

2-Methyl-3,5-dinitrobenzoic acid

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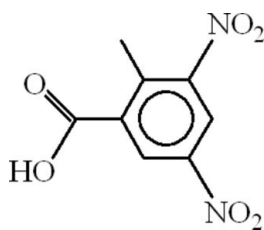
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; disorder in main residue; R factor = 0.035; wR factor = 0.098; data-to-parameter ratio = 10.7.

In the title compound, $\text{C}_8\text{H}_6\text{N}_2\text{O}_6$, the O atoms of the nitro groups, the methyl H atoms and the carboxyl C=O and C—OH groups are disordered over two sets of sites with an occupancy ratio of 0.595 (16):0.405 (16). In the crystal, inversion dimers linked by pairs of O—H···O hydrogen bonds arise for both carboxyl disorder components and C—H···O bonds and weak C—H··· π interactions consolidate the packing.

Related literature

For general background to isocoumarins, see: Hill (1986); Varanda *et al.* (2004). For related structures, see: Prince *et al.* (1991); Sarma & Nagaraju (2000).



Experimental

Crystal data

$\text{C}_8\text{H}_6\text{N}_2\text{O}_6$
 $M_r = 226.15$
 Monoclinic, $C2/c$
 $a = 26.8441$ (16) Å

$b = 5.1044$ (3) Å
 $c = 13.8853$ (10) Å
 $\beta = 104.544$ (3)°
 $V = 1841.6$ (2) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹

$T = 296$ K
 $0.28 \times 0.09 \times 0.08$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.985$, $T_{\max} = 0.987$

8618 measured reflections
 2019 independent reflections
 1626 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.098$
 $S = 1.07$
 2019 reflections
 189 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O2 ⁱ	0.83 (4)	1.80 (4)	2.6216 (16)	175 (3)
C8—H8B···O5A ⁱⁱ	0.96	2.55	3.385 (11)	145
C8—H8C···O3A	0.96	2.43	3.023 (11)	120
C8—H8A···Cg1 ⁱⁱⁱ	0.96	2.96	3.781 (2)	144
C8—H8E···Cg1 ⁱⁱⁱ	0.96	2.96	3.781 (2)	144

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $x, y - 1, z$. Cg1 is the centroid of the C1–C6 benzene ring.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); 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) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5136).

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supporting information

Acta Cryst. (2009). E65, o2819 [https://doi.org/10.1107/S1600536809042627]

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S1. Comment

Isocoumarins are secondary metabolites, derived from acetate pathway, which are structurally related to coumarins but with inverted lactone ring. Isocoumarins shows a wide range of applications and biological activities including anti-cancer (Varanda *et al.*, 2004), anti-tumor (Hill *et al.*, 1986) *etc.*

The title compound (I, Fig. 1) is an intermediate towards the synthesis of substituted homophthallic acid that is a precursor for the synthesis of isocoumarins.

The crystal structures of (II) 2,4-Dinitrotoluene (Sarma & Nagaraju 2000), (III) 3,5-Dinitrobenzoic acid (Prince *et al.*, 1991) have been reported. The title compound contains both of these moieties.

The O-atoms of nitro groups are disordered over two sets of sites with occupancy ratio of 0.595 (16):0.405 (16). Due to this disorder the H-atoms of CH₃ and OH groups are also disordered with same occupancy ratio. The title compound consist of conventional carboxylate dimers (Fig. 2). The benzene ring A (C1–C6) and carboxyl group B (O1/C7/O2) are oriented at a dihedral angle of 23.82 (15)°. The disordered nitro groups C (O3A/N1/O4A), D (O3B/N1/O4B), E (O5A/N2/O6A) and F (O5B/N1/O6B) are certainly planar. The values of dihedral angles for C/E and D/F are 57 (1) and 76 (1)°, respectively. The molecules are stabilized due to H-bondings and C—H... π interactions (Table 1).

S2. Experimental

HNO₃ (28.0 g, 0.7 mol) was added as drops to an ice-chilled (273 K) solution of *o*-toluic acid (13.6 g, 0.1 mol) in H₂SO₄ (110.4 g, 11.2 mol) with constant stirring. The reaction mixture was stirred for 15 minutes, left overnight on stirring at room temperature and then refluxed at 373 K for 4 h. More HNO₃ (21.0 g, 0.69 mol) was added after cooling to room temperature and refluxed for further 3 h. The reaction mixture was cooled to room temperature and poured to ice. The precipitates were filtered, washed with distilled water to remove free sulfates and nitrates. Recrystallization from methanol/water (1:1) afforded yellow needles of (I) suitable for *x*-ray diffraction. Yield 92%.

S3. Refinement

The O-atoms of NO₂ groups along with H-atoms of CH₃ and OH groups are disordered. The coordinates of H-atoms of hydroxy group were refined.

H-atoms were positioned geometrically, with C—H = 0.93 and 0.96 Å for aryl and methyl H, respectively and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C}, \text{O})$, where $x = 1.5$ for methyl and 1.2 for all other H atoms.

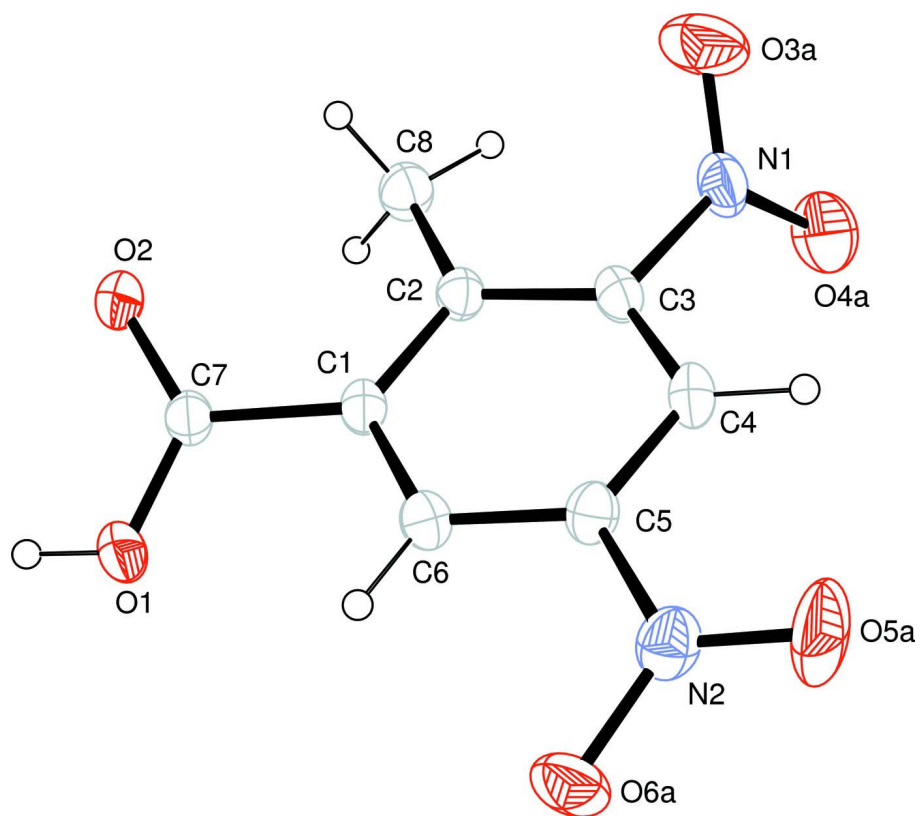


Figure 1

View of (I) with the atom numbering scheme having atoms of greater occupancy ratio. The displacement ellipsoids are drawn at the 30% probability level. H-atoms are shown by small circles of arbitrary radii.

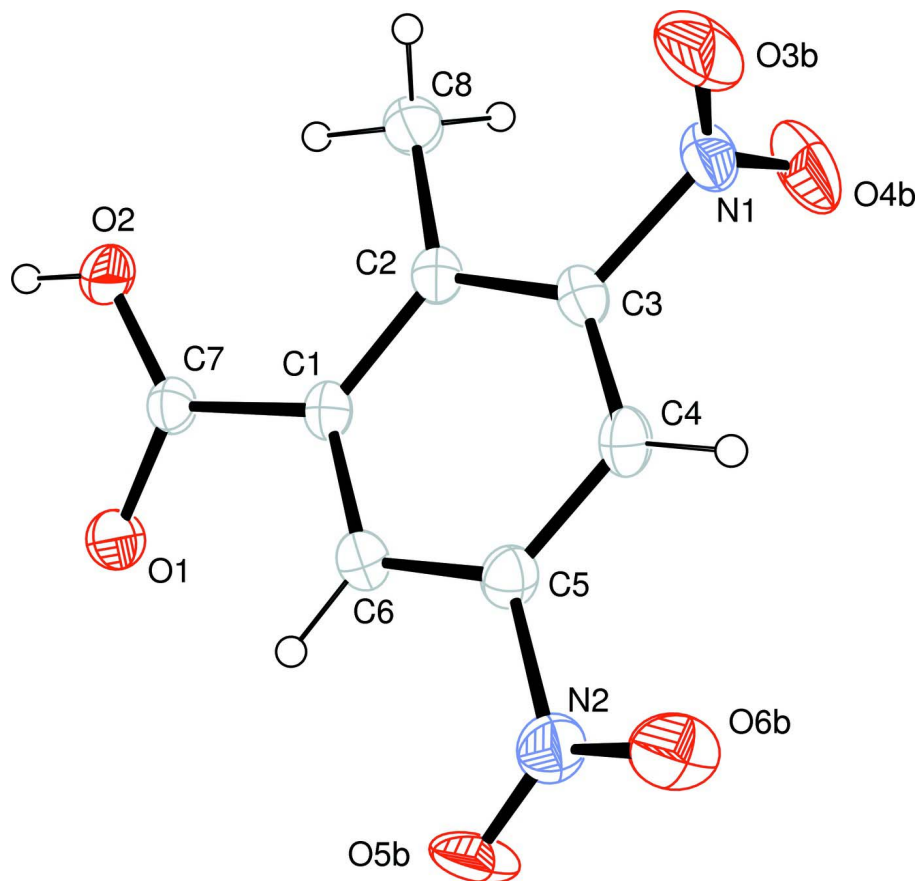


Figure 2

View of (I) with the atom numbering scheme having atoms of smaller occupancy ratio. The displacement ellipsoids are drawn at the 30% probability level. H-atoms are shown by small circles of arbitrary radii.

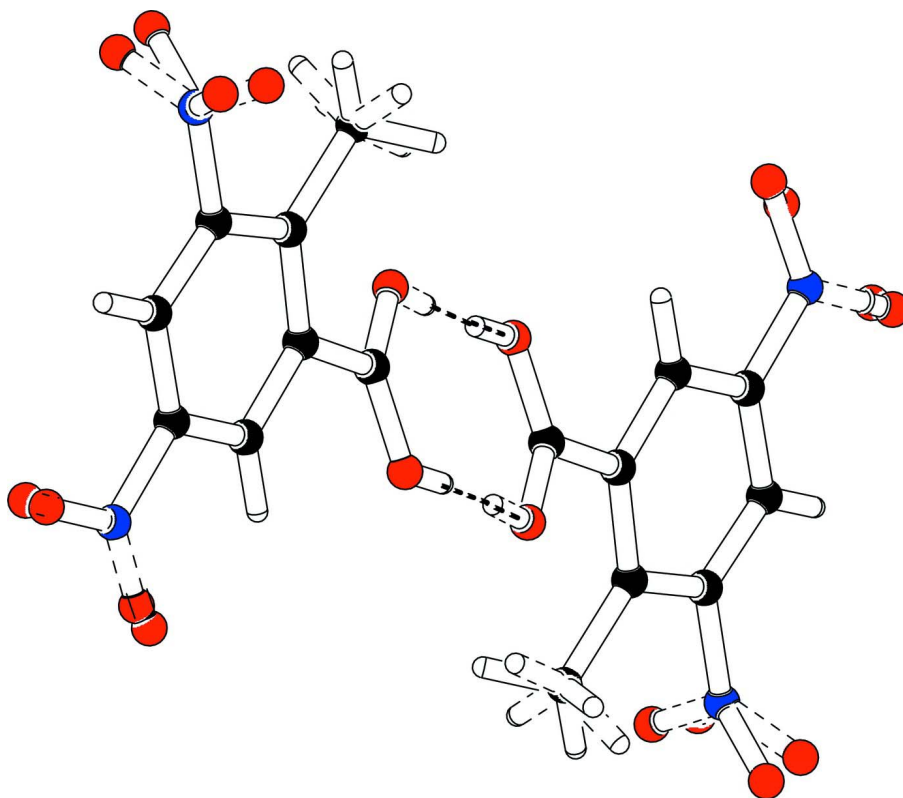


Figure 3

The partial packing of (I), which shows that molecules form inversion dimers.

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$M_r = 226.15$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 26.8441 (16) \text{ \AA}$

$b = 5.1044 (3) \text{ \AA}$

$c = 13.8853 (10) \text{ \AA}$

$\beta = 104.544 (3)^\circ$

$V = 1841.6 (2) \text{ \AA}^3$

$Z = 8$

$F(000) = 928$

$D_x = 1.631 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 2019 reflections

$\theta = 3.0\text{--}27.1^\circ$

$\mu = 0.14 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle, yellow

$0.28 \times 0.09 \times 0.08 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $7.60 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2005)

$T_{\min} = 0.985$, $T_{\max} = 0.987$

8618 measured reflections

2019 independent reflections

1626 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 27.1^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -34 \rightarrow 21$

$k = -6 \rightarrow 6$

$l = -16 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.098$

$S = 1.07$

2019 reflections

189 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 atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.7672P]$

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

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

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

$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.01701 (4)	0.2581 (2)	0.43564 (8)	0.0512 (3)	
O2	0.05404 (4)	-0.13177 (19)	0.47311 (8)	0.0478 (3)	
O3A	0.2288 (4)	-0.200 (2)	0.3383 (8)	0.083 (2)	0.595 (16)
O4A	0.2604 (2)	0.1735 (16)	0.3731 (8)	0.0879 (18)	0.595 (16)
O5A	0.1204 (4)	0.696 (2)	0.1252 (9)	0.082 (3)	0.595 (16)
O6A	0.0510 (4)	0.781 (2)	0.1802 (7)	0.0573 (14)	0.595 (16)
N1	0.22362 (4)	0.0323 (3)	0.35244 (10)	0.0497 (4)	
N2	0.09302 (5)	0.6426 (3)	0.17734 (9)	0.0485 (4)	
C1	0.09152 (4)	0.1704 (2)	0.38137 (9)	0.0325 (3)	
C2	0.14060 (4)	0.0536 (2)	0.39970 (9)	0.0335 (3)	
C3	0.17128 (4)	0.1421 (3)	0.33837 (10)	0.0367 (4)	
C4	0.15720 (5)	0.3269 (3)	0.26482 (10)	0.0399 (4)	
C5	0.10921 (5)	0.4375 (3)	0.25252 (9)	0.0371 (4)	
C6	0.07666 (4)	0.3649 (3)	0.31037 (9)	0.0360 (4)	
C7	0.05193 (4)	0.0909 (3)	0.43530 (9)	0.0346 (4)	
C8	0.16097 (5)	-0.1411 (3)	0.48095 (11)	0.0448 (4)	
O4B	0.2566 (3)	0.149 (3)	0.4132 (8)	0.084 (3)	0.405 (16)
O5B	0.0598 (5)	0.750 (3)	0.1754 (11)	0.061 (2)	0.405 (16)
O6B	0.1179 (7)	0.655 (3)	0.1105 (11)	0.061 (2)	0.405 (16)
O3B	0.2269 (6)	-0.152 (3)	0.3038 (13)	0.094 (4)	0.405 (16)
H8B	0.15619	-0.07488	0.54272	0.0672*	0.595 (16)
H8C	0.19697	-0.16935	0.48691	0.0672*	0.595 (16)
H8A	0.14278	-0.30373	0.46522	0.0672*	0.595 (16)
H1	-0.0046 (14)	0.209 (6)	0.465 (2)	0.0614*	0.595 (16)
H4	0.17896	0.37504	0.22525	0.0479*	

H6	0.04484	0.44612	0.30177	0.0432*	
H2	0.0315 (19)	-0.169 (9)	0.498 (4)	0.0614*	0.405 (16)
H8D	0.19134	-0.07189	0.52575	0.0672*	0.405 (16)
H8E	0.16930	-0.30148	0.45242	0.0672*	0.405 (16)
H8F	0.13531	-0.17459	0.51669	0.0672*	0.405 (16)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0444 (5)	0.0495 (6)	0.0706 (7)	0.0066 (4)	0.0349 (5)	0.0127 (5)
O2	0.0450 (5)	0.0407 (5)	0.0658 (7)	-0.0019 (4)	0.0293 (5)	0.0092 (5)
O3A	0.058 (2)	0.064 (3)	0.121 (5)	0.0211 (19)	0.012 (3)	-0.014 (3)
O4A	0.0343 (13)	0.091 (2)	0.142 (5)	-0.0100 (13)	0.029 (3)	-0.005 (3)
O5A	0.068 (3)	0.114 (5)	0.071 (5)	-0.004 (3)	0.031 (3)	0.051 (4)
O6A	0.052 (3)	0.060 (2)	0.061 (2)	0.027 (2)	0.016 (2)	0.0131 (16)
N1	0.0356 (6)	0.0591 (8)	0.0593 (8)	0.0035 (6)	0.0213 (6)	0.0073 (7)
N2	0.0488 (7)	0.0541 (7)	0.0416 (7)	-0.0018 (6)	0.0093 (6)	0.0104 (6)
C1	0.0303 (6)	0.0364 (6)	0.0325 (6)	-0.0048 (5)	0.0109 (5)	-0.0019 (5)
C2	0.0315 (6)	0.0354 (6)	0.0345 (6)	-0.0036 (5)	0.0100 (5)	-0.0024 (5)
C3	0.0295 (6)	0.0424 (7)	0.0401 (7)	-0.0005 (5)	0.0124 (5)	-0.0016 (6)
C4	0.0364 (6)	0.0489 (8)	0.0388 (7)	-0.0063 (6)	0.0175 (5)	0.0012 (6)
C5	0.0374 (6)	0.0421 (7)	0.0320 (6)	-0.0034 (5)	0.0089 (5)	0.0039 (5)
C6	0.0300 (6)	0.0414 (7)	0.0368 (7)	-0.0013 (5)	0.0090 (5)	-0.0003 (5)
C7	0.0316 (6)	0.0369 (6)	0.0376 (7)	-0.0031 (5)	0.0128 (5)	-0.0007 (5)
C8	0.0416 (7)	0.0468 (8)	0.0466 (8)	0.0033 (6)	0.0124 (6)	0.0089 (6)
O4B	0.029 (3)	0.115 (5)	0.102 (5)	0.000 (3)	0.005 (3)	-0.011 (4)
O5B	0.064 (5)	0.068 (4)	0.064 (3)	0.046 (3)	0.039 (3)	0.032 (3)
O6B	0.075 (5)	0.075 (3)	0.040 (2)	0.020 (3)	0.027 (2)	0.017 (2)
O3B	0.070 (5)	0.074 (6)	0.152 (10)	0.020 (3)	0.053 (6)	-0.025 (6)

Geometric parameters (Å, °)

O1—C7	1.2686 (17)	C1—C6	1.3854 (18)
O2—C7	1.2473 (18)	C1—C7	1.5015 (16)
O3A—N1	1.216 (10)	C2—C3	1.3999 (17)
O3B—N1	1.174 (16)	C2—C8	1.4999 (19)
O4A—N1	1.198 (7)	C3—C4	1.372 (2)
O4B—N1	1.215 (12)	C4—C5	1.377 (2)
O5A—N2	1.186 (12)	C5—C6	1.3779 (18)
O5B—N2	1.041 (14)	C4—H4	0.9300
O6A—N2	1.340 (11)	C6—H6	0.9300
O6B—N2	1.274 (17)	C8—H8A	0.9600
O1—H1	0.83 (4)	C8—H8B	0.9600
O2—H2	0.79 (5)	C8—H8C	0.9600
N1—C3	1.4794 (17)	C8—H8D	0.9600
N2—C5	1.465 (2)	C8—H8E	0.9600
C1—C2	1.4098 (16)	C8—H8F	0.9600

C7—O1—H1	114 (2)	C4—C5—C6	121.86 (13)
C7—O2—H2	116 (3)	N2—C5—C4	118.82 (12)
O4A—N1—C3	120.1 (4)	N2—C5—C6	119.31 (12)
O3B—N1—C3	115.7 (8)	C1—C6—C5	119.75 (11)
O3A—N1—C3	119.5 (5)	O2—C7—C1	119.55 (11)
O3B—N1—O4B	130.2 (10)	O1—C7—O2	124.54 (12)
O4B—N1—C3	114.1 (6)	O1—C7—C1	115.86 (12)
O3A—N1—O4A	120.3 (6)	C3—C4—H4	122.00
O5A—N2—O6A	123.5 (7)	C5—C4—H4	122.00
O5B—N2—C5	119.6 (8)	C1—C6—H6	120.00
O6B—N2—C5	116.0 (7)	C5—C6—H6	120.00
O5B—N2—O6B	123.9 (11)	C2—C8—H8A	109.00
O6A—N2—C5	117.2 (4)	C2—C8—H8B	109.00
O5A—N2—C5	118.7 (5)	C2—C8—H8C	109.00
C2—C1—C7	122.82 (10)	C2—C8—H8D	109.00
C2—C1—C6	121.37 (10)	C2—C8—H8E	109.00
C6—C1—C7	115.80 (10)	C2—C8—H8F	109.00
C3—C2—C8	120.82 (11)	H8A—C8—H8B	109.00
C1—C2—C8	124.31 (11)	H8A—C8—H8C	109.00
C1—C2—C3	114.81 (11)	H8B—C8—H8C	109.00
N1—C3—C2	118.80 (12)	H8D—C8—H8E	109.00
N1—C3—C4	115.71 (12)	H8D—C8—H8F	109.00
C2—C3—C4	125.49 (12)	H8E—C8—H8F	109.00
C3—C4—C5	116.64 (12)		
O3A—N1—C3—C2	63.2 (6)	C2—C1—C7—O1	158.86 (11)
O3A—N1—C3—C4	-117.2 (6)	C2—C1—C7—O2	-23.53 (18)
O4A—N1—C3—C2	-120.3 (6)	C6—C1—C7—O1	-22.16 (17)
O4A—N1—C3—C4	59.4 (6)	C6—C1—C7—O2	155.46 (12)
O5A—N2—C5—C4	4.6 (6)	C1—C2—C3—N1	179.58 (12)
O5A—N2—C5—C6	-176.9 (6)	C1—C2—C3—C4	-0.1 (2)
O6A—N2—C5—C4	-167.3 (5)	C8—C2—C3—N1	2.39 (19)
O6A—N2—C5—C6	11.2 (5)	C8—C2—C3—C4	-177.24 (14)
C6—C1—C2—C3	-2.47 (17)	N1—C3—C4—C5	-178.07 (13)
C6—C1—C2—C8	174.61 (12)	C2—C3—C4—C5	1.6 (2)
C7—C1—C2—C3	176.46 (12)	C3—C4—C5—N2	177.87 (13)
C7—C1—C2—C8	-6.46 (18)	C3—C4—C5—C6	-0.6 (2)
C2—C1—C6—C5	3.43 (19)	N2—C5—C6—C1	179.73 (12)
C7—C1—C6—C5	-175.58 (12)	C4—C5—C6—C1	-1.8 (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>
O1—H1...O2 ⁱ	0.83 (4)	1.80 (4)	2.6216 (16)	175 (3)
C8—H8B...O5A ⁱⁱ	0.96	2.55	3.385 (11)	145
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