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Ethyl 4-ethylamino-3-nitrobenzoate

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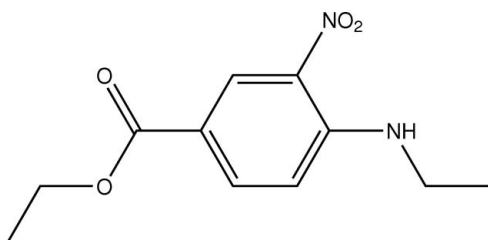
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.077; wR factor = 0.173; data-to-parameter ratio = 6.9.

In the molecule of the title compound, $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$, a bifurcated intra/intermolecular $\text{N}-\text{H}\cdots(\text{O},\text{O})$ hydrogen bond occurs. The intramolecular component results in a non-planar six-membered ring with a flattened-boat conformation. In the crystal structure, the intermolecular interaction links the molecules into chains parallel to the b axis.

Related literature

For a related structure, see: Ates-Alagoz *et al.* (2001). For bond-length data, see: Allen *et al.* (1987). For ring-puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$
 $M_r = 238.24$
 Monoclinic, $P2_1$
 $a = 4.2360$ (8) Å

$b = 16.180$ (3) Å
 $c = 8.4890$ (17) Å
 $\beta = 95.80$ (3)°
 $V = 578.8$ (2) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹

$T = 294$ (2) K
 $0.30 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\text{min}} = 0.969$, $T_{\text{max}} = 0.990$
 1213 measured reflections

1066 independent reflections
 841 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.173$
 $S = 1.01$
 1066 reflections
 154 parameters

4 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O2}$	0.86	2.00	2.645 (10)	131
$\text{N1}-\text{H1A}\cdots\text{O3}^i$	0.86	2.45	3.053 (10)	128

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2598).

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supplementary materials

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Ethyl 4-ethylamino-3-nitrobenzoate

H.-Y. Li, B.-N. Liu, S.-G. Tang and C. Guo

Comment

Some derivatives of benzoic acid are important chemical materials. We report herein the crystal structure of the title compound.

In the molecule of the title compound (Fig 1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. Ring A (C3-C8) is, of course, planar. The intramolecular N-H \cdots O hydrogen bond (Table 1) results in a nonplanar six-membered ring B (O2/N1/N2/C3/C4/H1A), having total puckering amplitude, Q_T , of 0.163 (2) Å, flattened-boat conformation [$\varphi = 52.00$ (3)° and $\theta = 19.29$ (4)°] (Cremer & Pople, 1975).

In the crystal structure, intermolecular N-H \cdots O hydrogen bonds (Table 1) link the molecules into chains parallel to the *b* axis (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, ethyl 4-chloro-3-nitrobenzoate (5.3 g, 0.023 mol) was refluxed in ethyl amine (20 ml) and tetrahydrofuran (50 ml) for 2 h. Then, solvents were evaporated and water was added to give yellow precipitate. It was collected by filtration and washed with cold ethanol (2 X 15 ml) to afford the yellow solid (yield; 4.4 g, 80%) (Ates-Alagoz *et al.*, 2001). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

Refinement

H atoms were positioned geometrically, with N-H = 0.86 Å (for NH) and C-H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C,N})$, where $x = 1.5$ for methyl H and $x = 1.2$ for all other H atoms.

Figures

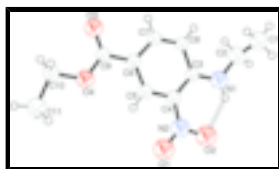


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Hydrogen bond is shown as dashed line.

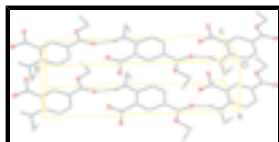


Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

Ethyl 4-ethylamino-3-nitrobenzoate

Crystal data

$C_{11}H_{14}N_2O_4$

$M_r = 238.24$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 4.2360$ (8) Å

$b = 16.180$ (3) Å

$c = 8.4890$ (17) Å

$\beta = 95.80$ (3)°

$V = 578.8$ (2) Å³

$Z = 2$

$F_{000} = 252$

$D_x = 1.367$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10$ – 12°

$\mu = 0.11$ mm⁻¹

$T = 294$ (2) K

Block, colorless

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ (2) K

$\omega/2\theta$ scans

Absorption correction: ψ scan
(North *et al.*, 1968)

$T_{\min} = 0.969$, $T_{\max} = 0.990$

1213 measured reflections

1066 independent reflections

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

$R_{\text{int}} = 0.018$

$\theta_{\max} = 25.2^\circ$

$\theta_{\min} = 2.4^\circ$

$h = -5 \rightarrow 5$

$k = 0 \rightarrow 19$

$l = 0 \rightarrow 10$

3 standard reflections

every 120 min

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.077$

$wR(F^2) = 0.173$

$S = 1.01$

1066 reflections

154 parameters

4 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

$$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.25P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.30$ e Å⁻³

Extinction correction: none

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7012 (15)	1.1050 (4)	0.7940 (7)	0.0772 (18)
O2	0.9134 (16)	1.1622 (4)	0.5988 (8)	0.083 (2)
O3	0.9764 (13)	0.7330 (4)	0.7615 (6)	0.0589 (15)
O4	0.7965 (13)	0.8254 (3)	0.9244 (6)	0.0564 (14)
N1	1.2210 (17)	1.0712 (5)	0.4054 (8)	0.065 (2)
H1A	1.1591	1.1204	0.4256	0.078*
N2	0.8667 (17)	1.0957 (5)	0.6810 (9)	0.0659 (19)
C1	1.212 (2)	1.0329 (6)	0.1174 (10)	0.071 (2)
H1B	1.3443	1.0259	0.0328	0.106*
H1C	1.0571	1.0750	0.0891	0.106*
H1D	1.1069	0.9818	0.1355	0.106*
C2	1.414 (2)	1.0581 (6)	0.2654 (10)	0.071 (3)
H2A	1.5246	1.1089	0.2453	0.085*
H2B	1.5719	1.0157	0.2925	0.085*
C3	1.1440 (15)	1.0085 (4)	0.4988 (7)	0.0383 (15)
C4	0.9754 (15)	1.0194 (5)	0.6315 (8)	0.0416 (16)
C5	0.9015 (15)	0.9543 (4)	0.7232 (8)	0.0401 (17)
H5A	0.7858	0.9646	0.8086	0.048*
C6	0.9927 (16)	0.8715 (4)	0.6946 (8)	0.0404 (16)
C7	1.1639 (14)	0.8632 (4)	0.5582 (7)	0.0393 (16)
H7A	1.2333	0.8105	0.5348	0.047*
C8	1.2314 (16)	0.9232 (4)	0.4633 (8)	0.0377 (16)
H8A	1.3342	0.9118	0.3740	0.045*
C9	0.9235 (16)	0.8047 (4)	0.7942 (8)	0.0376 (15)
C10	0.7087 (18)	0.7563 (5)	1.0314 (8)	0.0483 (19)
H10A	0.8916	0.7222	1.0650	0.058*
H10B	0.5432	0.7217	0.9787	0.058*
C11	0.590 (2)	0.8020 (6)	1.1726 (9)	0.060 (2)
H11A	0.5211	0.7625	1.2463	0.090*
H11B	0.4157	0.8372	1.1357	0.090*
H11C	0.7590	0.8348	1.2240	0.090*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.095 (4)	0.068 (4)	0.073 (4)	0.010 (4)	0.028 (4)	0.005 (4)
O2	0.094 (5)	0.079 (5)	0.078 (5)	-0.004 (4)	0.019 (4)	0.003 (4)
O3	0.068 (3)	0.052 (4)	0.059 (3)	0.004 (3)	0.015 (3)	0.002 (3)
O4	0.070 (3)	0.049 (3)	0.051 (3)	0.005 (3)	0.009 (3)	-0.002 (3)
N1	0.072 (4)	0.063 (5)	0.059 (4)	-0.011 (4)	0.005 (4)	-0.008 (4)
N2	0.068 (4)	0.068 (5)	0.061 (4)	0.001 (4)	0.002 (4)	-0.003 (4)
C1	0.083 (6)	0.070 (6)	0.061 (5)	0.008 (5)	0.012 (4)	0.004 (5)
C2	0.071 (5)	0.075 (7)	0.067 (6)	0.008 (5)	0.012 (4)	-0.005 (5)
C3	0.043 (3)	0.037 (4)	0.033 (3)	-0.006 (3)	-0.003 (3)	0.003 (3)
C4	0.040 (3)	0.045 (4)	0.039 (4)	-0.002 (3)	0.003 (3)	0.004 (3)
C5	0.039 (3)	0.043 (4)	0.038 (4)	0.001 (3)	0.002 (3)	-0.001 (3)
C6	0.044 (4)	0.034 (4)	0.043 (4)	0.002 (3)	0.006 (3)	-0.002 (3)
C7	0.044 (4)	0.037 (4)	0.037 (4)	0.004 (3)	0.005 (3)	-0.002 (3)
C8	0.050 (4)	0.029 (4)	0.035 (4)	-0.005 (3)	0.009 (3)	0.005 (3)
C9	0.047 (4)	0.029 (4)	0.037 (4)	0.002 (3)	0.004 (3)	-0.001 (3)
C10	0.055 (4)	0.052 (5)	0.038 (4)	0.002 (4)	0.005 (3)	0.006 (4)
C11	0.062 (5)	0.064 (5)	0.053 (5)	0.003 (4)	0.007 (4)	-0.002 (4)

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

O1—N2	1.253 (9)	C3—C8	1.467 (9)
O2—N2	1.308 (10)	C4—C5	1.365 (10)
O3—C9	1.219 (9)	C5—C6	1.422 (9)
O4—C9	1.320 (8)	C5—H5A	0.9300
O4—C10	1.510 (8)	C6—C9	1.420 (9)
N1—C2	1.523 (11)	C6—C7	1.434 (9)
N1—C3	1.349 (10)	C7—C8	1.311 (9)
N1—H1A	0.8600	C7—H7A	0.9300
N2—C4	1.397 (10)	C8—H8A	0.9300
C1—C2	1.502 (12)	C10—C11	1.535 (10)
C1—H1B	0.9600	C10—H10A	0.9700
C1—H1C	0.9600	C10—H10B	0.9700
C1—H1D	0.9600	C11—H11A	0.9600
C2—H2A	0.9700	C11—H11B	0.9600
C2—H2B	0.9700	C11—H11C	0.9600
C3—C4	1.405 (9)		
C2—N1—H1A	118.9	C4—C5—H5A	118.4
C3—N1—C2	122.3 (8)	C6—C5—H5A	118.4
C3—N1—H1A	118.9	C9—C6—C5	122.6 (6)
O1—N2—O2	115.9 (8)	C9—C6—C7	124.2 (6)
O1—N2—C4	124.3 (8)	C5—C6—C7	113.2 (6)
O2—N2—C4	119.6 (7)	C8—C7—C6	126.0 (7)
C9—O4—C10	117.5 (6)	C8—C7—H7A	117.0
C2—C1—H1B	109.5	C6—C7—H7A	117.0

C2—C1—H1C	109.5	C7—C8—C3	119.6 (6)
H1B—C1—H1C	109.5	C7—C8—H8A	120.2
C2—C1—H1D	109.5	C3—C8—H8A	120.2
H1B—C1—H1D	109.5	O3—C9—O4	122.1 (7)
H1C—C1—H1D	109.5	O3—C9—C6	122.3 (6)
C1—C2—N1	112.7 (7)	O4—C9—C6	115.6 (6)
C1—C2—H2A	109.0	O4—C10—C11	103.4 (6)
N1—C2—H2A	109.0	O4—C10—H10A	111.1
C1—C2—H2B	109.0	C11—C10—H10A	111.1
N1—C2—H2B	109.0	O4—C10—H10B	111.1
H2A—C2—H2B	107.8	C11—C10—H10B	111.1
N1—C3—C4	123.3 (7)	H10A—C10—H10B	109.0
N1—C3—C8	120.4 (6)	C10—C11—H11A	109.5
C4—C3—C8	116.3 (6)	C10—C11—H11B	109.5
C5—C4—N2	114.2 (6)	H11A—C11—H11B	109.5
C5—C4—C3	121.6 (7)	C10—C11—H11C	109.5
N2—C4—C3	124.2 (7)	H11A—C11—H11C	109.5
C4—C5—C6	123.2 (6)	H11B—C11—H11C	109.5
C3—N1—C2—C1	84.9 (10)	C4—C5—C6—C7	-1.2 (9)
C2—N1—C3—C4	177.9 (6)	C9—C6—C7—C8	179.8 (7)
C2—N1—C3—C8	-3.1 (11)	C5—C6—C7—C8	-1.2 (9)
O1—N2—C4—C5	-3.6 (10)	C6—C7—C8—C3	3.4 (10)
O2—N2—C4—C5	-177.5 (7)	N1—C3—C8—C7	177.8 (7)
O1—N2—C4—C3	175.8 (7)	C4—C3—C8—C7	-3.1 (9)
O2—N2—C4—C3	1.9 (10)	C10—O4—C9—O3	-1.7 (10)
N1—C3—C4—C5	179.9 (7)	C10—O4—C9—C6	178.0 (6)
C8—C3—C4—C5	0.9 (8)	C5—C6—C9—O3	173.2 (7)
N1—C3—C4—N2	0.6 (10)	C7—C6—C9—O3	-7.9 (11)
C8—C3—C4—N2	-178.5 (6)	C5—C6—C9—O4	-6.5 (10)
N2—C4—C5—C6	-179.3 (6)	C7—C6—C9—O4	172.4 (6)
C3—C4—C5—C6	1.3 (9)	C9—O4—C10—C11	176.7 (6)
C4—C5—C6—C9	177.8 (6)		

Hydrogen-bond geometry (Å, °)

<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—H1A \cdots O2	0.86	2.00	2.645 (10)	131
N1—H1A \cdots O3 ⁱ	0.86	2.45	3.053 (10)	128

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

Fig. 1

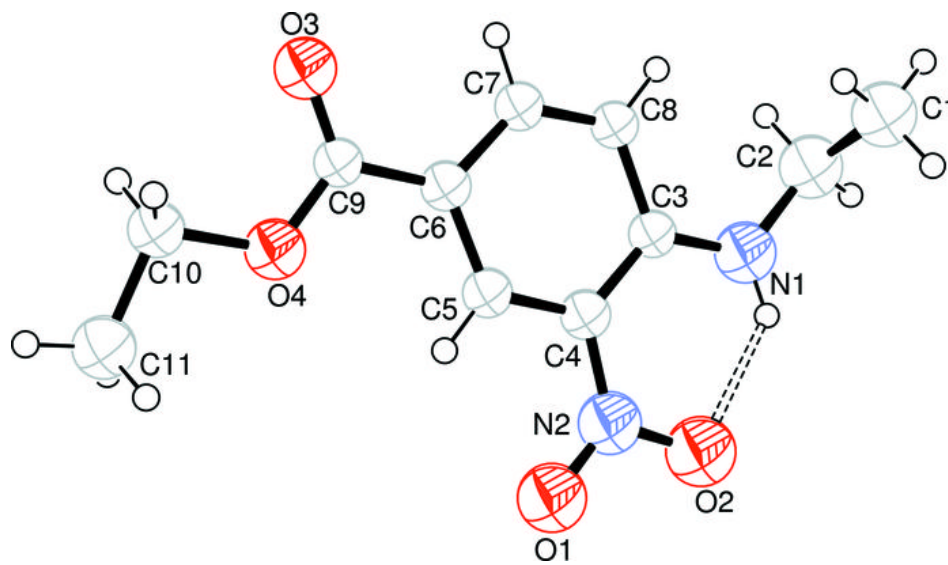


Fig. 2

