Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Ethyl 3-nitro-4-(*n*-propylamino)benzoate

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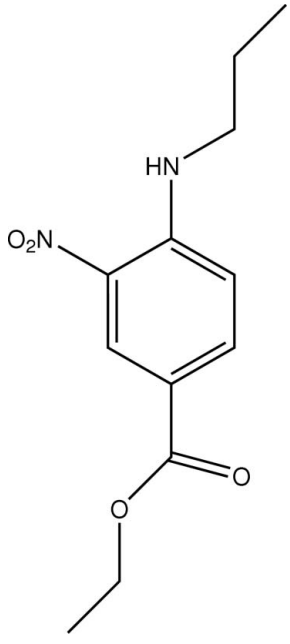
Received 14 May 2009; accepted 18 May 2009

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.006 Å; R factor = 0.067; wR factor = 0.165; data-to-parameter ratio = 14.5.

In the molecule of the title compound, $C_{12}H_{16}N_2O_4$, an intramolecular N—H···O hydrogen bond results in the formation of a six-membered ring having an envelope conformation. In the crystal structure, a bifurcated intra/intermolecular N—H···(O,O) hydrogen bond generates inversion dimers.

Related literature

For bond-length data, see: Allen *et al.* (1987). For the synthesis, see: Ates-Alagoz & Buyukbingol (2001); Oezden *et al.* (2005).



Experimental

Crystal data

$C_{12}H_{16}N_2O_4$
M_r = 252.27
Triclinic, $P\overline{1}$
a = 4.4400 (9) Å
b = 12.606 (3) Å
c = 13.209 (3) Å
α = 61.710 (19)°
β = 83.02 (3)°
γ = 81.75 (3)°
V = 643.1 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 294 K
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.981, T_{max} = 0.990
2593 measured reflections
2281 independent reflections
924 reflections with $I > 2\sigma(I)$
R_{int} = 0.083
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.165
S = 1.00
2281 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O4	0.86	2.02	2.635 (5)	128
N2—H2A···O4^{i}	0.86	2.55	3.324 (6)	150

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

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) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The authors thank the Center of Testing and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2690).

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supporting information

Acta Cryst. (2009). E**65**, o1380 [doi:10.1107/S160053680901873X]

Ethyl 3-nitro-4-(*n*-propylamino)benzoate

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S1. 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 (C4-C9) is, of course, planar. Intramolecular N-H···O hydrogen bond (Table 1) results in the formation of a six-membered ring B (O4/N1/N2/C6/C7/H2A) having envelope conformation with atom O4 displaced by -0.116 (3) Å from the plane of the other ring atoms.

In the crystal structure, intra- and intermolecular N-H···O interactions (Table 1) link the molecules into centrosymmetric dimers (Fig. 2), in which they may be effective in the stabilization of the structure.

S2. Experimental

For the preparation of the title compound, ethyl 4-chloro-3-nitrobenzoate (5.3 g, 23 mmol) was refluxed in n-propyl amine (25 ml) and tetrahydrofuran (50 ml) for 2 h. Then, solvents were evaporated and water was added to give yellow precipate, which was collected by filtration and washed with cold ethanol (2 × 15 ml) to afford the yellow solid (yield; 4.8 g). Crystals suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution.

S3. 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 $U_{iso}(H) = xU_{eq}(C,N)$, where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

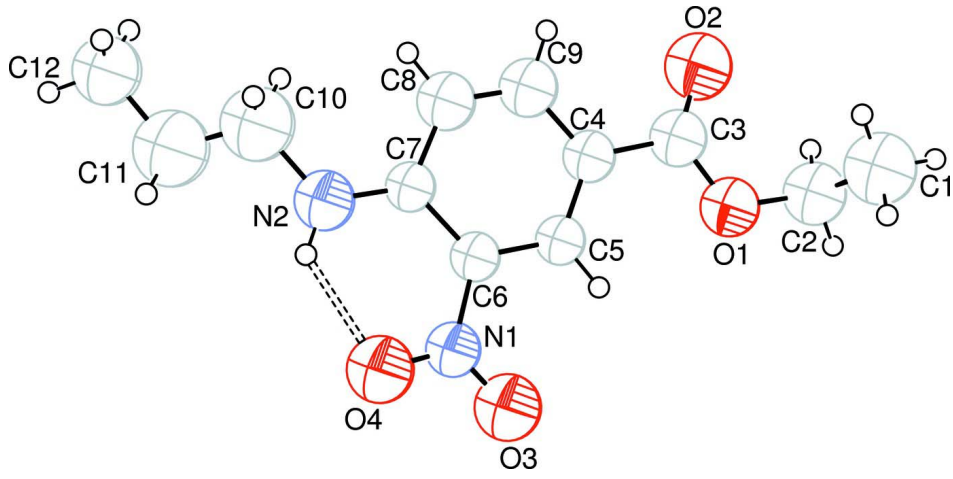

Figure 1

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

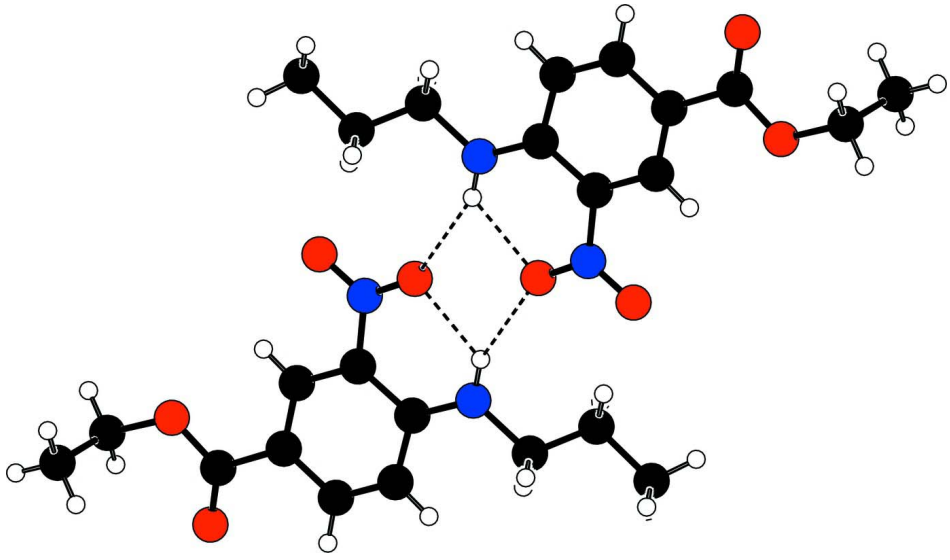

Figure 2

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

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Crystal data

$C_{12}H_{16}N_2O_4$
$M_r = 252.27$
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$\gamma = 81.75\ (3)°$
$V = 643.1\ (3)$ Å^3
$Z = 2$
$F(000) = 268$
$D_x = 1.303$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9–11°$
$\mu = 0.10$ mm^{-1}
$T = 294$ K
Block, colorless
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.981, T_{max} = 0.990
2593 measured reflections
2281 independent reflections
924 reflections with $I > 2\sigma(I)$
R_{int} = 0.083
θ_{max} = 25.2°, θ_{min} = 1.8°
h = 0→5
k = −14→15
l = −15→15
3 standard reflections every 120 min
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.165
S = 1.00
2281 reflections
157 parameters
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
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	−0.3870 (7)	−0.0274 (2)	0.8647 (2)	0.0865 (10)
O2	−0.2837 (8)	−0.1310 (3)	0.7632 (3)	0.1130 (12)
O3	−0.0492 (8)	0.3592 (2)	0.7202 (2)	0.1056 (12)
O4	0.2630 (7)	0.4310 (3)	0.5801 (2)	0.104
N1	0.1072 (8)	0.3526 (3)	0.6413 (3)	0.0706 (10)
N2	0.4396 (8)	0.3293 (3)	0.4457 (3)	0.0842 (11)
H2A	0.4491	0.3936	0.4521	0.101*
C1	−0.3968 (13)	−0.2145 (4)	1.0388 (4)	0.127 (2)
H1A	−0.5267	−0.2746	1.0918	0.190*
H1B	−0.3079	−0.1811	1.0788	0.190*
H1C	−0.2379	−0.2511	1.0058	0.190*
C2	−0.5738 (10)	−0.1193 (4)	0.9484 (4)	0.1006 (16)
H2B	−0.7339	−0.0825	0.9819	0.121*
H2C	−0.6696	−0.1538	0.9100	0.121*
C3	−0.2502 (11)	−0.0448 (4)	0.7781 (4)	0.0809 (13)
C4	−0.0655 (9)	0.0540 (3)	0.6944 (3)	0.0664 (11)

C5	−0.0537 (8)	0.1582 (3)	0.7019 (3)	0.0592 (10)
H5A	−0.1638	0.1678	0.7620	0.071*
C6	0.1163 (8)	0.2486 (3)	0.6230 (3)	0.0584 (10)
C7	0.2859 (8)	0.2413 (3)	0.5268 (3)	0.0588 (10)
C8	0.2554 (10)	0.1315 (4)	0.5233 (3)	0.0820 (13)
H8A	0.3503	0.1217	0.4612	0.098*
C9	0.1030 (11)	0.0445 (4)	0.6018 (4)	0.0834 (14)
H9A	0.1064	−0.0264	0.5961	0.100*
C10	0.5976 (13)	0.3193 (4)	0.3427 (4)	0.129 (2)
H10A	0.8040	0.2821	0.3610	0.155*
H10B	0.4927	0.2659	0.3281	0.155*
C11	0.6104 (14)	0.4292 (5)	0.2425 (4)	0.138 (2)
H11A	0.7199	0.4821	0.2561	0.165*
H11B	0.4046	0.4674	0.2246	0.165*
C12	0.7633 (11)	0.4158 (4)	0.1409 (3)	0.1116 (17)
H12A	0.7768	0.4944	0.0758	0.167*
H12B	0.6465	0.3692	0.1229	0.167*
H12C	0.9645	0.3752	0.1591	0.167*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.082 (2)	0.0819 (19)	0.0924 (19)	−0.0227 (18)	−0.0007 (18)	−0.0351 (17)
O2	0.149 (3)	0.0806 (19)	0.122 (2)	−0.028 (2)	−0.029 (2)	−0.0475 (19)
O3	0.128 (3)	0.103 (2)	0.104 (2)	−0.035 (2)	0.038 (2)	−0.0672 (19)
O4	0.123	0.115	0.097	−0.056	0.021	−0.063
N1	0.068 (2)	0.076 (2)	0.0711 (19)	−0.031 (2)	0.0100 (19)	−0.0344 (17)
N2	0.073 (3)	0.088 (2)	0.074 (2)	0.010 (2)	0.006 (2)	−0.0304 (18)
C1	0.133 (5)	0.088 (3)	0.104 (3)	0.007 (4)	0.004 (4)	−0.007 (3)
C2	0.070 (4)	0.089 (3)	0.126 (4)	−0.012 (3)	−0.017 (3)	−0.033 (3)
C3	0.079 (4)	0.063 (3)	0.094 (3)	0.001 (3)	−0.041 (3)	−0.025 (3)
C4	0.058 (3)	0.066 (2)	0.084 (3)	0.016 (2)	−0.030 (2)	−0.041 (2)
C5	0.050 (3)	0.065 (2)	0.067 (2)	0.002 (2)	−0.010 (2)	−0.034 (2)
C6	0.053 (3)	0.071 (2)	0.059 (2)	0.005 (2)	−0.013 (2)	−0.037 (2)
C7	0.043 (2)	0.064 (2)	0.054 (2)	0.021 (2)	−0.0114 (19)	−0.0212 (19)
C8	0.092 (4)	0.090 (3)	0.068 (3)	0.036 (3)	−0.019 (3)	−0.049 (2)
C9	0.104 (4)	0.069 (3)	0.089 (3)	0.014 (3)	−0.023 (3)	−0.048 (2)
C10	0.132 (4)	0.115 (4)	0.088 (3)	0.026 (3)	0.038 (3)	−0.026 (3)
C11	0.155 (5)	0.133 (4)	0.091 (3)	0.031 (4)	0.014 (4)	−0.041 (3)
C12	0.106 (4)	0.132 (4)	0.066 (2)	0.012 (3)	0.005 (3)	−0.030 (3)

Geometric parameters (Å, º)

O1—C3	1.326 (5)	C4—C9	1.400 (5)
O1—C2	1.446 (4)	C5—C6	1.373 (4)
O2—C3	1.223 (4)	C5—H5A	0.9300
O3—N1	1.211 (3)	C6—C7	1.432 (4)
O4—N1	1.188 (3)	C7—C8	1.432 (5)

N1—C6	1.436 (4)	C8—C9	1.304 (5)
N2—C7	1.326 (4)	C8—H8A	0.9300
N2—C10	1.505 (5)	C9—H9A	0.9300
N2—H2A	0.8600	C10—C11	1.393 (5)
C1—C2	1.443 (5)	C10—H10A	0.9700
C1—H1A	0.9600	C10—H10B	0.9700
C1—H1B	0.9600	C11—C12	1.500 (5)
C1—H1C	0.9600	C11—H11A	0.9700
C2—H2B	0.9700	C11—H11B	0.9700
C2—H2C	0.9700	C12—H12A	0.9600
C3—C4	1.488 (5)	C12—H12B	0.9600
C4—C5	1.372 (4)	C12—H12C	0.9600

C3—O1—C2	117.2 (3)	C5—C6—N1	115.8 (3)
O4—N1—O3	120.0 (3)	C7—C6—N1	121.9 (3)
O4—N1—C6	119.2 (3)	N2—C7—C6	123.9 (4)
O3—N1—C6	120.8 (3)	N2—C7—C8	123.4 (3)
C7—N2—C10	121.4 (4)	C6—C7—C8	112.6 (3)
C7—N2—H2A	119.3	C9—C8—C7	124.2 (4)
C10—N2—H2A	119.3	C9—C8—H8A	117.9
C2—C1—H1A	109.5	C7—C8—H8A	117.9
C2—C1—H1B	109.5	C8—C9—C4	122.3 (4)
H1A—C1—H1B	109.5	C8—C9—H9A	118.8
C2—C1—H1C	109.5	C4—C9—H9A	118.8
H1A—C1—H1C	109.5	C11—C10—N2	114.4 (4)
H1B—C1—H1C	109.5	C11—C10—H10A	108.7
C1—C2—O1	111.7 (4)	N2—C10—H10A	108.7
C1—C2—H2B	109.3	C11—C10—H10B	108.7
O1—C2—H2B	109.3	N2—C10—H10B	108.7
C1—C2—H2C	109.3	H10A—C10—H10B	107.6
O1—C2—H2C	109.3	C10—C11—C12	113.1 (4)
H2B—C2—H2C	107.9	C10—C11—H11A	109.0
O2—C3—O1	123.7 (4)	C12—C11—H11A	109.0
O2—C3—C4	121.8 (5)	C10—C11—H11B	109.0
O1—C3—C4	114.4 (4)	C12—C11—H11B	109.0
C5—C4—C9	116.8 (4)	H11A—C11—H11B	107.8
C5—C4—C3	122.8 (4)	C11—C12—H12A	109.5
C9—C4—C3	120.4 (4)	C11—C12—H12B	109.5
C4—C5—C6	121.8 (3)	H12A—C12—H12B	109.5
C4—C5—H5A	119.1	C11—C12—H12C	109.5
C6—C5—H5A	119.1	H12A—C12—H12C	109.5
C5—C6—C7	122.2 (3)	H12B—C12—H12C	109.5

C3—O1—C2—C1	87.3 (5)	C5—C6—C7—N2	176.3 (4)
C2—O1—C3—O2	3.0 (6)	N1—C6—C7—N2	−2.0 (6)
C2—O1—C3—C4	179.2 (3)	C5—C6—C7—C8	0.2 (5)
O2—C3—C4—C5	172.1 (4)	N1—C6—C7—C8	−178.1 (3)
O1—C3—C4—C5	−4.1 (6)	N2—C7—C8—C9	−179.4 (4)

O2—C3—C4—C9	−6.9 (7)	C6—C7—C8—C9	−3.2 (6)
O1—C3—C4—C9	176.9 (4)	C7—C8—C9—C4	4.6 (7)
C9—C4—C5—C6	−0.4 (6)	C5—C4—C9—C8	−2.6 (6)
C3—C4—C5—C6	−179.4 (4)	C3—C4—C9—C8	176.5 (4)
C4—C5—C6—C7	1.5 (6)	C7—N2—C10—C11	148.5 (5)
C4—C5—C6—N1	179.9 (3)	N2—C10—C11—C12	−178.8 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O4	0.86	2.02	2.635 (5)	128
N2—H2*A*···O4^{i}	0.86	2.55	3.324 (6)	150

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