

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N-(3-Chloro-4-methylphenyl)succinamic acid

 U. Chaithanya,^a Sabine Foro^b and B. Thimme Gowda^{a*}
^aDepartment of Chemistry, Mangalore University, Mangalagangothri 574 199, Mangalore, India, and ^bInstitute of Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany

Correspondence e-mail: gowdabt@yahoo.com

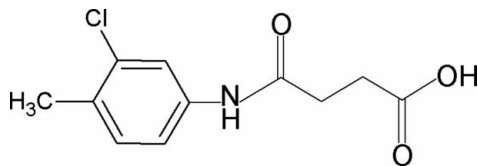
Received 17 February 2012; accepted 20 February 2012

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.083; wR factor = 0.159; data-to-parameter ratio = 13.4.

In the crystal structure of the title compound, $\text{C}_{11}\text{H}_{12}\text{ClNO}_3$, the asymmetric unit contains two independent molecules. The N—H bond in the amide segment is *anti* to the *meta*-Cl atom in the benzene ring, in both molecules. The amide and carboxyl C=O bonds are also *anti* to each other and *anti* to the H atoms on the adjacent $-\text{CH}_2$ groups. Furthermore, the C=O and O—H bonds of the acid group are in *syn* positions with respect to each other. The dihedral angles between the benzene ring and the amide group are 40.6 (2) and 44.9 (3)° in the two independent molecules. In the crystal, molecules are packed into sheets parallel to the $(11\bar{3})$ plane through O—H...O and N—H...O hydrogen bonds.

Related literature

For our studies on the effects of substituents on the structures and other aspects of *N*-(aryl)-amides, see: Gowda *et al.* (2000); Chaithanya *et al.* (2012). For *N*-(aryl)-methanesulfonamides, see: Gowda *et al.* (2007). For *N*-chloroarylamides, see: Gowda *et al.* (2003); Jyothi & Gowda (2004). For *N*-bromoaryl-sulfonamides, see: Usha & Gowda (2006).



Experimental

Crystal data

 $\text{C}_{11}\text{H}_{12}\text{ClNO}_3$
 $M_r = 241.67$

 Triclinic, $P\bar{1}$
 $a = 6.8788$ (9) Å

 $b = 7.9713$ (9) Å
 $c = 21.119$ (3) Å
 $\alpha = 86.76$ (1)°
 $\beta = 86.48$ (1)°
 $\gamma = 79.45$ (1)°
 $V = 1135.1$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.33$ mm⁻¹
 $T = 293$ K
 $0.42 \times 0.14 \times 0.08$ mm

Data collection

 Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector
 Absorption correction: multi-scan (*CrysAlis RED*; Oxford)

 Diffraction, 2009)
 $T_{\min} = 0.875$, $T_{\max} = 0.974$
 6890 measured reflections
 4066 independent reflections
 2649 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.083$
 $wR(F^2) = 0.159$
 $S = 1.26$
 4066 reflections
 303 parameters
 4 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.29$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O4}^i$	0.85 (2)	2.05 (2)	2.882 (5)	165 (5)
$\text{O3}-\text{H3O}\cdots\text{O2}^{ii}$	0.83 (2)	1.83 (2)	2.654 (5)	173 (7)
$\text{N2}-\text{H2N}\cdots\text{O1}^{iii}$	0.84 (2)	2.07 (2)	2.891 (5)	165 (5)
$\text{O6}-\text{H6O}\cdots\text{O5}^{iv}$	0.83 (2)	1.90 (3)	2.703 (5)	164 (7)

 Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+2, -y+3, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

BTG thanks the University Grants Commission, Government of India, New Delhi, for a UGC-BSR one-time grant to faculty.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5820).

References

- Chaithanya, U., Foro, S. & Gowda, B. T. (2012). *Acta Cryst.* **E68**, o785.
 Gowda, B. T., D'Souza, J. D. & Kumar, B. H. A. (2003). *Z. Naturforsch. Teil A*, **58**, 51–56.
 Gowda, B. T., Foro, S. & Fuess, H. (2007). *Acta Cryst.* **E63**, o2570.
 Gowda, B. T., Paulus, H. & Fuess, H. (2000). *Z. Naturforsch. Teil A*, **55**, 711–720.
 Jyothi, K. & Gowda, B. T. (2004). *Z. Naturforsch. Teil A*, **59**, 64–68.
 Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Usha, K. M. & Gowda, B. T. (2006). *J. Chem. Sci.* **118**, 351–359.

supporting information

Acta Cryst. (2012). E68, o835 [doi:10.1107/S1600536812007623]

N*-(3-Chloro-4-methylphenyl)succinamic acid*U. Chaithanya, Sabine Foro and B. Thimme Gowda****S1. Comment**

As part of our studies on the substituent effects on the structures and other aspects of *N*-(aryl)-amides (Gowda *et al.*, 2000; Chaithanya *et al.*, 2012), *N*-(aryl)-methanesulfonamides (Gowda *et al.*, 2007), *N*-chloroarylsulfonamides (Gowda *et al.*, 2003; Jyothi & Gowda, 2004) and *N*-bromoarylsulfonamides (Usha & Gowda, 2006), in the present work, the crystal structure of *N*-(3-Chloro-4-methylphenyl)succinamic acid has been determined (Fig. 1). The asymmetric unit of the structure contains two independent molecules. The conformations of the N—H bonds in the amide segments are *anti* to the *meta*-chloro atoms in the benzene rings of both the molecules, in contrast to the *syn* conformation observed between the N—H bond and *ortho*-chloro atom in *N*-(2-Chloro-4-methylphenyl)-succinamic acid (I) (Chaithanya *et al.*, 2012).

Further, the conformations of the amide oxygen and the carboxyl oxygen of the acid segments are *anti* to each other and both are *anti* to the H atoms on the adjacent —CH₂ groups.

The C=O and O—H bonds of the acid groups are in *syn* position to each other, similar to that observed in (I).

The dihedral angles between the phenyl ring and the amide group in the two independent molecules are 40.58 (22)° and 44.93 (27)°, compared to the value of 48.39 (12)° in (I).

In the structure, the pairs of O—H···O and N—H···O intermolecular hydrogen bonds pack the molecules into infinite chains (Table 1, Fig.2).

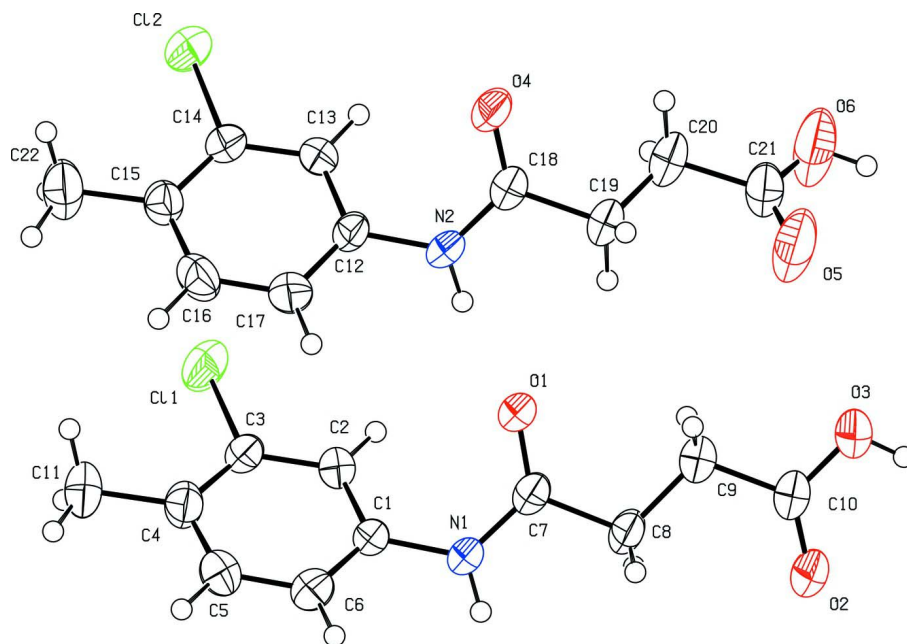
S2. Experimental

The solution of succinic anhydride (0.01 mole) in toluene (25 ml) was treated dropwise with the solution of 3-chloro,4-methylaniline (0.01 mole) also in toluene (20 ml) with constant stirring. The resulting mixture was stirred for about one hour and set aside for an additional hour at room temperature for completion of the reaction. The mixture was then treated with dilute hydrochloric acid to remove the unreacted 3-chloro-4-methyl- aniline. The resultant title compound was filtered under suction and washed thoroughly with water to remove the unreacted succinic anhydride and succinic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked and characterized by its infrared and NMR spectra.

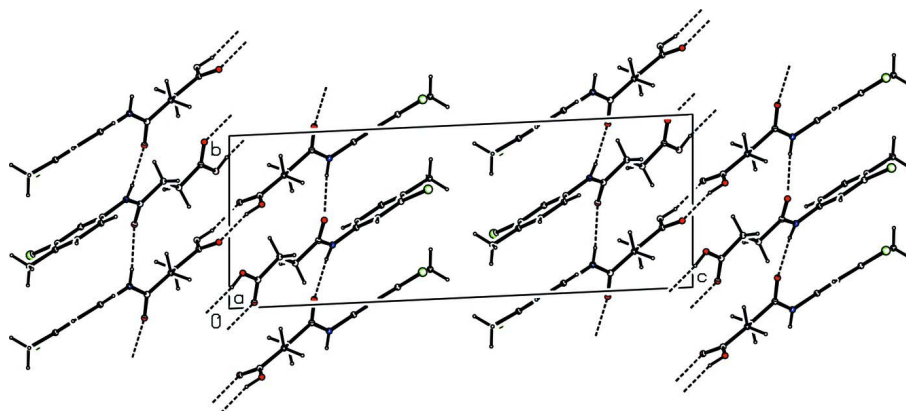
Needle like colorless single crystals used in X-ray diffraction studies were grown in ethanolic solution by slow evaporation of the solvent at room temperature.

S3. Refinement

The H atoms of the NH group and the OH group were located in a difference map and later restrained to N—H = 0.86 (2) Å and O—H = 0.82 (2) Å, respectively. The other H atoms were positioned with idealized geometry using a riding model with aromatic C—H = 0.93 Å and methylene C—H = 0.97 Å. All H atoms were refined with isotropic displacement parameters set at 1.2 U_{eq} (C-aromatic, N) and 1.5 U_{eq} (C-methyl).

**Figure 1**

Molecular structure of the title compound, showing the atom labelling scheme and with displacement ellipsoids drawn at the 50% probability level.

**Figure 2**

Molecular packing of the title compound with hydrogen bonding shown as dashed lines.

***N*-(3-Chloro-4-methylphenyl)succinamic acid**

Crystal data

$C_{11}H_{12}ClNO_3$

$M_r = 241.67$

Triclinic, $P1$

Hall symbol: $-P 1$

$a = 6.8788$ (9) Å

$b = 7.9713$ (9) Å

$c = 21.119$ (3) Å

$\alpha = 86.76$ (1)°

$\beta = 86.48$ (1)°

$\gamma = 79.45$ (1)°

$V = 1135.1$ (3) Å³

$Z = 4$

$F(000) = 504$

$D_x = 1.414$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1965 reflections

$\theta = 2.6$ – 27.8 °

$\mu = 0.33$ mm⁻¹

$T = 293$ K $0.42 \times 0.14 \times 0.08$ mm
 Needle, colourless

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector	6890 measured reflections 4066 independent reflections
Radiation source: fine-focus sealed tube	2649 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{\text{int}} = 0.028$
Rotation method data acquisition using ω and phi scans	$\theta_{\text{max}} = 25.3^\circ$, $\theta_{\text{min}} = 2.6^\circ$ $h = -8 \rightarrow 7$
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2009)	$k = -9 \rightarrow 5$ $l = -25 \rightarrow 24$
$T_{\text{min}} = 0.875$, $T_{\text{max}} = 0.974$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.083$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.159$	$w = 1/[\sigma^2(F_o^2) + (0.0164P)^2 + 2.1147P]$
$S = 1.26$	where $P = (F_o^2 + 2F_c^2)/3$
4066 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
303 parameters	$\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
4 restraints	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. *CrysAlis RED* (Oxford Diffraction, 2009) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9701 (7)	0.4350 (5)	0.2737 (2)	0.0373 (11)
C2	0.8270 (7)	0.4875 (6)	0.3209 (2)	0.0395 (11)
H2	0.6996	0.4647	0.3192	0.047*
C3	0.8765 (7)	0.5746 (6)	0.3707 (2)	0.0406 (11)
C4	1.0621 (8)	0.6124 (6)	0.3758 (2)	0.0462 (12)
C5	1.2006 (7)	0.5579 (6)	0.3278 (2)	0.0508 (13)
H5	1.3280	0.5803	0.3297	0.061*
C6	1.1575 (7)	0.4713 (6)	0.2771 (2)	0.0492 (13)
H6	1.2545	0.4376	0.2454	0.059*
C7	0.7569 (7)	0.3702 (6)	0.1926 (2)	0.0442 (12)
C8	0.7444 (8)	0.2452 (6)	0.1422 (2)	0.0520 (14)

H8A	0.8542	0.2459	0.1111	0.062*
H8B	0.7571	0.1310	0.1618	0.062*
C9	0.5540 (8)	0.2863 (7)	0.1088 (3)	0.0643 (16)
H9A	0.4443	0.2925	0.1402	0.077*
H9B	0.5453	0.3979	0.0872	0.077*
C10	0.5339 (9)	0.1589 (7)	0.0616 (3)	0.0625 (16)
C11	1.1143 (8)	0.7015 (7)	0.4315 (2)	0.0641 (16)
H11A	1.0990	0.6329	0.4698	0.077*
H11B	1.0282	0.8103	0.4347	0.077*
H11C	1.2491	0.7180	0.4258	0.077*
N1	0.9276 (6)	0.3407 (5)	0.22252 (18)	0.0444 (10)
H1N	1.019 (5)	0.261 (4)	0.210 (2)	0.053*
O1	0.6196 (5)	0.4867 (4)	0.20492 (16)	0.0577 (10)
O2	0.6511 (6)	0.0290 (5)	0.0539 (2)	0.0819 (14)
O3	0.3768 (7)	0.2020 (6)	0.0292 (2)	0.1039 (18)
H3O	0.370 (11)	0.124 (6)	0.006 (3)	0.125*
C11	0.6908 (2)	0.63733 (18)	0.42917 (6)	0.0627 (4)
C12	0.5122 (7)	1.0684 (5)	0.7315 (2)	0.0391 (11)
C13	0.6607 (7)	0.9993 (6)	0.6890 (2)	0.0422 (12)
H13	0.7919	1.0053	0.6953	0.051*
C14	0.6131 (7)	0.9208 (5)	0.6365 (2)	0.0397 (11)
C15	0.4223 (7)	0.9079 (6)	0.6246 (2)	0.0415 (11)
C16	0.2766 (7)	0.9777 (7)	0.6688 (2)	0.0534 (14)
H16	0.1457	0.9702	0.6628	0.064*
C17	0.3185 (7)	1.0581 (6)	0.7213 (2)	0.0473 (12)
H17	0.2168	1.1048	0.7497	0.057*
C18	0.7041 (8)	1.1042 (7)	0.8223 (2)	0.0573 (15)
C19	0.7225 (8)	1.2230 (7)	0.8742 (3)	0.0707 (18)
H19A	0.6436	1.3344	0.8645	0.085*
H19B	0.6696	1.1790	0.9141	0.085*
C20	0.9289 (9)	1.2424 (8)	0.8816 (3)	0.0722 (18)
H20A	0.9796	1.2907	0.8422	0.087*
H20B	1.0086	1.1303	0.8893	0.087*
C21	0.9521 (10)	1.3530 (7)	0.9343 (3)	0.0619 (16)
C22	0.3714 (8)	0.8265 (7)	0.5666 (2)	0.0644 (16)
H22A	0.4427	0.7112	0.5655	0.077*
H22B	0.4072	0.8903	0.5292	0.077*
H22C	0.2317	0.8261	0.5682	0.077*
N2	0.5543 (6)	1.1566 (5)	0.78445 (19)	0.0485 (11)
H2N	0.485 (6)	1.254 (4)	0.790 (2)	0.058*
O4	0.8183 (7)	0.9688 (5)	0.8168 (2)	0.0951 (17)
O5	0.8321 (7)	1.3876 (6)	0.9774 (2)	0.0946 (16)
O6	1.1205 (9)	1.4050 (7)	0.9300 (2)	0.1004 (16)
H6O	1.122 (11)	1.457 (8)	0.963 (2)	0.121*
Cl2	0.8053 (2)	0.84014 (18)	0.58273 (6)	0.0599 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.038 (3)	0.036 (3)	0.037 (2)	0.001 (2)	-0.008 (2)	-0.010 (2)
C2	0.038 (3)	0.042 (3)	0.040 (3)	-0.007 (2)	-0.007 (2)	-0.009 (2)
C3	0.044 (3)	0.038 (3)	0.038 (3)	0.001 (2)	-0.005 (2)	-0.011 (2)
C4	0.056 (3)	0.040 (3)	0.045 (3)	-0.009 (2)	-0.013 (2)	-0.006 (2)
C5	0.040 (3)	0.056 (3)	0.059 (3)	-0.012 (2)	-0.009 (2)	-0.012 (3)
C6	0.046 (3)	0.056 (3)	0.044 (3)	0.000 (2)	-0.001 (2)	-0.015 (2)
C7	0.051 (3)	0.040 (3)	0.040 (3)	-0.001 (2)	-0.006 (2)	-0.014 (2)
C8	0.068 (4)	0.038 (3)	0.048 (3)	0.004 (2)	-0.020 (3)	-0.019 (2)
C9	0.057 (4)	0.069 (4)	0.068 (4)	0.001 (3)	-0.020 (3)	-0.037 (3)
C10	0.063 (4)	0.064 (4)	0.063 (4)	-0.002 (3)	-0.020 (3)	-0.032 (3)
C11	0.068 (4)	0.072 (4)	0.059 (3)	-0.017 (3)	-0.017 (3)	-0.025 (3)
N1	0.044 (3)	0.042 (2)	0.046 (2)	0.0057 (19)	-0.0109 (19)	-0.0200 (19)
O1	0.053 (2)	0.055 (2)	0.061 (2)	0.0148 (18)	-0.0208 (17)	-0.0312 (18)
O2	0.081 (3)	0.067 (3)	0.097 (3)	0.016 (2)	-0.042 (2)	-0.051 (2)
O3	0.088 (3)	0.095 (3)	0.126 (4)	0.029 (3)	-0.065 (3)	-0.073 (3)
C11	0.0659 (9)	0.0708 (9)	0.0511 (8)	-0.0068 (7)	0.0061 (6)	-0.0275 (7)
C12	0.047 (3)	0.030 (2)	0.041 (3)	-0.002 (2)	-0.009 (2)	-0.010 (2)
C13	0.030 (3)	0.049 (3)	0.048 (3)	-0.002 (2)	-0.006 (2)	-0.014 (2)
C14	0.041 (3)	0.034 (3)	0.043 (3)	-0.001 (2)	-0.003 (2)	-0.007 (2)
C15	0.041 (3)	0.044 (3)	0.042 (3)	-0.012 (2)	-0.004 (2)	-0.005 (2)
C16	0.034 (3)	0.072 (4)	0.057 (3)	-0.014 (3)	-0.008 (2)	-0.010 (3)
C17	0.038 (3)	0.055 (3)	0.048 (3)	-0.003 (2)	-0.001 (2)	-0.011 (2)
C18	0.059 (4)	0.055 (3)	0.057 (3)	0.006 (3)	-0.017 (3)	-0.028 (3)
C19	0.068 (4)	0.072 (4)	0.070 (4)	0.010 (3)	-0.024 (3)	-0.045 (3)
C20	0.082 (5)	0.066 (4)	0.071 (4)	-0.006 (3)	-0.019 (3)	-0.040 (3)
C21	0.073 (4)	0.061 (4)	0.055 (4)	-0.011 (3)	-0.021 (3)	-0.019 (3)
C22	0.066 (4)	0.082 (4)	0.054 (3)	-0.029 (3)	-0.010 (3)	-0.017 (3)
N2	0.049 (3)	0.041 (2)	0.053 (2)	0.0089 (19)	-0.011 (2)	-0.024 (2)
O4	0.105 (3)	0.072 (3)	0.097 (3)	0.048 (3)	-0.062 (3)	-0.058 (2)
O5	0.109 (4)	0.111 (4)	0.077 (3)	-0.045 (3)	0.005 (3)	-0.053 (3)
O6	0.121 (4)	0.126 (4)	0.071 (3)	-0.053 (3)	-0.001 (3)	-0.049 (3)
C12	0.0528 (8)	0.0685 (9)	0.0563 (8)	0.0000 (7)	0.0034 (6)	-0.0261 (7)

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

C1—C6	1.378 (6)	C12—C13	1.375 (6)
C1—C2	1.384 (6)	C12—C17	1.380 (6)
C1—N1	1.424 (5)	C12—N2	1.426 (5)
C2—C3	1.385 (6)	C13—C14	1.387 (6)
C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.376 (7)	C14—C15	1.375 (6)
C3—C11	1.746 (4)	C14—C12	1.743 (4)
C4—C5	1.380 (7)	C15—C16	1.387 (6)
C4—C11	1.502 (6)	C15—C22	1.507 (6)
C5—C6	1.382 (6)	C16—C17	1.383 (6)

C5—H5	0.9300	C16—H16	0.9300
C6—H6	0.9300	C17—H17	0.9300
C7—O1	1.223 (5)	C18—O4	1.220 (6)
C7—N1	1.344 (6)	C18—N2	1.334 (6)
C7—C8	1.516 (6)	C18—C19	1.515 (6)
C8—C9	1.499 (7)	C19—C20	1.475 (8)
C8—H8A	0.9700	C19—H19A	0.9700
C8—H8B	0.9700	C19—H19B	0.9700
C9—C10	1.492 (6)	C20—C21	1.491 (7)
C9—H9A	0.9700	C20—H20A	0.9700
C9—H9B	0.9700	C20—H20B	0.9700
C10—O2	1.202 (6)	C21—O5	1.200 (7)
C10—O3	1.297 (6)	C21—O6	1.297 (7)
C11—H11A	0.9600	C22—H22A	0.9600
C11—H11B	0.9600	C22—H22B	0.9600
C11—H11C	0.9600	C22—H22C	0.9600
N1—H1N	0.853 (19)	N2—H2N	0.843 (19)
O3—H3O	0.83 (2)	O6—H6O	0.83 (2)
C6—C1—C2	119.4 (4)	C13—C12—C17	119.5 (4)
C6—C1—N1	119.7 (4)	C13—C12—N2	121.0 (4)
C2—C1—N1	120.9 (4)	C17—C12—N2	119.5 (4)
C1—C2—C3	118.9 (4)	C12—C13—C14	119.4 (4)
C1—C2—H2	120.5	C12—C13—H13	120.3
C3—C2—H2	120.5	C14—C13—H13	120.3
C4—C3—C2	123.3 (4)	C15—C14—C13	123.0 (4)
C4—C3—C11	119.6 (3)	C15—C14—C12	119.1 (3)
C2—C3—C11	117.1 (4)	C13—C14—C12	117.8 (4)
C3—C4—C5	116.0 (4)	C14—C15—C16	116.0 (4)
C3—C4—C11	122.3 (5)	C14—C15—C22	122.7 (4)
C5—C4—C11	121.6 (5)	C16—C15—C22	121.3 (5)
C4—C5—C6	122.7 (5)	C17—C16—C15	122.5 (5)
C4—C5—H5	118.7	C17—C16—H16	118.7
C6—C5—H5	118.7	C15—C16—H16	118.7
C1—C6—C5	119.7 (4)	C12—C17—C16	119.6 (4)
C1—C6—H6	120.1	C12—C17—H17	120.2
C5—C6—H6	120.1	C16—C17—H17	120.2
O1—C7—N1	123.6 (4)	O4—C18—N2	123.1 (4)
O1—C7—C8	121.7 (4)	O4—C18—C19	121.3 (5)
N1—C7—C8	114.7 (4)	N2—C18—C19	115.6 (4)
C9—C8—C7	112.8 (4)	C20—C19—C18	112.7 (5)
C9—C8—H8A	109.0	C20—C19—H19A	109.1
C7—C8—H8A	109.0	C18—C19—H19A	109.1
C9—C8—H8B	109.0	C20—C19—H19B	109.1
C7—C8—H8B	109.0	C18—C19—H19B	109.1
H8A—C8—H8B	107.8	H19A—C19—H19B	107.8
C10—C9—C8	113.5 (4)	C19—C20—C21	113.7 (5)
C10—C9—H9A	108.9	C19—C20—H20A	108.8

C8—C9—H9A	108.9	C21—C20—H20A	108.8
C10—C9—H9B	108.9	C19—C20—H20B	108.8
C8—C9—H9B	108.9	C21—C20—H20B	108.8
H9A—C9—H9B	107.7	H20A—C20—H20B	107.7
O2—C10—O3	122.9 (5)	O5—C21—O6	122.6 (5)
O2—C10—C9	123.8 (5)	O5—C21—C20	124.6 (6)
O3—C10—C9	113.3 (5)	O6—C21—C20	112.8 (6)
C4—C11—H11A	109.5	C15—C22—H22A	109.5
C4—C11—H11B	109.5	C15—C22—H22B	109.5
H11A—C11—H11B	109.5	H22A—C22—H22B	109.5
C4—C11—H11C	109.5	C15—C22—H22C	109.5
H11A—C11—H11C	109.5	H22A—C22—H22C	109.5
H11B—C11—H11C	109.5	H22B—C22—H22C	109.5
C7—N1—C1	125.1 (4)	C18—N2—C12	125.3 (4)
C7—N1—H1N	118 (3)	C18—N2—H2N	118 (4)
C1—N1—H1N	117 (3)	C12—N2—H2N	116 (3)
C10—O3—H3O	109 (5)	C21—O6—H6O	105 (5)
C6—C1—C2—C3	-0.4 (7)	C17—C12—C13—C14	0.1 (7)
N1—C1—C2—C3	178.1 (4)	N2—C12—C13—C14	-177.3 (4)
C1—C2—C3—C4	0.1 (7)	C12—C13—C14—C15	0.0 (7)
C1—C2—C3—C11	-179.8 (3)	C12—C13—C14—C12	178.3 (4)
C2—C3—C4—C5	-0.1 (7)	C13—C14—C15—C16	-0.5 (7)
C11—C3—C4—C5	179.8 (4)	C12—C14—C15—C16	-178.8 (4)
C2—C3—C4—C11	-177.7 (5)	C13—C14—C15—C22	178.3 (5)
C11—C3—C4—C11	2.1 (7)	C12—C14—C15—C22	0.0 (7)
C3—C4—C5—C6	0.4 (8)	C14—C15—C16—C17	1.0 (8)
C11—C4—C5—C6	178.0 (5)	C22—C15—C16—C17	-177.8 (5)
C2—C1—C6—C5	0.6 (7)	C13—C12—C17—C16	0.3 (7)
N1—C1—C6—C5	-177.9 (4)	N2—C12—C17—C16	177.8 (5)
C4—C5—C6—C1	-0.6 (8)	C15—C16—C17—C12	-0.9 (8)
O1—C7—C8—C9	2.6 (8)	O4—C18—C19—C20	44.0 (9)
N1—C7—C8—C9	-178.3 (5)	N2—C18—C19—C20	-137.0 (6)
C7—C8—C9—C10	-176.6 (5)	C18—C19—C20—C21	-177.5 (5)
C8—C9—C10—O2	5.2 (9)	C19—C20—C21—O5	19.0 (9)
C8—C9—C10—O3	-174.7 (6)	C19—C20—C21—O6	-163.0 (6)
O1—C7—N1—C1	2.5 (8)	O4—C18—N2—C12	-3.1 (10)
C8—C7—N1—C1	-176.6 (4)	C19—C18—N2—C12	178.0 (5)
C6—C1—N1—C7	-141.8 (5)	C13—C12—N2—C18	-44.3 (8)
C2—C1—N1—C7	39.7 (7)	C17—C12—N2—C18	138.3 (6)

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>
N1—H1N...O4 ⁱ	0.85 (2)	2.05 (2)	2.882 (5)	165 (5)
O3—H3O...O2 ⁱⁱ	0.83 (2)	1.83 (2)	2.654 (5)	173 (7)

N2—H2N \cdots O1 ⁱⁱⁱ	0.84 (2)	2.07 (2)	2.891 (5)	165 (5)
O6—H6O \cdots O5 ^{iv}	0.83 (2)	1.90 (3)	2.703 (5)	164 (7)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+2, -y+3, -z+2$.