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Bis(4-methoxy-3,4-dihydroquinazolin-1-ium) chloranilate

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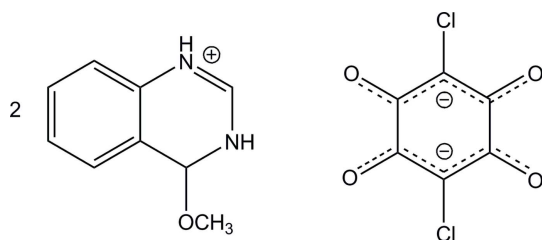
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.082; wR factor = 0.177; data-to-parameter ratio = 15.7.

In the title compound [systematic name: bis(4-methoxy-3,4-dihydroquinazolin-1-ium) 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate], $2\text{C}_9\text{H}_{11}\text{N}_2\text{O}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$, the chloranilate anion lies about an inversion center. The 4-methoxy-3,4-dihydroquinazolin-1-ium cations are linked on both sides of the anion *via* bifurcated $\text{N}-\text{H}\cdots(\text{O},\text{O})$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, giving a centrosymmetric 2:1 aggregate. The 2:1 aggregates are linked by another $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond into a tape running along $[\bar{1}10]$. The tapes are further linked by a $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond into a layer parallel to the *ab* plane.

Related literature

For NMR and nuclear quadrupole resonance (NQR) studies on proton-transfer in the short hydrogen-bond of the diazine-chloranilic acid (2:1) system, see: Nihei *et al.* (2000); Seliger *et al.* (2009). For a related structure, see: Gotoh & Ishida (2011). For the double π system of the chloranilate anion, see: Andersen (1967); Benchekroun & Savariault (1995).



Experimental

Crystal data

$2\text{C}_9\text{H}_{11}\text{N}_2\text{O}^+\cdot\text{C}_6\text{Cl}_2\text{O}_4^{2-}$

$M_r = 533.37$

Triclinic, $P\bar{1}$
 $a = 4.9971$ (4) Å
 $b = 8.6363$ (4) Å
 $c = 13.5808$ (9) Å
 $\alpha = 97.869$ (4)°
 $\beta = 91.660$ (6)°
 $\gamma = 100.968$ (5)°

$V = 569.06$ (7) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.34$ mm⁻¹
 $T = 200$ K
 $0.45 \times 0.35 \times 0.04$ mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
 Absorption correction: numerical (NUMABS; Higashi, 1999)
 $T_{\min} = 0.887$, $T_{\max} = 0.987$

7422 measured reflections
 2692 independent reflections
 1913 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.199$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.177$
 $S = 0.84$
 2692 reflections
 172 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.89$ e Å⁻³
 $\Delta\rho_{\min} = -0.54$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.95 (3)	1.79 (3)	2.706 (2)	160 (3)
$\text{N1}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.95 (3)	2.56 (3)	3.229 (3)	127 (2)
$\text{N2}-\text{H2}\cdots\text{O2}^{\text{ii}}$	0.90 (3)	1.87 (3)	2.762 (3)	171 (3)
$\text{C4}-\text{H4}\cdots\text{O1}^{\text{iii}}$	0.95	2.34	3.214 (3)	152
$\text{C10}-\text{H10}\cdots\text{O1}$	0.95	2.52	3.230 (3)	131

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

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); 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, 2012); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5342).

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supporting information

Acta Cryst. (2013). E69, o1482 [doi:10.1107/S1600536813023635]

Bis(4-methoxy-3,4-dihydroquinazolin-1-ium) chloranilate**Kazuma Gotoh and Hiroyuki Ishida****S1. Comment**

The title compound was accidentally obtained in the preparation process of bis(quinazolinium) chloranilate, which is an interesting candidate for the study on proton-transfer in short hydrogen-bonded systems (Nihei *et al.*, 2000, Seliger *et al.*, 2009) and also for the study on $D-H\cdots A$ hydrogen bonding ($D = N, O, \text{ or } C; A = N, O \text{ or } Cl$) in amine-chloranilic acid systems (Gotoh & Ishida, 2011).

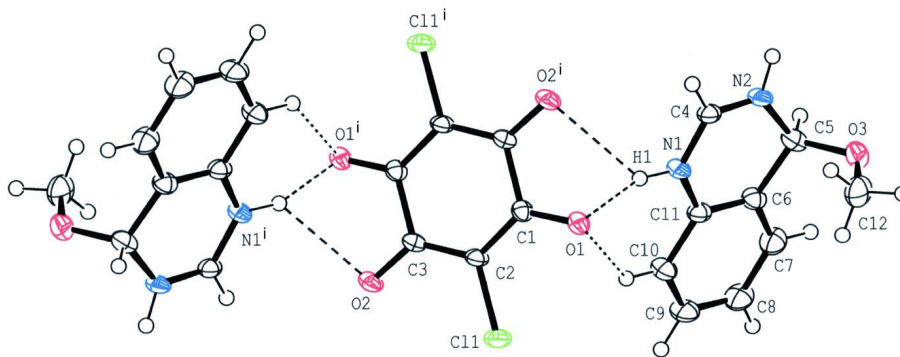
In the crystal structure of the title compound, an acid-base interaction involving proton transfer is observed between chloranilic acid and 4-methoxy-3,4-dihydroquinazoline. The chloranilate ion shows a characteristic structure having four short C—C bonds and two extremely long C—C bonds, and C—O with similar bond lengths, which is explainable in terms of the double π system of the anion (Andersen, 1967; Benchekroun & Savariault, 1995). One chloranilate anion and two 4-methoxy-3,4-dihydroquinazolin-1-ium cations are linked by bifurcated N—H \cdots (O,O) and weak C—H \cdots O hydrogen bonds (N1—H1 \cdots O1, N1—H1 \cdots O2ⁱ and C10—H10 \cdots O1; symmetry code as in Table 1) to afford a centrosymmetric 2:1 aggregate (Fig. 1). The 2:1 aggregates are linked by another N—H \cdots O hydrogen bond (N2—H2 \cdots O2ⁱⁱ; symmetry code as in Table 1), forming a tape along the $[1\bar{1}0]$ direction (Fig. 2). The tapes are further linked by a C—H \cdots O hydrogen bond (C4—H4 \cdots O1ⁱⁱⁱ; symmetry code as in Table 1) into a layer parallel to the ab plane.

S2. Experimental

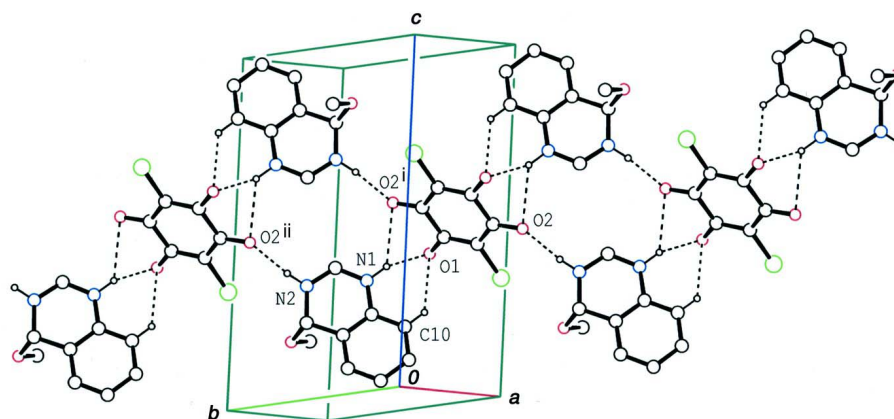
To a solution of chloranilic acid (183 mg) in acetonitrile (40 ml), a solution of quinazoline (228 mg) in acetonitrile (40 ml) was added at room temperature. A brown precipitate, which was immediately formed after mixing the solutions, was collected by filtration and then dissolved in methanol (40 ml). Single crystals of the title compound were obtained by slow evaporation from the methanol solution for *ca* three months at room temperature. During the slow evaporation process, quinazoline reacted with methanol under an acidic condition of chloranilic acid, yielding 4-methoxy-3,4-dihydroquinazoline.

S3. Refinement

C-bound H atoms were positioned geometrically (C—H = 0.95 or 0.98 Å) and refined as riding, allowing for free rotation of the methyl group. $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The N-bound H atom was found in a difference Fourier map and refined isotropically. The refined N—H distances are 0.90 (3) and 0.95 (3) Å. The quality of the crystals studied were low as indicated by $R_{\text{int}} = 0.199$. This is possibly due to a small amount of quinazoline which remained without reacting with methanol and incorporated in the crystallization of the title compound as an impurity.

**Figure 1**

The molecular structure of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. The dashed lines indicate N—H...O and C—H...O hydrogen bonds. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

**Figure 2**

A partial packing diagram of the title compound. The dashed lines indicate N—H...O and C—H...O hydrogen bonds. H atoms of the not involved in the hydrogen bonds have been omitted. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x - 1, y + 1, z$.]

Bis(4-methoxy-3,4-dihydroquinazolin-1-ium) 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-diolate

Crystal data

$2C_9H_{11}N_2O^+ \cdot C_6Cl_2O_4^{2-}$

$M_r = 533.37$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 4.9971(4)$ Å

$b = 8.6363(4)$ Å

$c = 13.5808(9)$ Å

$\alpha = 97.869(4)^\circ$

$\beta = 91.660(6)^\circ$

$\gamma = 100.968(5)^\circ$

$V = 569.06(7)$ Å³

$Z = 1$

$F(000) = 276.00$

$D_x = 1.556$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 6359 reflections

$\theta = 3.0\text{--}28.0^\circ$

$\mu = 0.34$ mm⁻¹

$T = 200$ K

Platelet, brown

$0.45 \times 0.35 \times 0.04$ mm

Data collection

Rigaku R-AXIS RAPID II
diffractometer
Detector resolution: 10.00 pixels mm⁻¹
 ω scans
Absorption correction: numerical
(NUMABS; Higashi, 1999)
 $T_{\min} = 0.887$, $T_{\max} = 0.987$
7422 measured reflections

2692 independent reflections
1913 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.199$
 $\theta_{\text{max}} = 27.9^\circ$
 $h = -6 \rightarrow 6$
 $k = -11 \rightarrow 11$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.082$
 $wR(F^2) = 0.177$
 $S = 0.84$
2692 reflections
172 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
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.89 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.54 \text{ e } \text{Å}^{-3}$

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 (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.92850 (10)	-0.01581 (6)	0.33371 (4)	0.0289 (2)
O1	0.6877 (3)	0.26227 (17)	0.41520 (12)	0.0253 (4)
O2	0.6806 (3)	-0.27488 (17)	0.44963 (13)	0.0273 (4)
O3	0.0538 (3)	0.67492 (19)	0.17432 (13)	0.0325 (4)
N1	0.3013 (4)	0.3978 (2)	0.33662 (15)	0.0238 (4)
N2	0.0001 (4)	0.5674 (2)	0.32482 (16)	0.0264 (4)
C1	0.6067 (4)	0.1368 (2)	0.45169 (16)	0.0202 (5)
C2	0.6949 (4)	-0.0070 (2)	0.42490 (16)	0.0216 (5)
C3	0.6061 (4)	-0.1443 (2)	0.46922 (16)	0.0208 (5)
C4	0.1661 (4)	0.5056 (2)	0.37648 (17)	0.0239 (5)
H4	0.1907	0.5399	0.4462	0.029*
C5	-0.0403 (4)	0.5353 (3)	0.21674 (18)	0.0276 (5)
H5	-0.2413	0.5032	0.2003	0.033*
C6	0.0872 (4)	0.3967 (3)	0.17605 (18)	0.0252 (5)
C7	0.0414 (5)	0.3326 (3)	0.07619 (19)	0.0329 (5)
H7	-0.0787	0.3723	0.0350	0.039*

C8	0.1683 (6)	0.2118 (3)	0.0362 (2)	0.0375 (6)
H8	0.1365	0.1689	-0.0323	0.045*
C9	0.3429 (5)	0.1532 (3)	0.0965 (2)	0.0367 (6)
H9	0.4315	0.0707	0.0688	0.044*
C10	0.3890 (5)	0.2130 (3)	0.19591 (19)	0.0305 (5)
H10	0.5075	0.1721	0.2370	0.037*
C11	0.2585 (4)	0.3353 (3)	0.23554 (17)	0.0234 (5)
C12	0.3396 (6)	0.7357 (3)	0.1882 (2)	0.0405 (6)
H12A	0.3821	0.8406	0.1661	0.061*
H12B	0.4377	0.6626	0.1493	0.061*
H12C	0.3958	0.7459	0.2589	0.061*
H1	0.413 (6)	0.351 (3)	0.377 (2)	0.037 (7)*
H2	-0.097 (6)	0.628 (4)	0.362 (2)	0.043 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0312 (3)	0.0265 (4)	0.0301 (4)	0.0090 (2)	0.0144 (2)	0.0008 (3)
O1	0.0295 (8)	0.0181 (7)	0.0299 (9)	0.0075 (6)	0.0073 (6)	0.0041 (7)
O2	0.0324 (8)	0.0188 (8)	0.0327 (9)	0.0111 (6)	0.0113 (7)	0.0006 (7)
O3	0.0428 (10)	0.0251 (8)	0.0326 (10)	0.0131 (7)	0.0048 (7)	0.0057 (8)
N1	0.0288 (9)	0.0188 (9)	0.0246 (10)	0.0091 (7)	0.0052 (7)	-0.0013 (8)
N2	0.0314 (10)	0.0213 (9)	0.0281 (11)	0.0106 (8)	0.0125 (8)	0.0000 (9)
C1	0.0219 (9)	0.0162 (10)	0.0217 (11)	0.0032 (8)	0.0015 (8)	0.0005 (9)
C2	0.0234 (10)	0.0189 (10)	0.0223 (11)	0.0066 (8)	0.0073 (8)	-0.0020 (9)
C3	0.0219 (9)	0.0189 (10)	0.0217 (11)	0.0073 (8)	0.0033 (8)	-0.0019 (9)
C4	0.0289 (10)	0.0197 (10)	0.0230 (12)	0.0050 (8)	0.0097 (8)	0.0002 (10)
C5	0.0269 (10)	0.0238 (11)	0.0327 (13)	0.0090 (9)	0.0040 (9)	-0.0004 (10)
C6	0.0264 (10)	0.0198 (10)	0.0282 (12)	0.0033 (8)	0.0053 (8)	-0.0004 (10)
C7	0.0397 (13)	0.0296 (12)	0.0275 (13)	0.0038 (10)	0.0021 (10)	0.0015 (11)
C8	0.0561 (16)	0.0282 (13)	0.0248 (13)	0.0053 (11)	0.0078 (11)	-0.0054 (11)
C9	0.0522 (15)	0.0258 (12)	0.0325 (14)	0.0127 (11)	0.0153 (12)	-0.0040 (12)
C10	0.0366 (12)	0.0235 (11)	0.0333 (14)	0.0117 (10)	0.0092 (10)	0.0011 (11)
C11	0.0259 (10)	0.0195 (10)	0.0236 (12)	0.0035 (8)	0.0074 (8)	-0.0003 (9)
C12	0.0478 (15)	0.0276 (13)	0.0449 (16)	0.0002 (11)	0.0088 (12)	0.0095 (12)

Geometric parameters (Å, °)

C11—C2	1.730 (2)	C5—C6	1.508 (3)
O1—C1	1.255 (3)	C5—H5	1.0000
O2—C3	1.251 (2)	C6—C11	1.384 (3)
O3—C5	1.413 (3)	C6—C7	1.388 (4)
O3—C12	1.422 (3)	C7—C8	1.379 (3)
N1—C4	1.319 (2)	C7—H7	0.9500
N1—C11	1.399 (3)	C8—C9	1.389 (4)
N1—H1	0.95 (3)	C8—H8	0.9500
N2—C4	1.305 (3)	C9—C10	1.374 (4)
N2—C5	1.457 (3)	C9—H9	0.9500

N2—H2	0.90 (3)	C10—C11	1.398 (3)
C1—C2	1.401 (3)	C10—H10	0.9500
C1—C3 ⁱ	1.537 (3)	C12—H12A	0.9800
C2—C3	1.405 (3)	C12—H12B	0.9800
C3—C1 ⁱ	1.537 (3)	C12—H12C	0.9800
C4—H4	0.9500		
C5—O3—C12	115.09 (18)	C11—C6—C7	118.93 (19)
C4—N1—C11	120.69 (19)	C11—C6—C5	121.3 (2)
C4—N1—H1	120.9 (17)	C7—C6—C5	119.7 (2)
C11—N1—H1	118.0 (17)	C8—C7—C6	120.7 (2)
C4—N2—C5	124.17 (18)	C8—C7—H7	119.7
C4—N2—H2	114.4 (19)	C6—C7—H7	119.7
C5—N2—H2	121.4 (19)	C7—C8—C9	119.7 (2)
O1—C1—C2	124.72 (19)	C7—C8—H8	120.2
O1—C1—C3 ⁱ	116.54 (16)	C9—C8—H8	120.2
C2—C1—C3 ⁱ	118.73 (18)	C10—C9—C8	120.8 (2)
C1—C2—C3	123.38 (19)	C10—C9—H9	119.6
C1—C2—C11	118.46 (16)	C8—C9—H9	119.6
C3—C2—C11	118.15 (14)	C9—C10—C11	118.9 (2)
O2—C3—C2	126.28 (19)	C9—C10—H10	120.6
O2—C3—C1 ⁱ	115.86 (18)	C11—C10—H10	120.6
C2—C3—C1 ⁱ	117.85 (16)	C6—C11—C10	121.0 (2)
N2—C4—N1	123.2 (2)	C6—C11—N1	119.03 (18)
N2—C4—H4	118.4	C10—C11—N1	120.0 (2)
N1—C4—H4	118.4	O3—C12—H12A	109.5
O3—C5—N2	110.61 (19)	O3—C12—H12B	109.5
O3—C5—C6	113.51 (18)	H12A—C12—H12B	109.5
N2—C5—C6	110.36 (18)	O3—C12—H12C	109.5
O3—C5—H5	107.4	H12A—C12—H12C	109.5
N2—C5—H5	107.4	H12B—C12—H12C	109.5
C6—C5—H5	107.4		
O1—C1—C2—C3	178.1 (2)	O3—C5—C6—C7	-63.7 (3)
C3 ⁱ —C1—C2—C3	-2.3 (3)	N2—C5—C6—C7	171.5 (2)
O1—C1—C2—C11	-1.1 (3)	C11—C6—C7—C8	-1.3 (4)
C3 ⁱ —C1—C2—C11	178.50 (14)	C5—C6—C7—C8	176.3 (2)
C1—C2—C3—O2	-178.8 (2)	C6—C7—C8—C9	0.3 (4)
C11—C2—C3—O2	0.4 (3)	C7—C8—C9—C10	0.6 (4)
C1—C2—C3—C1 ⁱ	2.3 (3)	C8—C9—C10—C11	-0.5 (4)
C11—C2—C3—C1 ⁱ	-178.52 (14)	C7—C6—C11—C10	1.4 (3)
C5—N2—C4—N1	-5.1 (3)	C5—C6—C11—C10	-176.1 (2)
C11—N1—C4—N2	-4.4 (3)	C7—C6—C11—N1	-178.9 (2)
C12—O3—C5—N2	64.7 (2)	C5—C6—C11—N1	3.6 (3)
C12—O3—C5—C6	-60.0 (3)	C9—C10—C11—C6	-0.5 (3)
C4—N2—C5—O3	-114.4 (2)	C9—C10—C11—N1	179.8 (2)
C4—N2—C5—C6	12.1 (3)	C4—N1—C11—C6	4.8 (3)

O3—C5—C6—C11	113.8 (2)	C4—N1—C11—C10	-175.5 (2)
N2—C5—C6—C11	-11.0 (3)		

Symmetry code: (i) $-x+1, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...O1	0.95 (3)	1.79 (3)	2.706 (2)	160 (3)
N1—H1...O2 ⁱ	0.95 (3)	2.56 (3)	3.229 (3)	127 (2)
N2—H2...O2 ⁱⁱ	0.90 (3)	1.87 (3)	2.762 (3)	171 (3)
C4—H4...O1 ⁱⁱⁱ	0.95	2.34	3.214 (3)	152
C10—H10...O1	0.95	2.52	3.230 (3)	131

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