# organic compounds

# Methyl 2-hydroxy-3-nitrobenzoate

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The title compound, $C_8H_7NO_5$, assumes an approximately planar molecular structure with an intramolecular O—H⋯O hydrogen bond between the hydroxy and carboxylate groups. Weak intermolecular C—H⋯O hydrogen bonding is present in the crystal structure.

## Related literature

For the properties of 2-hydroxybenzoyl compounds, see: Konopacka *et al.* (2005); Sonar *et al.* (2007); Willian & Layne (2001); Huang *et al.* (1996). For bond-length data, see: Allen *et al.* (1987).
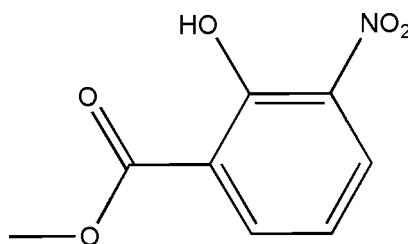


## Experimental

### Crystal data

$C_8H_7NO_5$
$M_r = 197.15$
Monoclinic, $P2_1/c$
$a = 7.6120 (10)$ Å
$b = 11.716 (2)$ Å
$c = 9.656 (2)$ Å
$\beta = 101.830 (10)°$

$V = 842.9 (3)$ Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.13$ mm$^{-1}$
$T = 291$ K
$0.30 \times 0.20 \times 0.20$ mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: none
4045 measured reflections

1473 independent reflections
965 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.110$
$S = 1.02$
1655 reflections

129 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å$^{-3}$
$\Delta\rho_{min} = -0.40$ e Å$^{-3}$

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| O1—H1$A$⋯O4 | 0.96 | 1.70 | 2.554 (2) | 146 |
| C4—H4$A$⋯O2$^i$ | 0.93 | 2.57 | 3.321 (3) | 138 |
| C6—H6$A$⋯O4$^{ii}$ | 0.93 | 2.49 | 3.336 (3) | 151 |
| C8—H8$B$⋯O1$^{ii}$ | 0.96 | 2.59 | 3.305 (3) | 131 |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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: *WinGX* (Farrugia, 1999).

## References

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# supporting information

## Methyl 2-hydroxy-3-nitrobenzoate

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### S1. Comment

Methyl salicylate and its analogues are useful intermediates in organic synthesis and show potential applications for functional materials and drugs (Konopacka *et al.*, 2005; Sonar *et al.*, 2007; Willian & Layne, 2001; Huang *et al.*, 1996). In this paper, the structure of the title compound is reported.

The molecular structure of (I) is shown in Fig. 1. The bond lengths and angles are within normal ranges (Allen *et al.*, 1987). There is an intramolecular hydrogen bond between the hydroxy group and the carboxyl group, and the whole molecule is planar except for the methyl H atoms. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonding (Table 1).

### S2. Experimental

The methyl salicylate (3 ml) and $Fe(NO_3)_3.9(H_2O)$ (3 g) were dissolved in ethyl acetate (50 ml), and the solution was refluxed for 1 h. The resulting mixture was cooled and filtered. The yellow single crystals were obtained from the filtrate by slowly evaporating ethyl acetate.

### S3. Refinement

H atoms were located geometrically and treated as riding atoms with C—H = 0.93 (aromatic), 0.96 Å (methyl) and O—H = 0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and $1.5U_{eq}(C,O)$ for the others.
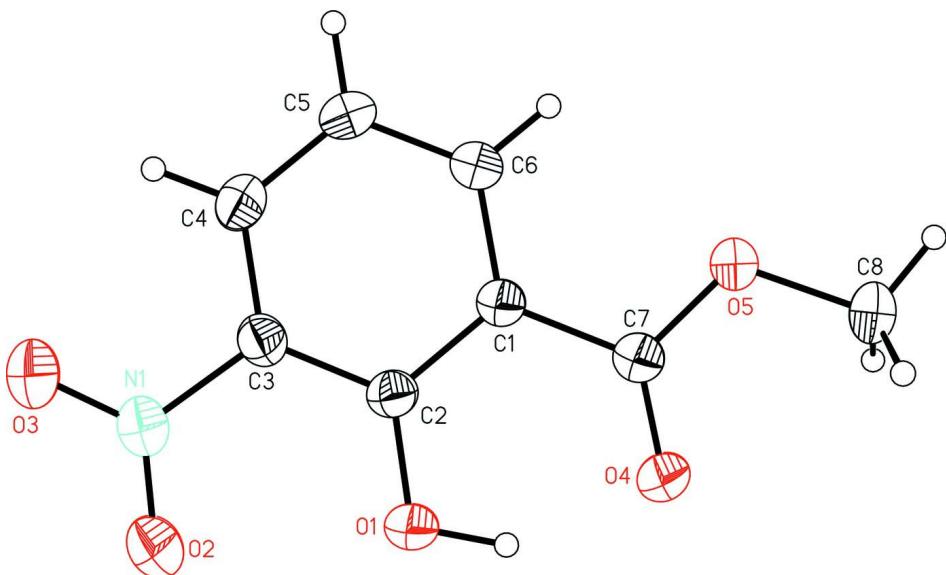
**Figure 1**

The molecular structure of the title compound with displacement ellipsoids at the 30% probability level. The dashed line indicates hydrogen bonding.

**Methyl 2-hydroxy-3-nitrobenzoate**

*Crystal data*

| | |
|---|---|
| $C_8H_7NO_5$ | $F(000) = 408$ |
| $M_r = 197.15$ | $D_x = 1.554$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2ybc | Cell parameters from 1211 reflections |
| $a = 7.612$ (1) Å | $\theta = 2.7–22.6°$ |
| $b = 11.716$ (2) Å | $\mu = 0.13$ mm$^{-1}$ |
| $c = 9.656$ (2) Å | $T = 291$ K |
| $\beta = 101.83$ (1)° | Block, yellow |
| $V = 842.9$ (3) Å$^3$ | $0.30 \times 0.20 \times 0.20$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 965 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.046$ |
| Graphite monochromator | $\theta_{max} = 26.0°$, $\theta_{min} = 2.7°$ |
| $\varphi$ and $\omega$ scans | $h = -8 \rightarrow 9$ |
| 4045 measured reflections | $k = -13 \rightarrow 13$ |
| 1473 independent reflections | $l = -11 \rightarrow 6$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | 0 restraints |
| Least-squares matrix: full | Primary atom site location: structure-invariant direct methods |
| $R[F^2 > 2\sigma(F^2)] = 0.055$ | |
| $wR(F^2) = 0.110$ | Secondary atom site location: difference Fourier map |
| $S = 1.02$ | |
| 1655 reflections | Hydrogen site location: inferred from neighbouring sites |
| 129 parameters | |

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.55P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å$^{-3}$

$\Delta\rho_{min} = -0.40$ e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$
Extinction coefficient: 0.010 (3)

*Special details*

**Experimental**. $^1$H-NMR (CDCl$_3$, 500 MHz): $\delta$4.03 (s, 3 H), 7.20(s, 1 H), 8.15-8.19 (d, 2 H), 12.02 (s, 1 H).
**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*          | $U_{iso}*/U_{eq}$ |
|------|------------|--------------|--------------|-------------------|
| C3   | 0.6545 (3) | 0.9162 (2)   | −0.0890 (2)  | 0.0465 (6)        |
| C4   | 0.6080 (3) | 0.8030 (2)   | −0.1125 (3)  | 0.0541 (7)        |
| H4A  | 0.5248     | 0.7822       | −0.1931      | 0.065*            |
| C5   | 0.6836 (4) | 0.7212 (2)   | −0.0176 (3)  | 0.0581 (8)        |
| H5A  | 0.6523     | 0.6448       | −0.0337      | 0.070*            |
| C6   | 0.8059 (3) | 0.7525 (2)   | 0.1011 (3)   | 0.0504 (7)        |
| H6A  | 0.8577     | 0.6966       | 0.1649       | 0.060*            |
| C1   | 0.8541 (3) | 0.8654 (2)   | 0.1281 (2)   | 0.0433 (6)        |
| C2   | 0.7769 (3) | 0.9507 (2)   | 0.0320 (2)   | 0.0449 (6)        |
| C7   | 0.9867 (3) | 0.8997 (2)   | 0.2543 (3)   | 0.0499 (7)        |
| C8   | 1.1859 (4) | 0.8424 (2)   | 0.4632 (3)   | 0.0654 (9)        |
| H8C  | 1.2856     | 0.8819       | 0.4384       | 0.098*            |
| H8B  | 1.2277     | 0.7740       | 0.5140       | 0.098*            |
| H8A  | 1.1297     | 0.8907       | 0.5217       | 0.098*            |
| N1   | 0.5694 (4) | 0.9981 (2)   | −0.1954 (3)  | 0.0726 (8)        |
| O2   | 0.6026 (3) | 1.09798 (19) | −0.1803 (2)  | 0.0830 (7)        |
| O3   | 0.4677 (4) | 0.96270 (19) | −0.2983 (2)  | 0.1045 (9)        |
| O1   | 0.8187 (3) | 1.06068 (13) | 0.05425 (19) | 0.0651 (6)        |
| H1A  | 0.9073     | 1.0676       | 0.1402       | 0.098*            |
| O4   | 1.0286 (3) | 0.99828 (15) | 0.2831 (2)   | 0.0692 (6)        |
| O5   | 1.0566 (2) | 0.81316 (14) | 0.33514 (18) | 0.0564 (5)        |

*Atomic displacement parameters (Å$^2$)*

|    | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$    | $U^{13}$    | $U^{23}$     |
|----|-------------|-------------|-------------|-------------|-------------|--------------|
| C3 | 0.0456 (15) | 0.0474 (15) | 0.0452 (15) | 0.0024 (12) | 0.0064 (12) | 0.0044 (12)  |
| C4 | 0.0541 (17) | 0.0566 (18) | 0.0479 (16) | −0.0064 (14)| 0.0016 (13) | −0.0055 (13) |
| C5 | 0.0686 (19) | 0.0408 (15) | 0.0602 (17) | −0.0089 (14)| 0.0021 (15) | −0.0062 (13) |
| C6 | 0.0570 (17) | 0.0389 (14) | 0.0523 (16) | 0.0003 (12) | 0.0043 (13) | 0.0024 (12)  |
| C1 | 0.0445 (14) | 0.0380 (14) | 0.0454 (14) | 0.0009 (11) | 0.0047 (11) | −0.0006 (11) |

| C2 | 0.0461 (15) | 0.0383 (14) | 0.0490 (15) | −0.0006 (12) | 0.0064 (12) | −0.0027 (12) |
| C7 | 0.0510 (16) | 0.0417 (15) | 0.0537 (16) | 0.0010 (13) | 0.0032 (12) | 0.0006 (13) |
| C8 | 0.0645 (19) | 0.0666 (18) | 0.0539 (17) | −0.0020 (15) | −0.0143 (14) | 0.0017 (14) |
| N1 | 0.088 (2) | 0.0614 (17) | 0.0573 (16) | 0.0015 (15) | −0.0116 (14) | 0.0065 (14) |
| O2 | 0.1039 (18) | 0.0617 (14) | 0.0704 (14) | 0.0079 (13) | −0.0123 (12) | 0.0118 (11) |
| O3 | 0.130 (2) | 0.0832 (17) | 0.0741 (16) | −0.0058 (15) | −0.0405 (15) | 0.0098 (13) |
| O1 | 0.0776 (14) | 0.0355 (10) | 0.0703 (13) | −0.0033 (9) | −0.0130 (10) | 0.0026 (9) |
| O4 | 0.0805 (14) | 0.0404 (11) | 0.0720 (13) | −0.0043 (10) | −0.0188 (11) | −0.0055 (9) |
| O5 | 0.0603 (12) | 0.0469 (11) | 0.0532 (11) | −0.0018 (9) | −0.0089 (9) | 0.0030 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C3—C4 | 1.380 (3) | C2—O1 | 1.334 (3) |
| C3—C2 | 1.396 (3) | C7—O4 | 1.215 (3) |
| C3—N1 | 1.457 (3) | C7—O5 | 1.323 (3) |
| C4—C5 | 1.369 (3) | C8—O5 | 1.455 (3) |
| C4—H4A | 0.9300 | C8—H8C | 0.9600 |
| C5—C6 | 1.371 (3) | C8—H8B | 0.9600 |
| C5—H5A | 0.9300 | C8—H8A | 0.9600 |
| C6—C1 | 1.383 (3) | N1—O2 | 1.200 (3) |
| C6—H6A | 0.9300 | N1—O3 | 1.201 (3) |
| C1—C2 | 1.408 (3) | O1—H1A | 0.9600 |
| C1—C7 | 1.470 (3) | | |
| | | | |
| C4—C3—C2 | 121.4 (2) | O1—C2—C1 | 121.7 (2) |
| C4—C3—N1 | 117.0 (2) | C3—C2—C1 | 117.6 (2) |
| C2—C3—N1 | 121.6 (2) | O4—C7—O5 | 122.6 (2) |
| C5—C4—C3 | 120.3 (2) | O4—C7—C1 | 123.6 (2) |
| C5—C4—H4A | 119.8 | O5—C7—C1 | 113.8 (2) |
| C3—C4—H4A | 119.8 | O5—C8—H8C | 109.5 |
| C4—C5—C6 | 119.5 (2) | O5—C8—H8B | 109.5 |
| C4—C5—H5A | 120.3 | H8C—C8—H8B | 109.5 |
| C6—C5—H5A | 120.3 | O5—C8—H8A | 109.5 |
| C5—C6—C1 | 121.5 (2) | H8C—C8—H8A | 109.5 |
| C5—C6—H6A | 119.2 | H8B—C8—H8A | 109.5 |
| C1—C6—H6A | 119.2 | O2—N1—O3 | 121.4 (2) |
| C6—C1—C2 | 119.7 (2) | O2—N1—C3 | 120.2 (2) |
| C6—C1—C7 | 121.9 (2) | O3—N1—C3 | 118.3 (3) |
| C2—C1—C7 | 118.4 (2) | C2—O1—H1A | 108.9 |
| O1—C2—C3 | 120.7 (2) | C7—O5—C8 | 116.16 (19) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···O4 | 0.96 | 1.70 | 2.554 (2) | 146 |
| C4—H4*A*···O2ⁱ | 0.93 | 2.57 | 3.321 (3) | 138 |

| C6—H6$A$···O4[ii] | 0.93 | 2.49 | 3.336 (3) | 151 |
|---|---|---|---|---|
| C8—H8$B$···O1[ii] | 0.96 | 2.59 | 3.305 (3) | 131 |

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