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4-Ethylamino-3-nitrobenzoic acid

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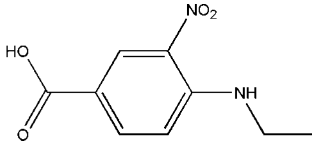
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.041; wR factor = 0.121; data-to-parameter ratio = 17.0.

In the title compound, $C_9H_{10}N_2O_4$, an intramolecular N—H⋯O hydrogen-bond interaction generates an $S(6)$ ring motif. The nitro group is slightly twisted away from its attached benzene ring [dihedral angle = 15.29 (15)°]. In the crystal structure, molecules are stacked down the a axis caused by short O⋯O($-1-x$, $-y$, $2-z$) contacts of 2.6481 (16) Å involving the O atoms of the nitro groups. The crystal packing is consolidated by intermolecular O—H⋯O hydrogen bonds, linking the molecules into centrosymmetric dimers.

Related literature

For reference bond lengths, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For information on the use of derivatives of nitro benzoic acid as precursors for heterocyclic compounds of biological interest, see: Ishida *et al.* (2006). For related structures, see: Mohd. Maidin *et al.* (2008); Narendra Babu *et al.* (2009). For the synthesis of ethyl 4-ethylamino-3-nitrobenzoate, see: Li *et al.* (2009).



Experimental

Crystal data

$C_9H_{10}N_2O_4$
M_r = 210.19
Triclinic, $P\bar{1}$
a = 3.9354 (4) Å
b = 8.4741 (9) Å
c = 13.8106 (15) Å
α = 89.256 (5)°
β = 84.730 (4)°
γ = 82.304 (4)°
V = 454.49 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 120 K
0.45 × 0.05 × 0.03 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.918, T_{max} = 0.996
7604 measured reflections
2410 independent reflections
1903 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.06
2410 reflections
142 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H1O4⋯O3^i	0.82	1.80	2.6092 (15)	168
N2—H1N2⋯O1	0.831 (19)	2.052 (18)	2.6634 (15)	130.0 (16)

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

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* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2618).

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4-Ethylamino-3-nitrobenzoic acid

Shivanagere Nagojappa Narendra Babu, Aisyah Saad Abdul Rahim, Shafida Abd Hamid, Ching Kheng Quah and Hoong-Kun Fun

S1. Comment

The derivatives of nitro benzoic acid are convenient precursors for the synthesis of various heterocyclic compounds of biological interest (Ishida *et al.*, 2006). As part of our ongoing studies on new nitro benzoic acid derivatives (Mohd. Maidin *et al.*, 2008; Narendra Babu *et al.*, 2009), we herein present the crystal structure of the title compound.

The molecular structure is stabilized by an intramolecular N2—H1N2···O1 hydrogen bond which generates an S(6) ring motif (Bernstein *et al.*, 1995). The bond lengths (Allen *et al.*, 1987) and angles in the molecule (Fig. 1) are within normal ranges. The nitro groups are slightly twisted away from the attached benzene ring as indicated by the torsion angles O1—N1—C2—C1 and O2—N1—C2—C3 being 165.34 (12)° and 165.04 (12)°, respectively.

In the crystal structure, (Fig. 2), the crystal packing is consolidated by an intermolecular O4—H1O4···O3^{i} hydrogen bond linking the molecules into dimers. There is a short O1···O1 contact (symmetry code: - 1 - *x*, - *y*, 2 - *z*) with distance = 2.6481 (16) which is shorter than the sum of van der Waals radii of the oxygen atoms, stacking the molecules along the *a* axis.

S2. Experimental

Ethyl 4-ethylamino-3-nitro-benzoate (1.80 g, 0.0075 mol) (Li *et al.*, 2009), and KOH (0.42 g, 0.0075 mol) was refluxed in aqueous ethanol (25 ml) for 3 h. After completion of the reaction, ethanol was distilled off and the reaction mixture was diluted with water (20 ml). The aqueous layer was washed with dichloromethane (10 x 2 ml) and then acidified with concentrated hydrochloric acid to afford a yellow precipitate as the crude product. Recrystallization of the crude product from hot ethyl acetate gave the title compound as yellow crystals suitable for X-ray analysis.

S3. Refinement

The H-atom attached to N2 was located from the difference Fourier map and refined freely. H atoms of the hydroxy groups were positioned using a rotating group model and constrained with a fixed distance of 0.82 Å. The rest of the hydrogen atoms were positioned geometrically and refined using a riding model with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). A rotating-group model was also applied for the methyl groups.

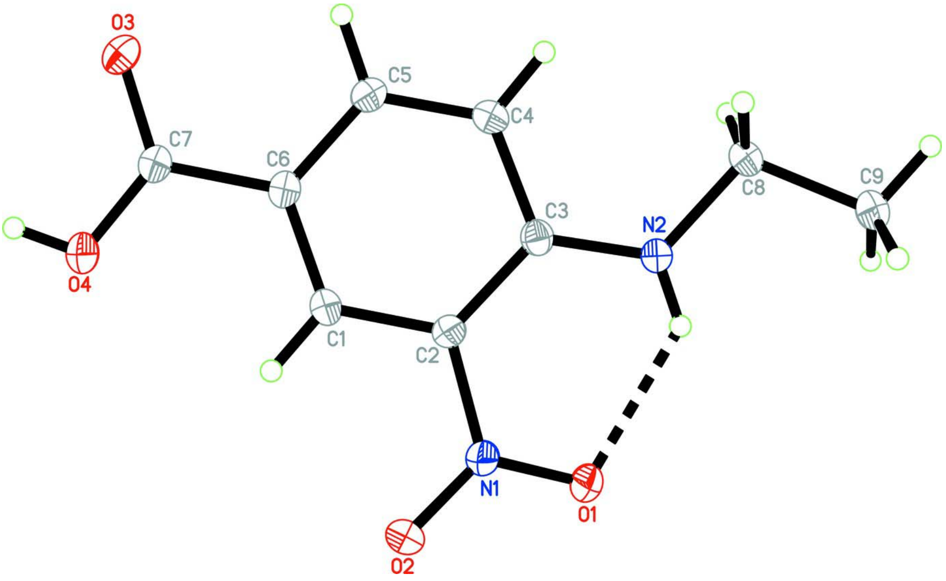

Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. The dashed line indicates an intramolecular hydrogen bond.

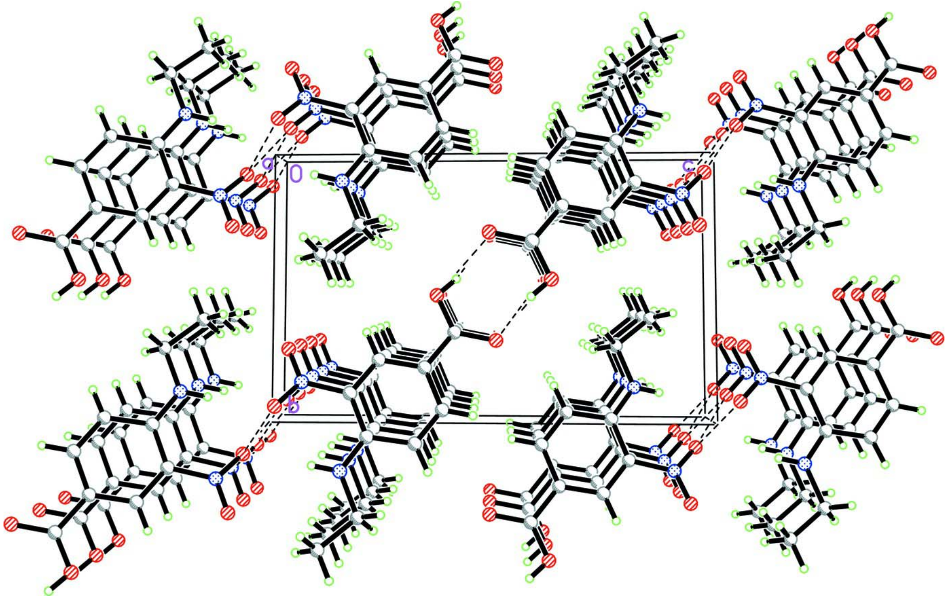

Figure 2

The crystal packing of the title compound,viewed along the *a* axis. Hydrogen bonds and the short O···O contacts are shown as dashed lines.

4-Ethylamino-3-nitrobenzoic acid

Crystal data

$C_9H_{10}N_2O_4$
$M_r = 210.19$
Triclinic, $P\overline{1}$

Hall symbol: -P 1
$a = 3.9354\ (4)$ Å
$b = 8.4741\ (9)$ Å

c = 13.8106 (15) Å
α = 89.256 (5)°
β = 84.730 (4)°
γ = 82.304 (4)°
V = 454.49 (8) Å^3
Z = 2
F(000) = 220
D_x = 1.536 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3018 reflections
θ = 1.5–29.0°
μ = 0.12 mm^{-1}
T = 120 K
Needle, yellow
0.45 × 0.05 × 0.03 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)
$T_{\min}$ = 0.918, $T_{\max}$ = 0.996

7604 measured reflections
2410 independent reflections
1903 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
$\theta_{\max}$ = 29.0°, $\theta_{\min}$ = 1.5°
h = −5→5
k = −11→11
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.121
S = 1.06
2410 reflections
142 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
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 0.1132P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.33 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat [Cosier, J. & Glazer, A. M. (1986). J. Appl. Cryst. 19, 105–107] operating at 120.0 (1) K.

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	−0.2816 (3)	0.09151 (12)	0.95790 (7)	0.0267 (3)
O2	0.0296 (3)	0.28327 (12)	0.93767 (7)	0.0260 (3)
O3	0.3986 (3)	0.31078 (13)	0.49289 (7)	0.0302 (3)
O4	0.3740 (3)	0.47173 (12)	0.62170 (8)	0.0272 (3)
H1O4	0.4493	0.5304	0.5797	0.041*
N1	−0.0961 (3)	0.17166 (13)	0.90601 (8)	0.0175 (2)

N2	−0.2305 (3)	−0.12944 (13)	0.82002 (8)	0.0174 (2)
C1	0.1130 (3)	0.24569 (15)	0.74460 (9)	0.0164 (3)
H1A	0.1501	0.3413	0.7714	0.020*
C2	−0.0252 (3)	0.13158 (15)	0.80371 (9)	0.0155 (3)
C3	−0.0921 (3)	−0.01649 (14)	0.76646 (9)	0.0152 (3)
C4	0.0068 (3)	−0.04224 (15)	0.66528 (9)	0.0179 (3)
H4A	−0.0235	−0.1381	0.6374	0.021*
C5	0.1453 (4)	0.07084 (16)	0.60827 (9)	0.0186 (3)
H5A	0.2077	0.0496	0.5427	0.022*
C6	0.1956 (3)	0.21795 (15)	0.64634 (9)	0.0175 (3)
C7	0.3311 (4)	0.34040 (16)	0.58304 (10)	0.0194 (3)
C8	−0.2853 (4)	−0.28286 (15)	0.78103 (10)	0.0177 (3)
H8A	−0.0688	−0.3375	0.7516	0.021*
H8B	−0.4447	−0.2657	0.7312	0.021*
C9	−0.4293 (4)	−0.38448 (16)	0.86180 (10)	0.0206 (3)
H9A	−0.4684	−0.4841	0.8355	0.031*
H9B	−0.6428	−0.3299	0.8910	0.031*
H9C	−0.2680	−0.4038	0.9101	0.031*
H1N2	−0.299 (5)	−0.109 (2)	0.8778 (14)	0.030 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0407 (6)	0.0221 (5)	0.0181 (5)	−0.0142 (4)	0.0083 (4)	−0.0012 (4)
O2	0.0395 (6)	0.0233 (5)	0.0178 (5)	−0.0145 (4)	−0.0011 (4)	−0.0033 (4)
O3	0.0478 (7)	0.0288 (6)	0.0155 (5)	−0.0165 (5)	0.0056 (4)	0.0006 (4)
O4	0.0415 (7)	0.0199 (5)	0.0215 (5)	−0.0142 (4)	0.0048 (4)	0.0009 (4)
N1	0.0222 (6)	0.0146 (5)	0.0155 (5)	−0.0032 (4)	−0.0002 (4)	0.0006 (4)
N2	0.0236 (6)	0.0144 (5)	0.0147 (5)	−0.0057 (4)	0.0004 (4)	0.0001 (4)
C1	0.0179 (6)	0.0142 (6)	0.0176 (6)	−0.0044 (5)	−0.0013 (5)	0.0004 (5)
C2	0.0181 (6)	0.0151 (6)	0.0133 (6)	−0.0025 (5)	−0.0007 (5)	0.0002 (4)
C3	0.0150 (6)	0.0142 (6)	0.0165 (6)	−0.0018 (5)	−0.0023 (5)	0.0011 (5)
C4	0.0215 (7)	0.0165 (6)	0.0162 (6)	−0.0047 (5)	−0.0016 (5)	−0.0022 (5)
C5	0.0215 (7)	0.0204 (6)	0.0143 (6)	−0.0056 (5)	0.0007 (5)	−0.0008 (5)
C6	0.0196 (7)	0.0166 (6)	0.0166 (6)	−0.0050 (5)	0.0002 (5)	0.0014 (5)
C7	0.0232 (7)	0.0192 (6)	0.0166 (6)	−0.0070 (5)	0.0007 (5)	0.0013 (5)
C8	0.0211 (7)	0.0147 (6)	0.0179 (6)	−0.0051 (5)	−0.0016 (5)	−0.0010 (5)
C9	0.0246 (7)	0.0164 (6)	0.0218 (7)	−0.0071 (5)	−0.0016 (5)	0.0007 (5)

Geometric parameters (Å, º)

O1—N1	1.2375 (14)	C3—C4	1.4273 (18)
O2—N1	1.2273 (14)	C4—C5	1.3700 (18)
O3—C7	1.2700 (17)	C4—H4A	0.9300
O4—C7	1.2784 (16)	C5—C6	1.4043 (18)
O4—H1O4	0.8200	C5—H5A	0.9300
N1—C2	1.4506 (16)	C6—C7	1.4711 (18)
N2—C3	1.3441 (16)	C8—C9	1.5155 (18)

N2—C8	1.4634 (16)	C8—H8A	0.9700
N2—H1N2	0.832 (19)	C8—H8B	0.9700
C1—C6	1.3818 (18)	C9—H9A	0.9600
C1—C2	1.3914 (17)	C9—H9B	0.9600
C1—H1A	0.9300	C9—H9C	0.9600
C2—C3	1.4278 (17)		

C7—O4—H1O4	109.5	C4—C5—H5A	119.2
O2—N1—O1	122.64 (11)	C6—C5—H5A	119.2
O2—N1—C2	118.90 (11)	C1—C6—C5	118.53 (12)
O1—N1—C2	118.46 (10)	C1—C6—C7	120.64 (12)
C3—N2—C8	123.74 (11)	C5—C6—C7	120.83 (12)
C3—N2—H1N2	117.9 (13)	O3—C7—O4	123.29 (12)
C8—N2—H1N2	118.3 (13)	O3—C7—C6	118.53 (12)
C6—C1—C2	120.49 (12)	O4—C7—C6	118.18 (12)
C6—C1—H1A	119.8	N2—C8—C9	109.98 (11)
C2—C1—H1A	119.8	N2—C8—H8A	109.7
C1—C2—C3	122.29 (11)	C9—C8—H8A	109.7
C1—C2—N1	115.93 (11)	N2—C8—H8B	109.7
C3—C2—N1	121.78 (11)	C9—C8—H8B	109.7
N2—C3—C4	120.00 (11)	H8A—C8—H8B	108.2
N2—C3—C2	124.66 (12)	C8—C9—H9A	109.5
C4—C3—C2	115.33 (11)	C8—C9—H9B	109.5
C5—C4—C3	121.59 (12)	H9A—C9—H9B	109.5
C5—C4—H4A	119.2	C8—C9—H9C	109.5
C3—C4—H4A	119.2	H9A—C9—H9C	109.5
C4—C5—C6	121.69 (12)	H9B—C9—H9C	109.5

C6—C1—C2—C3	−0.9 (2)	N2—C3—C4—C5	179.34 (13)
C6—C1—C2—N1	178.84 (11)	C2—C3—C4—C5	−2.10 (19)
O2—N1—C2—C1	−14.67 (18)	C3—C4—C5—C6	−0.3 (2)
O1—N1—C2—C1	165.34 (12)	C2—C1—C6—C5	−1.6 (2)
O2—N1—C2—C3	165.04 (12)	C2—C1—C6—C7	177.98 (12)
O1—N1—C2—C3	−14.95 (19)	C4—C5—C6—C1	2.2 (2)
C8—N2—C3—C4	0.74 (19)	C4—C5—C6—C7	−177.39 (13)
C8—N2—C3—C2	−177.68 (12)	C1—C6—C7—O3	−178.93 (12)
C1—C2—C3—N2	−178.83 (12)	C5—C6—C7—O3	0.7 (2)
N1—C2—C3—N2	1.5 (2)	C1—C6—C7—O4	0.9 (2)
C1—C2—C3—C4	2.69 (19)	C5—C6—C7—O4	−179.51 (13)
N1—C2—C3—C4	−177.01 (11)	C3—N2—C8—C9	177.29 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1*O*4···O3^{i}	0.82	1.80	2.6092 (15)	168
N2—H1*N*2···O1	0.831 (19)	2.052 (18)	2.6634 (15)	130.0 (16)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.