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Methyl 5-chloro-2-nitrobenzoate

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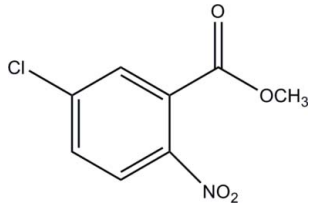
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.116; data-to-parameter ratio = 12.2.

In the title compound, $C_8H_6ClNO_4$, the nitro and acetoxy groups attached to the benzene ring at neighbouring positions are twisted from its plane by 29.4 (1) and 49.7 (1)°, respectively. In the crystal, weak C—H···O hydrogen bonds link molecules into layers parallel to (101). The crystal packing exhibits short intermolecular C···O distances of 2.925 (3) Å.

Related literature

The title compound is an intermediate of the oral vasopressin V_2-receptor antagonist tolvaptan. For applications of tolvaptan, see: Nemerovski & Hutchinson (2010). For the synthesis of the title compound, see: Kondo *et al.* (1999). For a related structure, see: Liu *et al.* (2008).



Experimental

Crystal data

$C_8H_6ClNO_4$
M_r = 215.59
Monoclinic, $P2_1/n$
a = 4.2616 (9) Å
b = 22.470 (5) Å
c = 9.3894 (19) Å
β = 90.64 (3)°
V = 899.1 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 113 K
0.16 × 0.14 × 0.12 mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.937, T_{max} = 0.952
5007 measured reflections
1564 independent reflections
1400 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
S = 1.07
1564 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1^{i}	0.93	2.53	3.206 (3)	130
C8—H8B···O3^{ii}	0.96	2.47	3.200 (3)	132

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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: *SHELXTL*.

The authors thank Mr Hai-Bin Song of Nankai University for his kind assistance with the X-ray structure determination and for helpful suggestions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5162).

References

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supporting information

Acta Cryst. (2011). E**67**, o3139 [https://doi.org/10.1107/S1600536811044072]

Methyl 5-chloro-2-nitrobenzoate

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S1. Comment

Tolvaptan is an oral nonpeptide selective vasopressin V_2-receptor antagonist indicated for the treatment of clinically relevant hypervolemic or euvolemic hyponatremia associated with heart failure, cirrhosis, or syndrome of inappropriate antidiuretic hormone (Nemerovski *et al.*, 2010). Now, we present the crystal structure of the title compound (I) (Kondo *et al.*, 1999), an intermediate of Tolvaptan.

In (I) (Fig. 1), all bond lengths and angles are normal and correspond to those observed in the analougs (Liu *et al.*, 2008). The acetoxy and nitro groups attached to the benzene ring at neighbouring positions are twisted from its plane at 49.7 (1) and 29.4 (1)°, respectively. In the crystal structure, weak C—H···O interactions (Table 1) link molecules into layers parallel to (101) plane. Short intermolecular C···O distances of 2.925 (3) Å observed in the structure.

S2. Experimental

To a stirred solution of the 5-chloro-2-nitrobenzoic acid (10 g, 50 mmol) in acetone(60 ml) was added K_2CO_3 (10.3 g, 74 mmol) and Me_2SO_4 (6.2 ml, 64.7 mmol). The mixture was heated at reflux for 30 min. The reaction mixture was then poured into an ice-water bath and extracted with ethyl acetate. The organic layer was separated and dried over $MgSO_4$. then the filtrate was concentrate under reduced pressure to afford the methyl ester as a white solid. Pure compound (I) was obstained by crystallizing from methanol. Crystals of (I) suitable for X-ray diffraction were obstained by slow evaporation of an methanol solution.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with d(C—H) = 0.95 - 0.99 Å, and U_{iso}(H) = 1.2 or 1.5 U_{eq}.

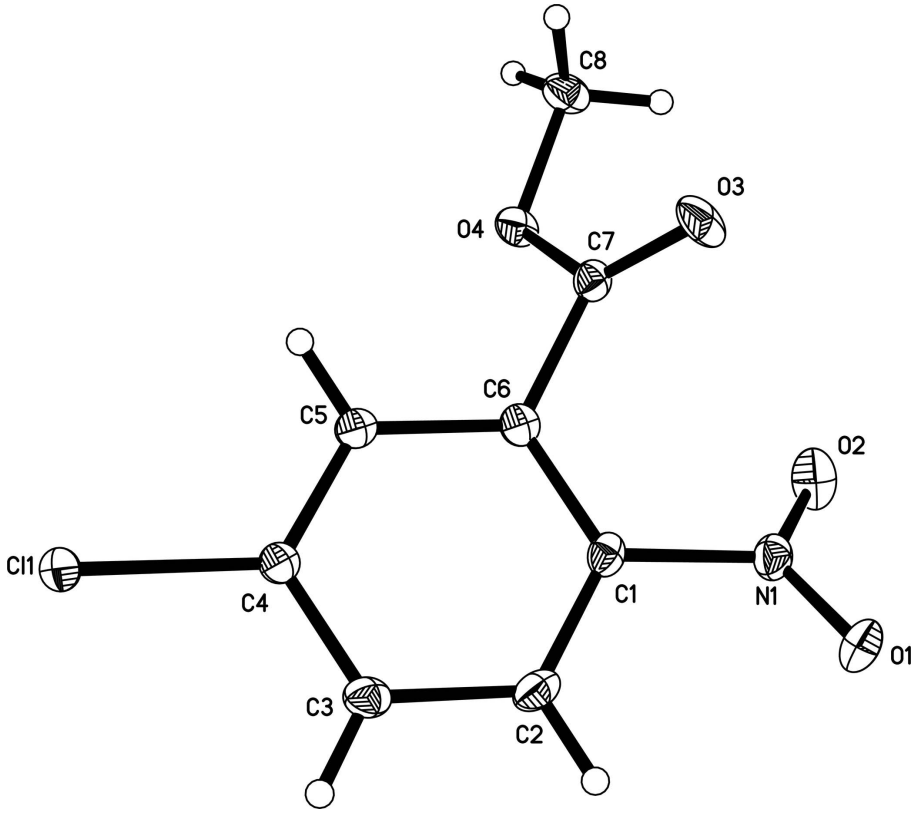

Figure 1

The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

Methyl 5-chloro-2-nitrobenzoate

Crystal data

$C_8H_6ClNO_4$
$M_r = 215.59$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 4.2616\ (9)$ Å
$b = 22.470\ (5)$ Å
$c = 9.3894\ (19)$ Å
$\beta = 90.64\ (3)°$
$V = 899.1\ (3)$ Å^3
$Z = 4$
$F(000) = 440$
$D_x = 1.593$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2662 reflections
$\theta = 1.8–27.5°$
$\mu = 0.41$ mm^{-1}
$T = 113$ K
Prism, colorless
0.16 × 0.14 × 0.12 mm

Data collection

Rigaku Saturn diffractometer
Radiation source: rotating anode
Confocal monochromator
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.937$, $T_{max} = 0.952$
5007 measured reflections
1564 independent reflections
1400 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
$h = -4\rightarrow5$
$k = -26\rightarrow20$
$l = -11\rightarrow11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.116$
$S = 1.07$
1564 reflections
128 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-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.3934P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.83432 (12)	0.09111 (2)	1.09984 (5)	0.0272 (2)
O1	0.1416 (4)	0.05968 (8)	0.42100 (17)	0.0423 (5)
O2	−0.1876 (4)	0.12282 (9)	0.48951 (17)	0.0409 (5)
O3	0.1575 (4)	0.22747 (7)	0.57507 (16)	0.0364 (4)
O4	−0.0357 (3)	0.22861 (6)	0.78230 (15)	0.0263 (4)
N1	0.0553 (5)	0.09256 (8)	0.51178 (19)	0.0282 (5)
C1	0.2555 (5)	0.09452 (9)	0.6557 (2)	0.0224 (5)
C2	0.4194 (5)	0.04329 (9)	0.7038 (2)	0.0273 (5)
H2	0.4148	0.0092	0.6478	0.033*
C3	0.6002 (5)	0.04214 (9)	0.8420 (2)	0.0263 (5)
H3	0.7041	0.0077	0.8707	0.032*
C4	0.6111 (5)	0.09270 (8)	0.9265 (2)	0.0215 (5)
C5	0.4463 (5)	0.14420 (9)	0.8781 (2)	0.0224 (5)
H5	0.4519	0.1783	0.9342	0.027*
C6	0.2642 (5)	0.14566 (9)	0.7406 (2)	0.0218 (5)
C7	0.1199 (5)	0.20438 (9)	0.6857 (2)	0.0228 (5)
C8	−0.1662 (6)	0.28749 (10)	0.7466 (2)	0.0323 (5)
H8A	0.0017	0.3157	0.7373	0.049*
H8B	−0.3039	0.3001	0.8209	0.049*
H8C	−0.2814	0.2850	0.6584	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0369 (4)	0.0243 (3)	0.0204 (3)	0.0011 (2)	−0.0024 (2)	0.00056 (18)

O1	0.0641 (13)	0.0388 (10)	0.0241 (9)	0.0017 (8)	0.0011 (8)	−0.0105 (7)
O2	0.0322 (10)	0.0596 (12)	0.0308 (9)	0.0044 (8)	0.0003 (7)	0.0013 (8)
O3	0.0481 (10)	0.0359 (9)	0.0256 (9)	0.0124 (7)	0.0201 (7)	0.0125 (7)
O4	0.0334 (9)	0.0244 (8)	0.0215 (8)	0.0032 (6)	0.0139 (6)	0.0031 (6)
N1	0.0335 (11)	0.0305 (10)	0.0206 (10)	−0.0064 (8)	0.0023 (8)	0.0002 (8)
C1	0.0231 (11)	0.0270 (11)	0.0174 (11)	−0.0047 (8)	0.0048 (8)	−0.0011 (8)
C2	0.0352 (12)	0.0223 (10)	0.0246 (11)	−0.0058 (9)	0.0087 (9)	−0.0063 (8)
C3	0.0331 (12)	0.0209 (10)	0.0252 (12)	−0.0008 (9)	0.0071 (9)	0.0024 (8)
C4	0.0255 (11)	0.0217 (10)	0.0176 (10)	−0.0033 (8)	0.0055 (8)	0.0018 (8)
C5	0.0280 (11)	0.0215 (10)	0.0178 (10)	−0.0035 (8)	0.0100 (8)	−0.0003 (8)
C6	0.0229 (11)	0.0252 (10)	0.0175 (10)	−0.0030 (8)	0.0099 (8)	0.0020 (8)
C7	0.0242 (10)	0.0258 (10)	0.0186 (11)	−0.0017 (8)	0.0049 (8)	−0.0004 (8)
C8	0.0416 (14)	0.0250 (11)	0.0307 (13)	0.0076 (10)	0.0123 (10)	0.0038 (9)

Geometric parameters (Å, º)

Cl1—C4	1.876 (2)	C2—H2	0.9300
O1—N1	1.189 (2)	C3—C4	1.386 (3)
O2—N1	1.254 (3)	C3—H3	0.9300
O3—C7	1.174 (2)	C4—C5	1.425 (3)
O4—C7	1.254 (2)	C5—C6	1.500 (3)
O4—C8	1.472 (3)	C5—H5	0.9300
N1—C1	1.590 (3)	C6—C7	1.542 (3)
C1—C6	1.399 (3)	C8—H8A	0.9600
C1—C2	1.418 (3)	C8—H8B	0.9600
C2—C3	1.502 (3)	C8—H8C	0.9600
C7—O4—C8	115.29 (16)	C4—C5—C6	122.73 (18)
O1—N1—O2	118.6 (2)	C4—C5—H5	118.6
O1—N1—C1	117.30 (18)	C6—C5—H5	118.6
O2—N1—C1	124.10 (17)	C1—C6—C5	118.89 (18)
C6—C1—C2	118.4 (2)	C1—C6—C7	120.30 (18)
C6—C1—N1	121.16 (18)	C5—C6—C7	120.47 (17)
C2—C1—N1	120.40 (17)	O3—C7—O4	121.8 (2)
C1—C2—C3	122.38 (18)	O3—C7—C6	128.04 (18)
C1—C2—H2	118.8	O4—C7—C6	110.01 (16)
C3—C2—H2	118.8	O4—C8—H8A	109.5
C4—C3—C2	119.62 (19)	O4—C8—H8B	109.5
C4—C3—H3	120.2	H8A—C8—H8B	109.5
C2—C3—H3	120.2	O4—C8—H8C	109.5
C3—C4—C5	118.0 (2)	H8A—C8—H8C	109.5
C3—C4—Cl1	119.63 (16)	H8B—C8—H8C	109.5
C5—C4—Cl1	122.36 (15)		
O1—N1—C1—C6	152.58 (19)	N1—C1—C6—C5	177.54 (15)
O2—N1—C1—C6	−28.3 (3)	C2—C1—C6—C7	173.45 (17)
O1—N1—C1—C2	−30.1 (3)	N1—C1—C6—C7	−9.2 (3)
O2—N1—C1—C2	149.0 (2)	C4—C5—C6—C1	−0.1 (3)

C6—C1—C2—C3	0.1 (3)	C4—C5—C6—C7	−173.43 (18)
N1—C1—C2—C3	−177.31 (16)	C8—O4—C7—O3	0.0 (3)
C1—C2—C3—C4	−0.4 (3)	C8—O4—C7—C6	175.57 (17)
C2—C3—C4—C5	0.4 (3)	C1—C6—C7—O3	−48.6 (3)
C2—C3—C4—Cl1	179.53 (14)	C5—C6—C7—O3	124.6 (2)
C3—C4—C5—C6	−0.1 (3)	C1—C6—C7—O4	136.20 (19)
Cl1—C4—C5—C6	−179.27 (14)	C5—C6—C7—O4	−50.6 (2)
C2—C1—C6—C5	0.2 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{i}	0.93	2.53	3.206 (3)	130
C8—H8*B*···O3^{ii}	0.96	2.47	3.200 (3)	132

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