	130.0 (3)	N2—C7—C9	110.88 (17)
C6—N2—H1N2	113 (3)	C8—C7—C9	109.04 (18)

C7—N2—H1N2	117 (3)	N2—C7—C9 ⁱ	110.88 (17)
C2—C1—C6	122.5 (3)	C8—C7—C9 ⁱ	109.04 (18)
C2—C1—H1A	118.7	C9—C7—C9 ⁱ	112.6 (3)
C6—C1—H1A	118.7	C7—C8—H8B	109.9
C1—C2—C3	121.4 (3)	C7—C8—H8C	109.3
C1—C2—H2A	119.3	H8B—C8—H8C	111.1
C3—C2—H2A	119.3	C7—C9—H9A	109.5
C4—C3—C2	118.5 (3)	C7—C9—H9B	109.5
C4—C3—C10	118.5 (3)	H9A—C9—H9B	109.5
C2—C3—C10	122.9 (3)	C7—C9—H9C	109.5
C3—C4—C5	121.0 (3)	H9A—C9—H9C	109.5
C3—C4—H4A	119.5	H9B—C9—H9C	109.5
C5—C4—H4A	119.5	O2—C10—O1	123.3 (3)
C4—C5—C6	121.7 (3)	O2—C10—C3	122.6 (3)
C4—C5—N1	115.8 (3)	O1—C10—C3	114.2 (3)
C6—C5—N1	122.5 (3)		
C6—C1—C2—C3	0.0	C2—C1—C6—N2	180.0
C1—C2—C3—C4	0.0	C2—C1—C6—C5	0.0
C1—C2—C3—C10	180.0	C4—C5—C6—N2	180.0
C2—C3—C4—C5	0.0	N1—C5—C6—N2	0.0
C10—C3—C4—C5	180.0	C4—C5—C6—C1	0.0
C3—C4—C5—C6	0.0	N1—C5—C6—C1	180.0
C3—C4—C5—N1	180.0	C6—N2—C7—C8	180.0
O3—N1—C5—C4	0.0	C6—N2—C7—C9	62.9 (2)
O4—N1—C5—C4	180.0	C6—N2—C7—C9 ⁱ	-62.9 (2)
O3—N1—C5—C6	180.0	C4—C3—C10—O2	0.0
O4—N1—C5—C6	0.0	C2—C3—C10—O2	180.0
C7—N2—C6—C1	0.0	C4—C3—C10—O1	180.0
C7—N2—C6—C5	180.0	C2—C3—C10—O1	0.0

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O1 \cdots O2 ⁱⁱ	0.82 (4)	1.83 (4)	2.655 (4)	178 (4)
C1—H1A \cdots O3 ⁱⁱⁱ	0.93	2.52	3.407 (4)	161
N2—H1N2 \cdots O4	0.81 (4)	1.97 (4)	2.641 (4)	139 (4)
C9—H9C \cdots O2 ^{iv}	0.96	2.53	3.437 (3)	158

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