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Methyl 2-amino-5-chlorobenzoate

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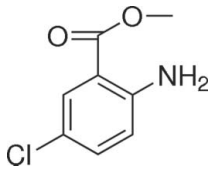
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.051; wR factor = 0.160; data-to-parameter ratio = 15.1.

The title compound, $C_8H_8ClNO_2$, is almost planar, with an r.m.s. deviation of 0.0410 Å from the plane through the non-hydrogen atoms. In the crystal structure, intermolecular N—H···O hydrogen bonds link the molecules into chains along the b axis. An intramolecular N—H···O hydrogen bond results in the formation of a six-membered ring.

Related literature

The title compound is a useful pharmaceutical intermediate, see: Dong & Xu (2009). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_8H_8ClNO_2$
M_r = 185.60
Monoclinic, $P2_1$
a = 3.9480 (8) Å
b = 9.0230 (18) Å
c = 12.018 (2) Å
β = 94.10 (3)°
V = 427.02 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 293 K
0.30 × 0.30 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.889, T_{max} = 0.980
1911 measured reflections
1663 independent reflections
1437 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.160
S = 1.01
1663 reflections
110 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Absolute structure: Flack (1983), 777 Friedel pairs
Flack parameter: 0.30 (14)

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H0A···O2^{i}	0.86	2.31	3.066 (5)	147
N—H0B···O2	0.86	2.08	2.713 (5)	129

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; 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: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2241).

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supporting information

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Methyl 2-amino-5-chlorobenzoate

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S1. Comment

Quinazolinones play an important role in the fields of natural products and medicinal chemistry. The title compound, methyl 2-amino-5-chlorobenzoate, (I), is a useful pharmaceutical intermediate (Dong *et al.* 2009). The molecule of (I) (Figure 1.) is almost planar (except the methyl hydrogens) with r. m. s. deviation of 0.0410 Å and the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The intramolecular N-H···O hydrogen bond (Table 1) results in the formation of a six-membered ring (C1/C6/C7/O2/H0B/N). In the crystal structure, intermolecular N-H0A···O2 hydrogen bonds link the molecules to form a stable structure (Table 1. and Figure 2.).

S2. Experimental

The title compound, methyl 2-amino-5-chlorobenzoate was prepared by the literature method (Dong *et al.*, 2009). To a solution of 2-aminobenzoic acid (10 g, 66 mmol) in DMF (40 mL) was added N-halosuccinimide (66 mmol) and the reaction mixture was heated at 100 °C for 40 min, cooled to room temperature, left stand overnight, and then slowly poured into ice-water (150 mL) to precipitate a white solid. The solid was filtered, washed with water (50 mL * 3), then taken up in ethyl acetate (600 mL). The ethyl acetate solution was dried over magnesium sulfate, evaporated under reduced pressure and the residual solid was washed with ether (30 mL * 3) to afford intermediate 2-amino-5-chloro-benzoic acid. To an alcohol solution (60 mL) containing 2-amino-5-chlorobenzoic acid (20 mmol) was added thionyl chloride (60 mmol), and the resulting suspension was refluxed overnight. The solvent was evaporated followed by addition of EtOAc, washed with 10% NaOH solution, dried, filtered, and evaporated to afford the desired anthranilic acid esters methyl 2-amino-5-chlorobenzoate. Crystals suitable for X-ray analysis were obtained by slow evaporation of an methanol solution.

S3. Refinement

H atoms were positioned geometrically, with N-H = 0.86 Å (for NH_2) and C-H = 0.93, 0.98 and 0.96 Å for aromatic, methine 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.

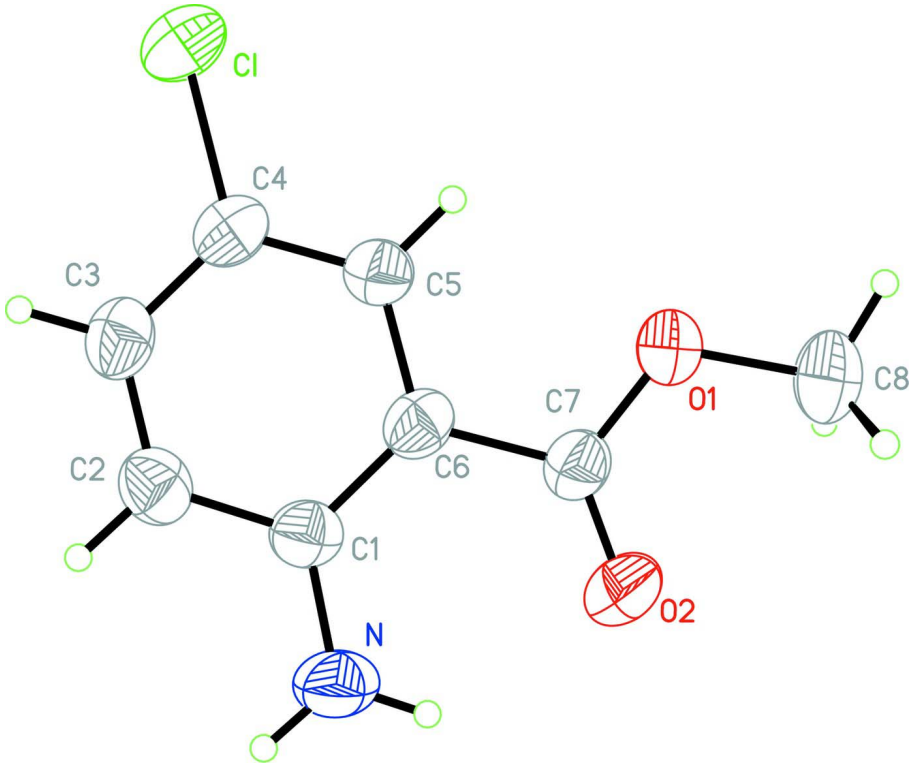

Figure 1

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

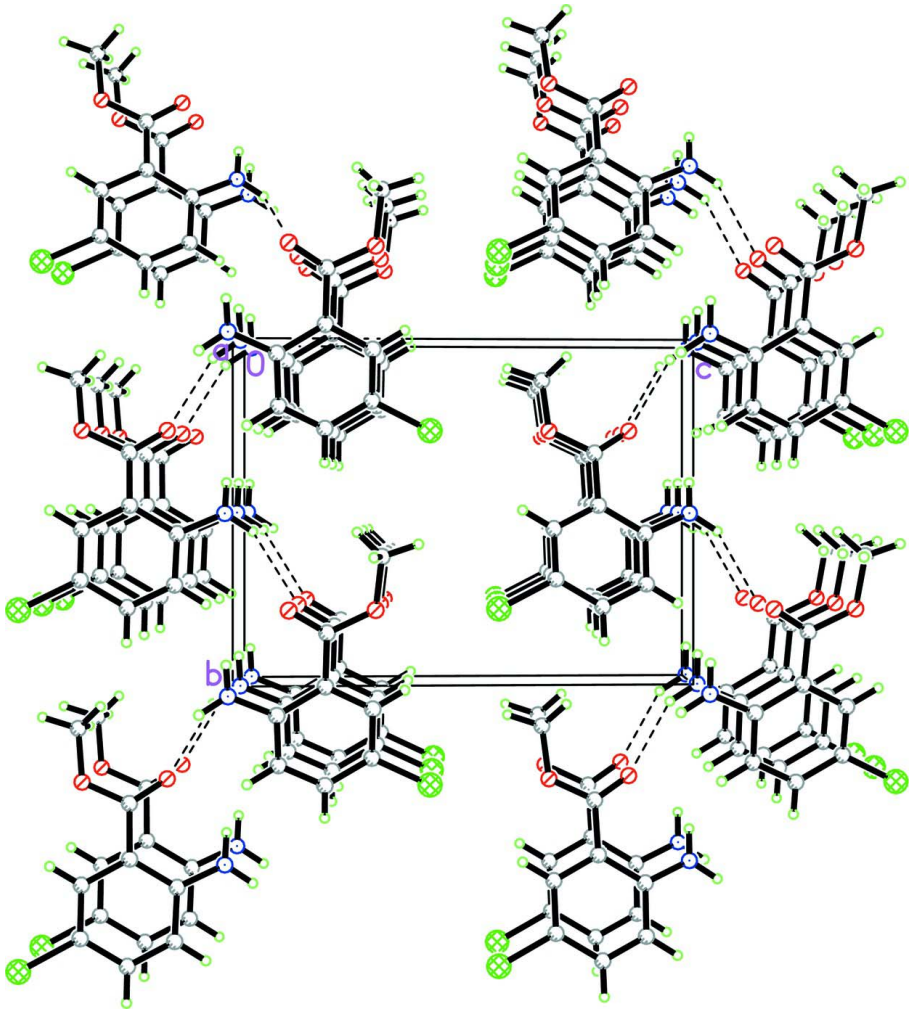

Figure 2

A packing diagram of (I). Hydrogen bond is shown as dashed line.

Methyl 2-amino-5-chlorobenzoate

Crystal data

$C_8H_8ClNO_2$
$M_r = 185.60$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 3.9480\ (8)$ Å
$b = 9.0230\ (18)$ Å
$c = 12.018\ (2)$ Å
$\beta = 94.10\ (3)°$
$V = 427.02\ (15)$ Å^3
$Z = 2$

$F(000) = 192$
$D_x = 1.444$ Mg m^{-3}
Melting point: 343 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–14°$
$\mu = 0.40$ mm^{-1}
$T = 293$ K
Block, colourless
0.30 × 0.30 × 0.05 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} = 0.889, T_{max} = 0.980
1911 measured reflections
1663 independent reflections
1437 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 26.0°, θ_{min} = 1.7°
h = 0→4
k = −11→11
l = −14→14
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.160
S = 1.01
1663 reflections
110 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.190P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.103 (19)
Absolute structure: Flack (1983), **777 Friedel pairs**
Absolute structure parameter: 0.30 (14)

Special details

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Cl	0.5983 (3)	0.76879 (13)	0.57288 (9)	0.0669 (4)
N	0.1559 (10)	0.5027 (4)	0.9873 (3)	0.0566 (10)
H0A	0.1791	0.5545	1.0474	0.068*
H0B	0.0700	0.4152	0.9888	0.068*
O1	0.1109 (8)	0.2663 (4)	0.6830 (2)	0.0570 (7)
C1	0.2559 (10)	0.5595 (4)	0.8894 (3)	0.0416 (8)
O2	−0.0279 (9)	0.2648 (4)	0.8588 (2)	0.0664 (8)
C2	0.3960 (10)	0.7029 (4)	0.8887 (4)	0.0471 (9)
H2A	0.4190	0.7567	0.9548	0.057*
C3	0.4982 (9)	0.7643 (5)	0.7937 (3)	0.0484 (8)
H3A	0.5884	0.8595	0.7954	0.058*
C4	0.4699 (10)	0.6870 (4)	0.6945 (3)	0.0459 (9)

C5	0.3416 (10)	0.5457 (4)	0.6914 (3)	0.0437 (9)
H5A	0.3266	0.4932	0.6246	0.052*
C6	0.2327 (9)	0.4797 (4)	0.7884 (3)	0.0410 (8)
C7	0.0929 (10)	0.3288 (4)	0.7827 (3)	0.0425 (8)
C8	−0.0251 (14)	0.1186 (5)	0.6689 (4)	0.0650 (13)
H8A	0.0020	0.0853	0.5941	0.097*
H8B	−0.2619	0.1192	0.6822	0.097*
H8C	0.0942	0.0528	0.7208	0.097*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl	0.0859 (8)	0.0590 (6)	0.0578 (6)	−0.0183 (6)	0.0195 (5)	0.0133 (5)
N	0.082 (3)	0.049 (2)	0.0405 (18)	0.0089 (18)	0.0160 (17)	0.0031 (16)
O1	0.0802 (18)	0.0415 (13)	0.0503 (14)	−0.0169 (17)	0.0130 (13)	−0.0067 (15)
C1	0.048 (2)	0.0374 (18)	0.0394 (19)	0.0079 (16)	0.0049 (16)	0.0026 (15)
O2	0.099 (2)	0.0470 (16)	0.0564 (16)	−0.009 (2)	0.0251 (15)	0.0092 (17)
C2	0.052 (2)	0.042 (2)	0.048 (2)	0.0045 (17)	0.0046 (16)	−0.0069 (17)
C3	0.050 (2)	0.0359 (17)	0.059 (2)	−0.002 (2)	0.0056 (16)	−0.002 (2)
C4	0.048 (2)	0.043 (2)	0.048 (2)	−0.0020 (18)	0.0067 (16)	0.0090 (17)
C5	0.050 (2)	0.041 (2)	0.041 (2)	−0.0016 (16)	0.0110 (16)	−0.0016 (16)
C6	0.0412 (19)	0.0360 (18)	0.046 (2)	0.0028 (15)	0.0068 (15)	0.0057 (15)
C7	0.048 (2)	0.0347 (17)	0.045 (2)	0.0013 (16)	0.0053 (16)	0.0034 (15)
C8	0.080 (3)	0.042 (2)	0.073 (3)	−0.018 (2)	0.007 (3)	−0.008 (2)

Geometric parameters (Å, º)

Cl—C4	1.744 (4)	C2—H2A	0.9300
N—C1	1.367 (5)	C3—C4	1.379 (6)
N—H0A	0.8600	C3—H3A	0.9300
N—H0B	0.8600	C4—C5	1.372 (5)
O1—C7	1.330 (5)	C5—C6	1.403 (5)
O1—C8	1.443 (5)	C5—H5A	0.9300
C1—C2	1.408 (6)	C6—C7	1.469 (5)
C1—C6	1.409 (5)	C8—H8A	0.9600
O2—C7	1.208 (5)	C8—H8B	0.9600
C2—C3	1.357 (6)	C8—H8C	0.9600
C1—N—H0A	120.0	C4—C5—C6	120.4 (4)
C1—N—H0B	120.0	C4—C5—H5A	119.8
H0A—N—H0B	120.0	C6—C5—H5A	119.8
C7—O1—C8	117.0 (3)	C5—C6—C1	119.6 (3)
N—C1—C2	119.1 (4)	C5—C6—C7	119.4 (4)
N—C1—C6	123.1 (4)	C1—C6—C7	121.0 (3)
C2—C1—C6	117.8 (3)	O2—C7—O1	121.9 (4)
C3—C2—C1	121.4 (4)	O2—C7—C6	125.1 (4)
C3—C2—H2A	119.3	O1—C7—C6	113.0 (3)
C1—C2—H2A	119.3	O1—C8—H8A	109.5

C2—C3—C4	120.7 (4)	O1—C8—H8B	109.5
C2—C3—H3A	119.6	H8A—C8—H8B	109.5
C4—C3—H3A	119.6	O1—C8—H8C	109.5
C5—C4—C3	120.0 (4)	H8A—C8—H8C	109.5
C5—C4—Cl	120.0 (3)	H8B—C8—H8C	109.5
C3—C4—Cl	120.0 (3)		
N—C1—C2—C3	−179.8 (4)	C2—C1—C6—C5	−1.3 (5)
C6—C1—C2—C3	1.6 (6)	N—C1—C6—C7	0.8 (5)
C1—C2—C3—C4	−0.5 (6)	C2—C1—C6—C7	179.3 (4)
C2—C3—C4—C5	−0.9 (6)	C8—O1—C7—O2	0.9 (6)
C2—C3—C4—Cl	179.3 (3)	C8—O1—C7—C6	−179.1 (4)
C3—C4—C5—C6	1.2 (6)	C5—C6—C7—O2	−175.1 (4)
Cl—C4—C5—C6	−179.0 (3)	C1—C6—C7—O2	4.3 (6)
C4—C5—C6—C1	0.0 (6)	C5—C6—C7—O1	4.9 (5)
C4—C5—C6—C7	179.3 (3)	C1—C6—C7—O1	−175.7 (3)
N—C1—C6—C5	−179.8 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H0*A*···O2^{i}	0.86	2.31	3.066 (5)	147
N—H0*B*···O2	0.86	2.08	2.713 (5)	129

Symmetry code: (i) −*x*, *y*+1/2, −*z*+2.