

Methyl 2,6-dihydroxy-3-nitrobenzoate

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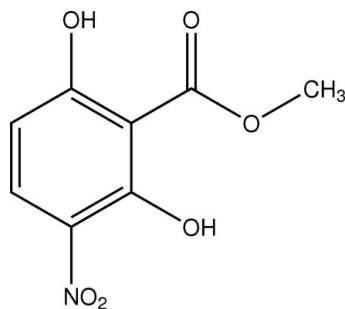
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Key indicators: single-crystal X-ray study; $T = 210$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.050; wR factor = 0.146; data-to-parameter ratio = 13.8.

Crystals of the title compound, $\text{C}_8\text{H}_7\text{NO}_6$, were obtained by the reaction of methyl 2,6-dihydroxybenzoate with nitric acid and crystallization of the product from ethyl acetate. In the molecule, the nitro group is essentially coplanar with the attached benzene ring [$\text{O}-\text{N}-\text{C}-\text{C} = 5.2(3)^\circ$] indicating conjugation with the π -electron system. The methoxy group of the ester group is *cis* with respect to the *ortho*-nitrohydroxyl group. The crystal structure is stabilized by intra- and intermolecular hydrogen bonds. The *ortho*-nitrohydroxy group forms an intramolecular hydrogen bond with the nitro group and the *para*-nitrohydroxy group forms an intramolecular hydrogen bond with the ester carbonyl function. In addition, there is intermolecular hydrogen bonding between the *ortho*-nitrohydroxyl of one molecule and the O atom of *para*-nitrohydroxyl of another molecule.

Related literature

For related literature, see: Wilson (1992).



Experimental

Crystal data

$\text{C}_8\text{H}_7\text{NO}_6$	$V = 853.15(8) \text{ \AA}^3$
$M_r = 213.15$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 3.8681(2) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$b = 18.3596(5) \text{ \AA}$	$T = 210(2) \text{ K}$
$c = 12.0186(9) \text{ \AA}$	$0.25 \times 0.22 \times 0.05 \text{ mm}$
$\beta = 91.682(2)^\circ$	

Data collection

Nonius KappaCCD diffractometer	7208 measured reflections
Absorption correction: multi-scan (<i>SCALEPACK</i> ; Otwinowski & Minor, 1997)	1922 independent reflections
$T_{\min} = 0.965$, $T_{\max} = 0.993$	1277 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	139 parameters
$wR(F^2) = 0.146$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
1922 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O3}-\text{H3} \cdots \text{O2}$	0.83	1.84	2.5636(16)	145
$\text{O3}-\text{H3} \cdots \text{O4}^i$	0.83	2.28	2.8816(15)	129
$\text{O3}-\text{H3} \cdots \text{N1}$	0.83	2.43	2.8797(19)	115
$\text{O4}-\text{H4} \cdots \text{O5}$	0.83	1.76	2.5028(16)	148

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

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and local procedures.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2413).

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supplementary materials

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Comment

X-ray crystallography confirmed the molecular structure and atom connectivity as illustrated in Fig. 1. In the title molecule the nitro group shows normal geometrical parameters. The torsion angles [O1—N1—C1—C6 = 5.2 (3)° and O2—N1—C1—C2 = 4.5 (3)°] indicate that there is not much deviation of the plane of the nitro group from the plane of phenyl ring, facilitating conjugation with the π electrons of the phenyl ring. Furthermore, the observed length of the N1—C1 bond [1.435 (2) Å] is shorter than the theoretical length for a C_{ar}—NO₂ bond of [1.468 (14) Å; Wilson, 1992], which indicates the formation of a conjugated π -electron system along this bond. There is an asymmetry of the exocyclic angles at the C1, C2, C3, and C4 atoms.

The mode of packing of along the b direction is illustrated in Fig.2. In addition to O—H \cdots O intra- and intermolecular hydrogen bonding, C—H \cdots O interactions contribute to the stabilization of the crystal structure.

Experimental

The title compound, methyl 2,6-dihydroxy-3-nitrobenzoate was prepared by nitration of methyl 2,6-dihydroxybenzoate and recrystallization of the resultant product from ethyl acetate to afford yellow colored crystals. ¹H NMR (DMSO-d₆, p.p.m.): δ 3.80 (s, 3H), 6.59 (d, 1H), 8.04 (d, 1H), 10.91 (s, 1H), 11.73 (s, 1H).

Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 0.94 Å (C_{ar}—H), 0.97 Å (CH₃) and 0.83 Å (O—H). $U_{\text{iso}}(\text{H})$ values were set to 1.2 $U_{\text{eq}}(\text{C}_{\text{ar}}\text{H}$ only) or 1.5 U_{eq} of the attached atom.

Figures

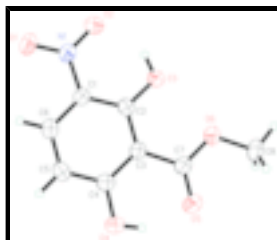


Fig. 1. A view of the molecular structure of the title compound, with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

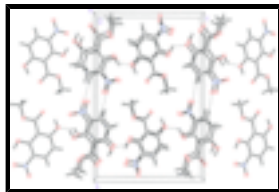


Fig. 2. The packing of the title compound, viewed along the *a* axis; showing hydrogen-bonding interactions (dashed lines).

Methyl 2,6-dihydroxy-3-nitrobenzoate

Crystal data

$C_8H_7NO_6$

$M_r = 213.15$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 3.8681$ (2) Å

$b = 18.3596$ (5) Å

$c = 12.0186$ (9) Å

$\beta = 91.682$ (2)°

$V = 853.15$ (8) Å³

$Z = 4$

$F_{000} = 440$

$D_x = 1.659$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3726 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 0.15$ mm⁻¹

$T = 210$ (2) K

Cut wedge, yellow

$0.25 \times 0.22 \times 0.05$ mm

Data collection

Nonius KappaCCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 18 pixels mm⁻¹

$T = 210$ (2) K

ω scans at fixed $\chi = 55$ °

Absorption correction: multi-scan
(SCALEPACK; Otwinowski & Minor, 1997)

$T_{\min} = 0.965$, $T_{\max} = 0.993$

7208 measured reflections

1922 independent reflections

1277 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 27.4$ °

$\theta_{\min} = 2.0$ °

$h = -5 \rightarrow 5$

$k = -23 \rightarrow 23$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.146$

$S = 1.03$

1922 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.37$ e Å⁻³

139 parameters

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Experimental. The crystals shattered on cooling to 90 K, 150 K 180 K but were stable at 210 K.

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.1783 (4)	0.09134 (8)	0.62514 (12)	0.0410 (4)
O1	0.2648 (4)	0.02998 (7)	0.59892 (13)	0.0726 (6)
O2	0.0072 (4)	0.10261 (7)	0.70927 (11)	0.0494 (4)
O3	0.0305 (3)	0.24073 (6)	0.67916 (9)	0.0384 (4)
H3	-0.0207	0.2028	0.7123	0.058*
O4	0.5981 (3)	0.31416 (7)	0.35145 (9)	0.0424 (4)
H4	0.5587	0.3551	0.3776	0.064*
O5	0.3713 (3)	0.40744 (7)	0.48250 (11)	0.0480 (4)
O6	0.1204 (3)	0.37470 (6)	0.63917 (10)	0.0431 (4)
C1	0.2763 (4)	0.15166 (9)	0.55705 (14)	0.0330 (4)
C2	0.2024 (4)	0.22407 (9)	0.58833 (13)	0.0299 (4)
C3	0.3148 (4)	0.28084 (9)	0.51908 (13)	0.0296 (4)
C4	0.4839 (4)	0.26314 (9)	0.42013 (14)	0.0327 (4)
C5	0.5425 (4)	0.19083 (10)	0.39009 (13)	0.0381 (5)
H5	0.6501	0.1800	0.3229	0.046*
C6	0.4435 (5)	0.13631 (10)	0.45810 (15)	0.0381 (5)
H6	0.4875	0.0877	0.4386	0.046*
C7	0.2707 (4)	0.35928 (9)	0.54468 (14)	0.0331 (4)
C8	0.0837 (6)	0.45169 (10)	0.66481 (18)	0.0508 (5)
H8A	0.3085	0.4750	0.6636	0.076*
H8B	-0.0118	0.4571	0.7381	0.076*
H8C	-0.0702	0.4743	0.6098	0.076*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0555 (10)	0.0268 (9)	0.0413 (9)	0.0013 (7)	0.0126 (7)	0.0011 (6)
O1	0.1201 (14)	0.0253 (8)	0.0751 (11)	0.0110 (8)	0.0504 (10)	0.0036 (7)

supplementary materials

O2	0.0724 (9)	0.0349 (8)	0.0423 (8)	0.0001 (6)	0.0246 (7)	0.0034 (6)
O3	0.0526 (8)	0.0294 (7)	0.0341 (7)	0.0010 (6)	0.0166 (6)	0.0004 (5)
O4	0.0549 (8)	0.0333 (8)	0.0399 (7)	-0.0008 (6)	0.0171 (6)	0.0045 (6)
O5	0.0657 (9)	0.0287 (7)	0.0506 (8)	-0.0012 (6)	0.0175 (7)	0.0038 (6)
O6	0.0600 (9)	0.0269 (7)	0.0432 (8)	0.0044 (6)	0.0157 (6)	-0.0038 (5)
C1	0.0398 (10)	0.0260 (9)	0.0334 (9)	0.0016 (7)	0.0074 (7)	0.0015 (7)
C2	0.0316 (9)	0.0300 (9)	0.0284 (8)	0.0020 (7)	0.0042 (7)	-0.0015 (7)
C3	0.0319 (9)	0.0260 (9)	0.0311 (8)	0.0013 (7)	0.0033 (7)	-0.0006 (7)
C4	0.0341 (10)	0.0319 (10)	0.0325 (9)	-0.0008 (7)	0.0047 (7)	0.0023 (7)
C5	0.0441 (10)	0.0376 (11)	0.0331 (9)	0.0050 (8)	0.0102 (7)	-0.0027 (8)
C6	0.0449 (10)	0.0296 (10)	0.0403 (10)	0.0056 (8)	0.0079 (8)	-0.0040 (8)
C7	0.0360 (9)	0.0287 (10)	0.0348 (9)	0.0002 (7)	0.0053 (7)	0.0003 (7)
C8	0.0679 (13)	0.0267 (11)	0.0588 (12)	0.0040 (9)	0.0170 (10)	-0.0077 (9)

Geometric parameters (Å, °)

N1—O1	1.2192 (19)	C1—C2	1.413 (2)
N1—O2	1.2420 (17)	C2—C3	1.410 (2)
N1—C1	1.435 (2)	C3—C4	1.412 (2)
O3—C2	1.3306 (19)	C3—C7	1.483 (2)
O3—H3	0.8300	C4—C5	1.396 (2)
O4—C4	1.3323 (19)	C5—C6	1.355 (2)
O4—H4	0.8300	C5—H5	0.9400
O5—C7	1.228 (2)	C6—H6	0.9400
O6—C7	1.322 (2)	C8—H8A	0.9700
O6—C8	1.455 (2)	C8—H8B	0.9700
C1—C6	1.399 (2)	C8—H8C	0.9700
O1—N1—O2	121.40 (15)	C5—C4—C3	121.29 (15)
O1—N1—C1	119.13 (15)	C6—C5—C4	119.73 (15)
O2—N1—C1	119.47 (14)	C6—C5—H5	120.1
C2—O3—H3	109.5	C4—C5—H5	120.1
C4—O4—H4	109.5	C5—C6—C1	120.65 (16)
C7—O6—C8	116.01 (14)	C5—C6—H6	119.7
C6—C1—C2	121.19 (15)	C1—C6—H6	119.7
C6—C1—N1	117.76 (15)	O5—C7—O6	121.58 (16)
C2—C1—N1	121.04 (14)	O5—C7—C3	122.15 (15)
O3—C2—C3	118.97 (14)	O6—C7—C3	116.27 (14)
O3—C2—C1	122.98 (14)	O6—C8—H8A	109.5
C3—C2—C1	118.04 (14)	O6—C8—H8B	109.5
C2—C3—C4	119.04 (15)	H8A—C8—H8B	109.5
C2—C3—C7	123.75 (14)	O6—C8—H8C	109.5
C4—C3—C7	117.20 (15)	H8A—C8—H8C	109.5
O4—C4—C5	116.69 (14)	H8B—C8—H8C	109.5
O4—C4—C3	122.02 (15)		
O1—N1—C1—C6	5.2 (3)	C2—C3—C4—C5	-0.2 (2)
O2—N1—C1—C6	-174.73 (15)	C7—C3—C4—C5	178.90 (15)
O1—N1—C1—C2	-175.62 (16)	O4—C4—C5—C6	177.77 (15)
O2—N1—C1—C2	4.5 (3)	C3—C4—C5—C6	-1.7 (3)
C6—C1—C2—O3	176.93 (16)	C4—C5—C6—C1	1.4 (3)

N1—C1—C2—O3	-2.3 (3)	C2—C1—C6—C5	0.7 (3)
C6—C1—C2—C3	-2.6 (3)	N1—C1—C6—C5	179.95 (16)
N1—C1—C2—C3	178.25 (15)	C8—O6—C7—O5	-0.3 (3)
O3—C2—C3—C4	-177.25 (14)	C8—O6—C7—C3	178.90 (14)
C1—C2—C3—C4	2.3 (2)	C2—C3—C7—O5	-179.95 (16)
O3—C2—C3—C7	3.7 (2)	C4—C3—C7—O5	1.0 (3)
C1—C2—C3—C7	-176.80 (15)	C2—C3—C7—O6	0.9 (2)
C2—C3—C4—O4	-179.62 (15)	C4—C3—C7—O6	-178.18 (14)
C7—C3—C4—O4	-0.5 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O3—H3 \cdots O2	0.83	1.84	2.5636 (16)	145
O3—H3 \cdots O4 ⁱ	0.83	2.28	2.8816 (15)	129
O3—H3 \cdots N1	0.83	2.43	2.8797 (19)	115
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Fig. 1

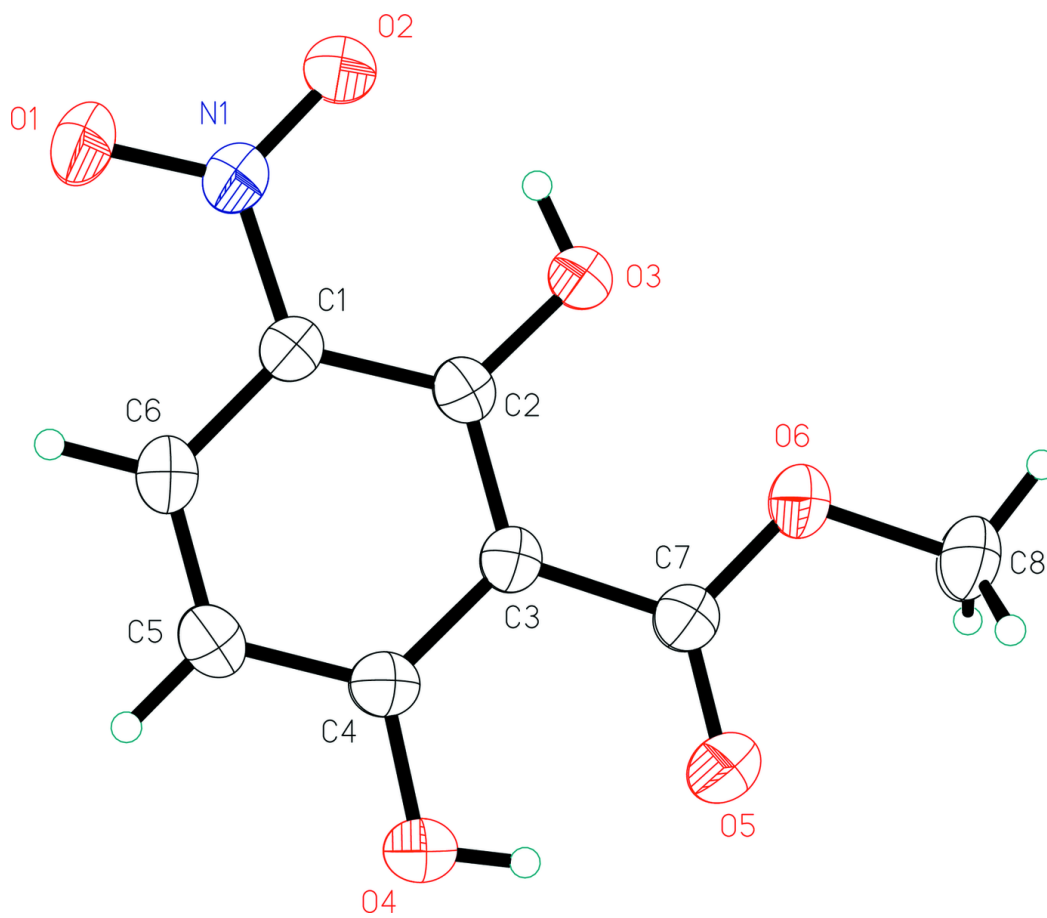


Fig. 2

