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Methyl 4-chloro-3-nitrobenzoate

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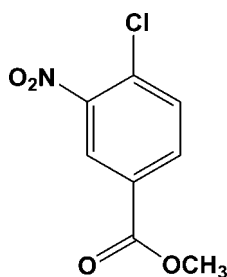
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.045; wR factor = 0.142; data-to-parameter ratio = 13.9.

In the title compound, $\text{C}_8\text{H}_6\text{ClNO}_4$, the molecules are linked by $\text{C}-\text{H}\cdots\text{O}$ interactions to form a chain parallel to the a axis. The chains are further connected by slipped $\pi-\pi$ stacking between symmetry-related benzene rings, with a centroid-to-centroid distance of 3.646 (2) Å and an interplanar distance of 3.474 Å, resulting in an offset of 1.106 Å.

Related literature

For related literature, see: de Souza *et al.* (2006); Jin & Xiao (2005); Spiniello & White (2003); Jönsson *et al.* (2004); Andrews & Ladlow (2003).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{ClNO}_4$	$\gamma = 118.95$ (3)°
$M_r = 215.59$	$V = 454.1$ (2) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.338$ (1) Å	Mo $K\alpha$ radiation
$b = 7.480$ (1) Å	$\mu = 0.41$ mm ⁻¹
$c = 9.715$ (2) Å	$T = 293$ (2) K
$\alpha = 98.39$ (3)°	0.40 × 0.10 × 0.10 mm
$\beta = 94.89$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	1773 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1389 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.854$, $T_{\max} = 0.961$	$R_{\text{int}} = 0.019$
1918 measured reflections	3 standard reflections every 200 reflections
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	128 parameters
$wR(F^2) = 0.142$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.21$ e Å ⁻³
1773 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C5}-\text{H5}\cdots\text{O2}^i$	0.93	2.47	3.272 (3)	145

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

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, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); 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: DN2295).

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supplementary materials

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Methyl 4-chloro-3-nitrobenzoate

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Comment

Some derivatives of benzoic acid are important chemical materials. We report here the crystal structure of the title compound, (I).

In compound (I) the nitro group is twisted with respect to the phenyl ring making a dihedral angle of $45.4(1)^\circ$ (Fig. 1). Similar twisted conformations are observed in related structures where the aryl ring bears nitro and halide adjacent to each other (de Souza *et al.*, 2006; Spiniello & White, 2003), whereas a planar conformation is observed in other case (Jin & Xiao, 2005).

The molecules of (I) are linked by C—H \cdots O interactions to form a chain parallel to the *a* axis (Table 1, Fig. 2). The chains are further connected by slipped π – π stacking between symmetry related phenyl rings with a centroid to centroid distance Cg1 \cdots Cg1i (Symmetry code: (i) $1 - x, 1 - y, 1 - z$) of 3.646 (2) Å and an interplanar distance of 3.474 Å resulting in an offset of 1.106 Å.

Experimental

4-Chloro-3-nitrobenzoic acid (35.0 g, 0.174 mol) was suspended in methanol (150 ml) and cooled to 0° . Concentrated sulfuric acid (15 ml) was slowly added with stirring, and then the mixture was heated at reflux for 17 h. Upon cooling to room temperature, a precipitate formed, which was collected by filtration and washed with cold methanol (2*50 ml) and hexane (2*50 ml) to afford the methyl ester as a white solid (31.8 g, 85%) (Andrews & Ladlow, 2003; Jönssen *et al.*, 2004). Pure compound (I) was obtained by crystallizing from methanol. Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution.

Refinement

All H atoms were placed geometrically and treated as riding on their parent C atoms with C—H = 0.93 Å (Caromatic) and 0.96 Å (Cmethyl) with $U_{\text{iso}}(\text{H}) = 1.2(\text{Caromatic})$ or $1.5(\text{methyl})U_{\text{eq}}(\text{C})$.

Figures

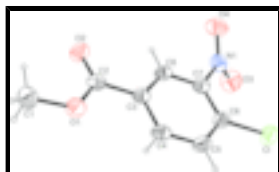


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

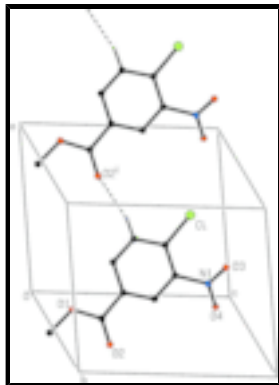


Fig. 2. Partial packing view of (I) showing the formation of the chain through C—H···O hydrogen bonds indicated as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity. [Symmetry code: (i) $1 + x, y, z$]

Methyl 4-chloro-3-nitrobenzoate

Crystal data

$C_8H_6ClNO_4$

$M_r = 215.59$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.338$ (1) Å

$b = 7.480$ (1) Å

$c = 9.715$ (2) Å

$\alpha = 98.39$ (3)°

$\beta = 94.89$ (3)°

$\gamma = 118.95$ (3)°

$V = 454.1$ (2) Å³

$Z = 2$

$F_{000} = 220$

$D_x = 1.577$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 9\text{--}13^\circ$

$\mu = 0.41$ mm⁻¹

$T = 293$ (2) K

Box, colourless

$0.40 \times 0.10 \times 0.10$ mm

Data collection

Enraf-Nonius CAD-4
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

$\omega/2\theta$ scans

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

$T_{\min} = 0.854$, $T_{\max} = 0.961$

1918 measured reflections

1773 independent reflections

1389 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 2.2^\circ$

$h = 0 \rightarrow 9$

$k = -9 \rightarrow 8$

$l = -11 \rightarrow 11$

3 standard reflections

every 200 reflections

intensity decay: none

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.046$$

$$wR(F^2) = 0.142$$

$$S = 1.12$$

1773 reflections

128 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.2181P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$$

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.2034 (5)	0.0805 (6)	0.0613 (3)	0.0722 (9)
H1A	−0.3435	−0.0080	0.0779	0.108*
H1B	−0.1832	0.0171	−0.0248	0.108*
H1C	−0.1857	0.2143	0.0536	0.108*
C2	−0.0585 (4)	0.1907 (4)	0.3056 (3)	0.0454 (6)
C3	0.1131 (4)	0.2225 (4)	0.4166 (3)	0.0417 (6)
C4	0.2701 (4)	0.1747 (4)	0.3866 (3)	0.0502 (7)
H4	0.2672	0.1180	0.2941	0.060*
C5	0.4285 (4)	0.2108 (4)	0.4925 (3)	0.0536 (7)
H5	0.5306	0.1769	0.4709	0.064*
C6	0.4376 (4)	0.2965 (4)	0.6299 (3)	0.0497 (6)
C7	0.2808 (4)	0.3452 (4)	0.6588 (3)	0.0459 (6)
C8	0.1197 (4)	0.3055 (4)	0.5547 (3)	0.0425 (6)
H8	0.0146	0.3344	0.5771	0.051*
Cl	0.63808 (12)	0.33572 (14)	0.75859 (9)	0.0731 (3)
N1	0.2849 (4)	0.4450 (4)	0.8022 (2)	0.0569 (6)
O1	−0.0490 (3)	0.1079 (3)	0.1782 (2)	0.0591 (5)
O2	−0.1910 (3)	0.2373 (3)	0.3279 (2)	0.0626 (6)
O3	0.4525 (4)	0.5930 (4)	0.8665 (2)	0.0838 (7)
O4	0.1169 (4)	0.3786 (4)	0.8445 (2)	0.0801 (7)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.075 (2)	0.089 (2)	0.0466 (17)	0.0412 (19)	0.0021 (15)	0.0024 (15)
C2	0.0449 (14)	0.0383 (13)	0.0488 (15)	0.0175 (11)	0.0148 (11)	0.0063 (11)
C3	0.0406 (13)	0.0343 (12)	0.0489 (14)	0.0170 (10)	0.0144 (11)	0.0086 (10)
C4	0.0533 (15)	0.0490 (15)	0.0560 (16)	0.0298 (13)	0.0225 (13)	0.0108 (12)
C5	0.0475 (15)	0.0572 (16)	0.0691 (18)	0.0328 (13)	0.0226 (13)	0.0198 (14)
C6	0.0412 (13)	0.0462 (14)	0.0633 (17)	0.0207 (12)	0.0122 (12)	0.0191 (12)
C7	0.0466 (14)	0.0388 (13)	0.0491 (15)	0.0187 (11)	0.0126 (11)	0.0085 (11)
C8	0.0399 (13)	0.0363 (12)	0.0532 (15)	0.0199 (10)	0.0147 (11)	0.0084 (10)
C1	0.0564 (5)	0.0836 (6)	0.0821 (6)	0.0363 (4)	0.0021 (4)	0.0278 (4)
N1	0.0682 (16)	0.0606 (15)	0.0451 (13)	0.0349 (13)	0.0112 (12)	0.0106 (11)
O1	0.0626 (12)	0.0725 (13)	0.0444 (10)	0.0400 (11)	0.0080 (9)	-0.0024 (9)
O2	0.0584 (12)	0.0832 (15)	0.0574 (12)	0.0468 (11)	0.0118 (9)	0.0049 (10)
O3	0.0794 (16)	0.0785 (16)	0.0661 (15)	0.0294 (13)	-0.0085 (12)	-0.0115 (12)
O4	0.0839 (17)	0.0938 (18)	0.0647 (14)	0.0446 (14)	0.0324 (13)	0.0128 (12)

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

C1—O1	1.450 (4)	C4—H4	0.9300
C1—H1A	0.9600	C5—C6	1.375 (4)
C1—H1B	0.9600	C5—H5	0.9300
C1—H1C	0.9600	C6—C7	1.402 (4)
C2—O2	1.207 (3)	C6—C1	1.725 (3)
C2—O1	1.324 (3)	C7—C8	1.370 (4)
C2—C3	1.486 (4)	C7—N1	1.471 (3)
C3—C8	1.380 (4)	C8—H8	0.9300
C3—C4	1.402 (3)	N1—O3	1.215 (3)
C4—C5	1.376 (4)	N1—O4	1.220 (3)
O1—C1—H1A	109.5	C6—C5—H5	119.6
O1—C1—H1B	109.5	C4—C5—H5	119.6
H1A—C1—H1B	109.5	C5—C6—C7	118.1 (3)
O1—C1—H1C	109.5	C5—C6—C1	118.7 (2)
H1A—C1—H1C	109.5	C7—C6—C1	123.1 (2)
H1B—C1—H1C	109.5	C8—C7—C6	121.6 (2)
O2—C2—O1	123.3 (3)	C8—C7—N1	117.2 (2)
O2—C2—C3	124.1 (2)	C6—C7—N1	121.2 (2)
O1—C2—C3	112.7 (2)	C7—C8—C3	120.1 (2)
C8—C3—C4	118.7 (2)	C7—C8—H8	120.0
C8—C3—C2	118.5 (2)	C3—C8—H8	120.0
C4—C3—C2	122.8 (2)	O3—N1—O4	125.0 (3)
C5—C4—C3	120.7 (2)	O3—N1—C7	117.8 (2)
C5—C4—H4	119.6	O4—N1—C7	117.1 (2)
C3—C4—H4	119.6	C2—O1—C1	116.9 (2)
C6—C5—C4	120.8 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C5—H5···O2 ⁱ	0.93	2.47	3.272 (3)	145

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

Fig. 1

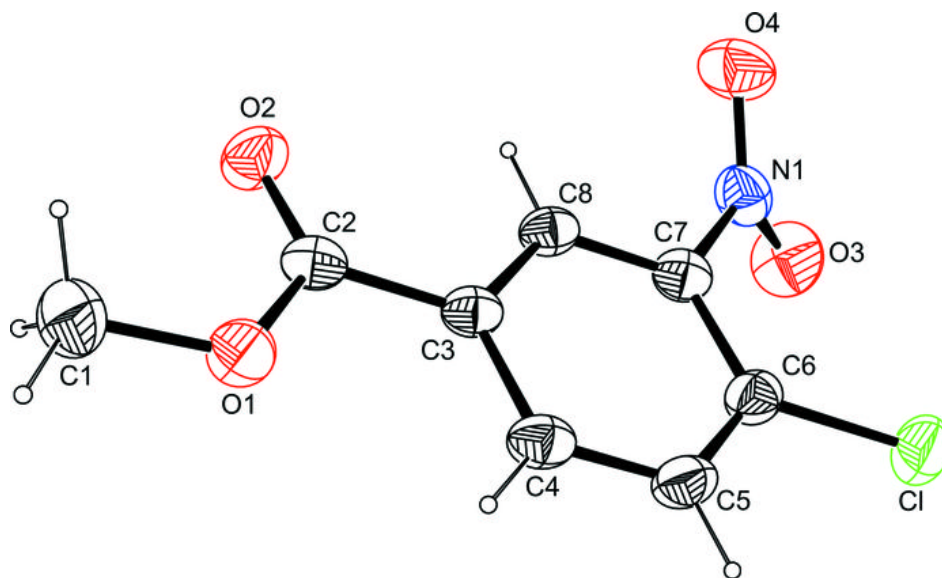


Fig. 2

