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2-Amino-6-chloropyridinium 3-carboxy-4-hydroxybenzenesulfonate

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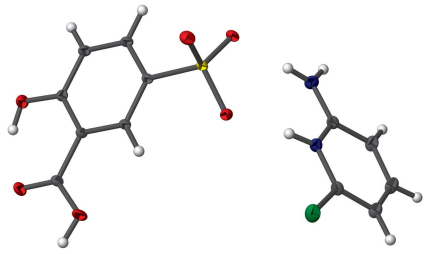
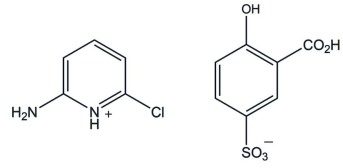
Structural data: full structural data are available from iucrdata.iucr.org

In the 3-carboxy-4-hydroxybenzenesulfonate anion of the title salt, $C_5H_6ClN_2^+\cdot C_7H_5O_6S^-$, an intramolecular O—H···O hydrogen bond with an $S(6)$ ring motif is observed. In the crystal, the anions are linked into a chain structure running along $[1\bar{1}0]$ *via* an O—H···O hydrogen bond formed between the carboxy and sulfonate groups. The 2-amino-6-chloropyridinium cations bridge the anion chains *via* N—H···O and C—H···O hydrogen bonds, forming a sheet parallel to the *ab* plane. In the sheet, a C—H···Cl interaction between the cations is also observed.

3D view



Chemical scheme



Structure description

Pyridine heterocycles and their derivatives have many applications in the fields of photochemical, electrochemical and catalytic processes (Katritzky *et al.*, 1996). Some pyridine derivatives possess non-linear optical (NLO) properties (Rajkumar *et al.*, 2015). 2-Aminopyridine derivatives are used in the synthesis of pharmaceutical drugs, especially for the treatment of neurological ailments (Schwid *et al.*, 1997). Several crystal structures of 2-aminopyridine co-crystals with carboxylic acid derivatives have been already reported (Hemamalini *et al.*, 2014). As part of our studies in this area, we now describe the synthesis and structure of the title salt.

In the 2-amino-6-chloropyridinium cation of the title compound, protonation at atom N1 leads to a slight increase in the C1—N1—C5 angle [121.72 (6)° compared with 116.8 (1)° in unprotonated 2-amino-6-chloropyridine (Hemamalini *et al.*, 2014)]. The 3-carboxy-4-hydroxybenzene sulfonate anion contains an intramolecular O—H···O hydrogen bond (O3—H1*O*3···O2; Table 1) with an $S(6)$ ring motif (Fig. 1). In the crystal, the anions are linked into a chain structure running along $[1\bar{1}0]$ *via* an O—H···O

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O1*···O6^{i}	0.871 (17)	1.775 (17)	2.6061 (7)	158.7 (16)
O3—H1*O3*···O2	0.850 (16)	1.829 (16)	2.6027 (8)	150.5 (16)
N1—H1*N1*···O5	0.881 (14)	1.854 (14)	2.7272 (8)	171.4 (13)
N2—H1*N2*···O6	0.890 (15)	1.992 (15)	2.8814 (8)	178.6 (15)
N2—H2*N2*···O4^{ii}	0.849 (14)	2.038 (14)	2.8823 (9)	173.1 (14)
C2—H2···O3^{iii}	0.931 (14)	2.389 (14)	3.2978 (9)	165.2 (12)
C3—H3···Cl1^{ii}	0.934 (15)	2.737 (15)	3.5834 (8)	151.1 (13)
C4—H4···O5^{ii}	0.941 (14)	2.340 (14)	3.2489 (9)	162.2 (11)

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

hydrogen bond formed between the carboxy and sulfonate groups (O1—H1*O1*···O6^{i}; symmetry code as in Table 1). The 2-amino-6-chloropyridinium cations bridge the anion chains *via* N—H···O and C—H···O hydrogen bonds (N1—H1*N1*···O5, N2—H1*N2*···O6, N2—H2*N2*···O4^{ii} and C4—H4···O5^{ii}; Table 1), forming a sheet parallel to the *ab* plane. In the sheet, a C—H···Cl interaction (C3—H3···Cl1^{ii}; Table 1) between the cations is also observed. The sheets are further linked *via* another C—H···O (C2—H2···O3^{iii}; Table 1) hydrogen bond, forming a three-dimensional network (Fig. 2).

Synthesis and crystallization

A hot methanol solution (20 ml) of 2-amino-6-chloropyridine (34 mg, Aldrich) and sulfosalicylic acid (54 mg, Merck) was allowed to cool slowly to room temperature and single crystals of the title compound appeared after a few days.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_5H_6ClN_2^+\cdot C_7H_5O_6S^-$
M_r	346.74
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	16.0043 (3), 7.4649 (2), 23.5799 (5)
β (°)	95.161 (1)
V (Å^3)	2805.68 (11)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.45
Crystal size (mm)	0.39 × 0.28 × 0.21
Data collection	
Diffractometer	Bruker *SMART* APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.842, 0.911
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26502, 7386, 6997
R_{int}	0.016
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.858
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.079, 1.14
No. of reflections	7386
No. of parameters	243
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.58, −0.41

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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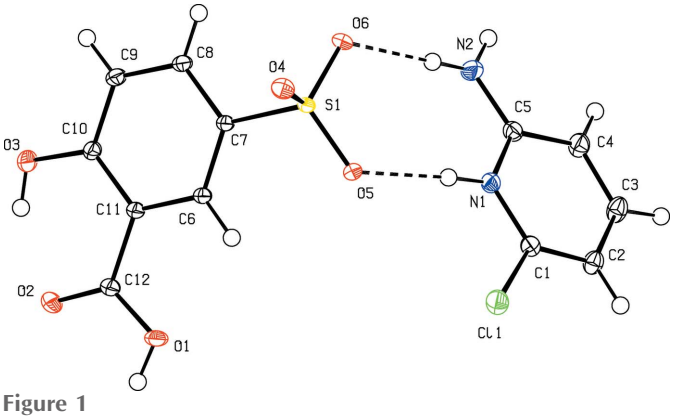

Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

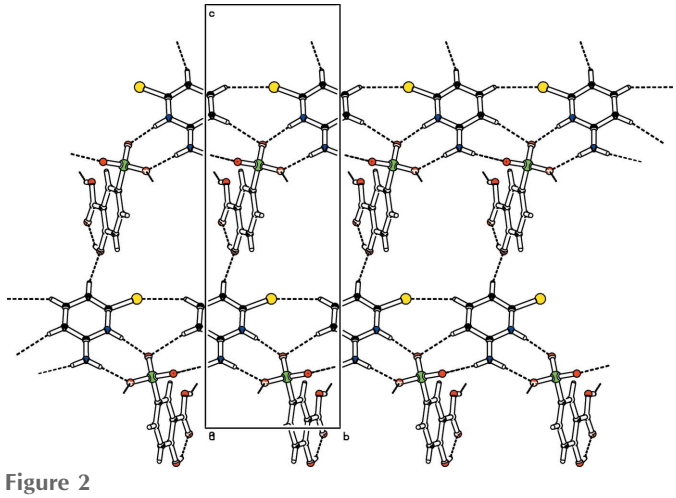

Figure 2
A packing diagram of the title compound, showing the hydrogen-bonded network (dashed lines).

full crystallographic data

IUCrData (2019). **4**, x190566 [https://doi.org/10.1107/S2414314619005662]

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2-Amino-6-chloropyridinium 3-carboxy-4-hydroxybenzenesulfonate

Crystal data

$C_5H_6ClN_2^+·C_7H_5O_6S^-$
M_r = 346.74
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 16.0043 (3) Å
b = 7.4649 (2) Å
c = 23.5799 (5) Å
β = 95.161 (1)°
V = 2805.68 (11) Å^3
Z = 8
F(000) = 1424
D_x = 1.642 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9829 reflections
θ = 2.6–37.6°
μ = 0.45 mm^{-1}
T = 100 K
Block, colourless
0.39 × 0.28 × 0.21 mm

Data collection

Bruker SMART APEXII CCD area detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.842, T_{max} = 0.911
26502 measured reflections
7386 independent reflections
6997 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 37.6°, θ_{min} = 2.6°
h = −27→27
k = −11→12
l = −40→27

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.079
S = 1.14
7386 reflections
243 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 1.5791P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat [Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107] operating at 100.0 (1) K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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.
All H atoms were located in a difference Fourier map and allowed to refine freely [N—H = 0.849 (14)–0.890 (15) Å, O—H = 0.850 (16)–0.870 (17) Å and C—H = 0.931 (14)–0.987 (13) Å].

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.194955 (9)	0.60531 (2)	0.120818 (6)	0.01019 (3)
O1	−0.11147 (3)	0.84652 (9)	0.08056 (2)	0.01856 (10)
O2	−0.14331 (3)	0.87680 (8)	−0.01363 (2)	0.01719 (10)
O3	−0.03230 (4)	0.78169 (9)	−0.08199 (2)	0.01771 (10)
O4	0.24938 (3)	0.76081 (8)	0.12876 (2)	0.01497 (9)
O5	0.14455 (3)	0.57579 (7)	0.16888 (2)	0.01358 (8)
O6	0.24046 (3)	0.44196 (7)	0.10735 (2)	0.01408 (8)
C6	0.04546 (4)	0.71656 (9)	0.06802 (3)	0.01147 (9)
C7	0.12440 (4)	0.64976 (9)	0.06087 (3)	0.01058 (9)
C8	0.15093 (4)	0.62660 (9)	0.00621 (3)	0.01268 (10)
C9	0.09758 (4)	0.67148 (10)	−0.04112 (3)	0.01408 (10)
C10	0.01735 (4)	0.73936 (9)	−0.03450 (3)	0.01221 (10)
C11	−0.00912 (4)	0.76231 (9)	0.02035 (3)	0.01131 (9)
C12	−0.09384 (4)	0.83327 (9)	0.02688 (3)	0.01288 (10)
N1	0.13605 (4)	0.27027 (8)	0.23152 (3)	0.01344 (9)
N2	0.19616 (4)	0.11253 (9)	0.16085 (3)	0.01786 (11)
Cl1	0.079291 (13)	0.48895 (2)	0.305211 (8)	0.01915 (4)
C1	0.09741 (4)	0.27792 (9)	0.28073 (3)	0.01322 (10)
C2	0.07675 (5)	0.12856 (10)	0.30926 (3)	0.01542 (11)
C3	0.09926 (5)	−0.03714 (10)	0.28634 (3)	0.01780 (12)
C4	0.13957 (5)	−0.04791 (10)	0.23772 (3)	0.01718 (12)
C5	0.15832 (4)	0.11192 (9)	0.20889 (3)	0.01376 (10)
H2	0.0514 (8)	0.1360 (19)	0.3432 (6)	0.021 (3)*
H3	0.0891 (10)	−0.145 (2)	0.3046 (7)	0.032 (4)*
H4	0.1526 (8)	−0.1600 (19)	0.2225 (6)	0.023 (3)*
H6	0.0274 (8)	0.7370 (19)	0.1064 (6)	0.019 (3)*
H8	0.2071 (8)	0.5821 (17)	0.0021 (5)	0.015 (3)*
H9	0.1142 (9)	0.656 (2)	−0.0780 (6)	0.024 (3)*
H1O1	−0.1623 (11)	0.888 (2)	0.0808 (7)	0.041 (4)*
H1O3	−0.0781 (10)	0.820 (2)	−0.0709 (7)	0.032 (4)*
H1N1	0.1436 (8)	0.3713 (18)	0.2134 (6)	0.019 (3)*
H1N2	0.2102 (9)	0.215 (2)	0.1449 (6)	0.028 (4)*

H2N2	0.2116 (9)	0.0121 (19)	0.1485 (6)	0.023 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.00848 (6)	0.01208 (6)	0.01013 (6)	0.00212 (4)	0.00147 (4)	−0.00012 (4)
O1	0.01210 (19)	0.0300 (3)	0.0140 (2)	0.00791 (19)	0.00350 (16)	0.00012 (19)
O2	0.01249 (19)	0.0226 (3)	0.0160 (2)	0.00428 (17)	−0.00103 (16)	0.00197 (18)
O3	0.0150 (2)	0.0267 (3)	0.01119 (19)	0.00370 (19)	−0.00049 (16)	0.00279 (18)
O4	0.01189 (18)	0.0154 (2)	0.0174 (2)	−0.00116 (16)	0.00033 (15)	−0.00181 (17)
O5	0.01388 (19)	0.0164 (2)	0.01106 (18)	0.00364 (16)	0.00411 (15)	0.00170 (15)
O6	0.01187 (18)	0.0148 (2)	0.0160 (2)	0.00497 (16)	0.00341 (15)	0.00015 (16)
C6	0.0094 (2)	0.0145 (2)	0.0107 (2)	0.00190 (18)	0.00201 (17)	0.00037 (18)
C7	0.0090 (2)	0.0127 (2)	0.0102 (2)	0.00151 (17)	0.00168 (16)	−0.00005 (18)
C8	0.0110 (2)	0.0160 (3)	0.0115 (2)	0.00172 (19)	0.00298 (17)	−0.00057 (19)
C9	0.0128 (2)	0.0192 (3)	0.0105 (2)	0.0021 (2)	0.00293 (18)	−0.0003 (2)
C10	0.0115 (2)	0.0147 (2)	0.0104 (2)	0.00023 (19)	0.00100 (17)	0.00095 (18)
C11	0.0092 (2)	0.0137 (2)	0.0112 (2)	0.00139 (18)	0.00165 (17)	0.00063 (18)
C12	0.0102 (2)	0.0148 (3)	0.0137 (2)	0.00172 (19)	0.00169 (18)	0.00027 (19)
N1	0.0151 (2)	0.0119 (2)	0.0135 (2)	0.00114 (17)	0.00169 (17)	0.00032 (17)
N2	0.0211 (3)	0.0158 (3)	0.0177 (2)	0.0036 (2)	0.0074 (2)	0.0010 (2)
Cl1	0.02752 (9)	0.01356 (7)	0.01658 (7)	0.00355 (6)	0.00307 (6)	−0.00200 (5)
C1	0.0145 (2)	0.0129 (2)	0.0120 (2)	0.00098 (19)	−0.00034 (18)	−0.00142 (19)
C2	0.0197 (3)	0.0146 (3)	0.0119 (2)	−0.0017 (2)	0.0009 (2)	−0.0006 (2)
C3	0.0260 (3)	0.0134 (3)	0.0142 (3)	−0.0020 (2)	0.0023 (2)	0.0003 (2)
C4	0.0236 (3)	0.0126 (3)	0.0155 (3)	0.0008 (2)	0.0027 (2)	−0.0003 (2)
C5	0.0145 (2)	0.0132 (2)	0.0136 (2)	0.00182 (19)	0.00097 (19)	−0.00013 (19)

Geometric parameters (Å, º)

S1—O4	1.4532 (6)	C10—C11	1.4072 (9)
S1—O5	1.4656 (5)	C11—C12	1.4765 (9)
S1—O6	1.4696 (5)	N1—C5	1.3577 (9)
S1—C7	1.7595 (6)	N1—C1	1.3643 (9)
O1—C12	1.3252 (9)	N1—H1N1	0.881 (14)
O1—H1O1	0.870 (17)	N2—C5	1.3317 (9)
O2—C12	1.2283 (8)	N2—H1N2	0.890 (15)
O3—C10	1.3509 (8)	N2—H2N2	0.849 (14)
O3—H1O3	0.850 (16)	Cl1—C1	1.7115 (7)
C6—C7	1.3824 (9)	C1—C2	1.3583 (10)
C6—C11	1.4024 (9)	C2—C3	1.4095 (11)
C6—H6	0.987 (13)	C2—H2	0.931 (14)
C7—C8	1.4036 (9)	C3—C4	1.3676 (11)
C8—C9	1.3840 (9)	C3—H3	0.932 (17)
C8—H8	0.972 (13)	C4—C5	1.4186 (10)
C9—C10	1.4020 (9)	C4—H4	0.941 (14)
C9—H9	0.939 (14)		

O4—S1—O5	112.69 (3)	C10—C11—C12	119.65 (6)
O4—S1—O6	112.81 (3)	O2—C12—O1	123.05 (6)
O5—S1—O6	111.12 (3)	O2—C12—C11	123.20 (6)
O4—S1—C7	106.66 (3)	O1—C12—C11	113.75 (6)
O5—S1—C7	106.94 (3)	C5—N1—C1	121.72 (6)
O6—S1—C7	106.12 (3)	C5—N1—H1N1	120.1 (9)
C12—O1—H1O1	108.1 (11)	C1—N1—H1N1	118.1 (9)
C10—O3—H1O3	106.5 (11)	C5—N2—H1N2	121.0 (10)
C7—C6—C11	120.03 (6)	C5—N2—H2N2	117.2 (9)
C7—C6—H6	120.9 (8)	H1N2—N2—H2N2	121.3 (13)
C11—C6—H6	119.0 (8)	C2—C1—N1	122.41 (6)
C6—C7—C8	120.77 (6)	C2—C1—Cl1	122.16 (5)
C6—C7—S1	119.84 (5)	N1—C1—Cl1	115.40 (5)
C8—C7—S1	119.29 (5)	C1—C2—C3	116.65 (7)
C9—C8—C7	119.68 (6)	C1—C2—H2	121.4 (9)
C9—C8—H8	120.8 (7)	C3—C2—H2	121.9 (9)
C7—C8—H8	119.5 (7)	C4—C3—C2	121.94 (7)
C8—C9—C10	120.16 (6)	C4—C3—H3	116.9 (10)
C8—C9—H9	120.8 (9)	C2—C3—H3	121.2 (10)
C10—C9—H9	119.0 (9)	C3—C4—C5	119.23 (7)
O3—C10—C9	117.94 (6)	C3—C4—H4	120.6 (9)
O3—C10—C11	122.00 (6)	C5—C4—H4	120.1 (9)
C9—C10—C11	120.05 (6)	N2—C5—N1	119.14 (6)
C6—C11—C10	119.32 (6)	N2—C5—C4	122.85 (7)
C6—C11—C12	121.03 (6)	N1—C5—C4	118.01 (6)

C11—C6—C7—C8	−0.09 (10)	O3—C10—C11—C12	0.52 (10)
C11—C6—C7—S1	176.17 (5)	C9—C10—C11—C12	−179.78 (6)
O4—S1—C7—C6	−96.71 (6)	C6—C11—C12—O2	179.20 (7)
O5—S1—C7—C6	24.08 (6)	C10—C11—C12—O2	−1.06 (11)
O6—S1—C7—C6	142.77 (6)	C6—C11—C12—O1	−0.49 (10)
O4—S1—C7—C8	79.60 (6)	C10—C11—C12—O1	179.25 (6)
O5—S1—C7—C8	−159.60 (5)	C5—N1—C1—C2	−1.85 (10)
O6—S1—C7—C8	−40.91 (6)	C5—N1—C1—Cl1	176.41 (5)
C6—C7—C8—C9	0.15 (10)	N1—C1—C2—C3	1.66 (10)
S1—C7—C8—C9	−176.13 (6)	Cl1—C1—C2—C3	−176.49 (6)
C7—C8—C9—C10	−0.15 (11)	C1—C2—C3—C4	−0.26 (11)
C8—C9—C10—O3	179.81 (7)	C2—C3—C4—C5	−0.94 (12)
C8—C9—C10—C11	0.10 (11)	C1—N1—C5—N2	−179.76 (7)
C7—C6—C11—C10	0.03 (10)	C1—N1—C5—C4	0.55 (10)
C7—C6—C11—C12	179.77 (6)	C3—C4—C5—N2	−178.87 (7)
O3—C10—C11—C6	−179.74 (6)	C3—C4—C5—N1	0.80 (11)
C9—C10—C11—C6	−0.04 (10)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···O6^{i}	0.871 (17)	1.775 (17)	2.6061 (7)	158.7 (16)

O3—H1*O*3···O2	0.850 (16)	1.829 (16)	2.6027 (8)	150.5 (16)
N1—H1*N*1···O5	0.881 (14)	1.854 (14)	2.7272 (8)	171.4 (13)
N2—H1*N*2···O6	0.890 (15)	1.992 (15)	2.8814 (8)	178.6 (15)
N2—H2*N*2···O4^{ii}	0.849 (14)	2.038 (14)	2.8823 (9)	173.1 (14)
C2—H2···O3^{iii}	0.931 (14)	2.389 (14)	3.2978 (9)	165.2 (12)
C3—H3···Cl1^{ii}	0.934 (15)	2.737 (15)	3.5834 (8)	151.1 (13)
C4—H4···O5^{ii}	0.941 (14)	2.340 (14)	3.2489 (9)	162.2 (11)

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